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An abstract painting of a parrot, likely a macaw, rendered in vibrant colors of red, blue, green, and yellow. The brushstrokes are visible, giving it a textured, expressive appearance. The parrot is shown in profile, facing right, with its wings and tail feathers partially visible.

Fate of riverine iron over estuarine salinity gradients

SIMON HERZOG | ENVIRONMENTAL SCIENCE | CEC | LUND UNIVERSITY



Fate of riverine iron over estuarine salinity gradients

Simon David Herzog



LUND
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DOCTORAL DISSERTATION

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To be defended in the Blue Hall, Ecology Building, Sölvegatan 37, Lund on
Friday 11th of January 2019, at 9:00 AM, for the degree of Doctor of Philosophy in
Environmental Science

Faculty opponent

Associate Research Professor Andrew Schroth

Department of Geology

University of Vermont

| | | |
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| <p>Abstract:</p> <p>Rivers have traditionally not been considered important sources of bioavailable iron (Fe) to the marine waters, since most Fe is lost by salinity-induced aggregation and sedimentation during estuarine mixing. However, recent studies from boreal rivers found a remarkably high Fe stability, probably due to the interaction with organic matter. Recent studies have suggested that Fe speciation is a key factor, i.e. that Fe (oxy)hydroxides are effectively removed by aggregation processes, but that organic Fe complexes (Fe-OM) are less affected by increasing salinity. This hypothesis has been supported by indirect assessments of Fe speciation (based on molecular size and Fe:C ratios). One aim of the current thesis was to directly assess variability in Fe speciation in boreal river waters, by X-ray absorbance spectroscopy (XAS), and to examine the link to Fe stability, which was assessed by artificial seawater mixing experiments. Another aim was to explore what factors may control temporal and spatial variability in Fe speciation within and across rivers. It has further been proposed that variation in Fe isotopic composition reflects Fe speciation, which was tested in this thesis by subjecting a set of samples to both analyses. Finally, to test how colloidal size distributions in river waters vary with regards to surface charge and Fe speciation, XAS analysis was combined with dynamic light scattering and zeta potential. The combination of these methods provided the potential for a comprehensive picture of the Fe phases present in river water and how they react to increasing salinity. The overarching aim of this thesis was to gain a better understanding of what factors determine the fate of Fe from boreal rivers across estuarine salinity gradients. For this purpose, 10 rivers, from the north to the south of Sweden, with different catchment characteristics were considered. Among the river mouths a significant, but variable contribution of Fe-OM in relation to Fe (oxy)hydroxides was detected. That Fe (oxy)hydroxides are more affected by increasing salinity than Fe-OM was confirmed by selective removal of Fe (oxy)hydroxides due to salinity-induced aggregation. Moreover, the relative contribution of Fe-OM correlated well with Fe transport capacity (FeTC), <i>i.e.</i> supporting that organic complexation of Fe favors Fe export to open waters. However, Fe-OM complexes were also found in the aggregated fraction, illustrating that the control of Fe stability is not simply explained by the prevalence of the respective Fe phases alone.</p> <p>The Fe-OM contribution was more dominant further upstream in a catchment than at the river mouth, and also more prevalent during high-flow than at low-flow conditions. Consequently, the higher contribution of Fe-OM during spring, when much of the annual Fe discharge is taking place, resulted in a higher FeTC. Separation of salinity-induced aggregates from the fraction remaining in suspension revealed that Fe (oxy)hydroxide displayed lower $\delta^{56}\text{Fe}$ values, and Fe-OM displayed higher $\delta^{56}\text{Fe}$ values than the in situ Fe. This points to the possibility of inferring Fe speciation of the fraction that survives the estuarine mixing zone from isotope analysis. The combination of XAS and DLS analysis demonstrated the existence of three size distributions; Fe (oxy)hydroxide were observed both as nanoparticles (10-40 nm) with positive surface charge, and larger aggregates with OM interactions (300-900 nm). An intermediate (100-200 nm) and negatively charged distribution was inferred to contain Fe-OM. After increasing salinity, the smallest Fe (oxy)hydroxide nanoparticles were no longer detected. Interestingly, both the larger size distributions were still detected at high salinity.</p> <p>In all, the results from this thesis support that boreal rivers may provide significant amounts of bioavailable Fe to marine waters beyond the estuary, due to significant contributions of Fe-OM complexes. Moreover, the results illustrates that a division between small Fe-OM complexes that "survive" estuarine salinity gradients and large Fe (oxy)hydroxides that are aggregated and lost to the sediment, is too simplistic, since both phases can be found in a wide size range.</p> | | |
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Fate of riverine iron over estuarine salinity gradients

Simon David Herzog



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MADE IN SWEDEN 

“No one ever steps in the same river twice” (Heraclitus)

Table of Contents

| | |
|---|-----|
| Popular Science Summary | 8 |
| Populärvetenskaplig sammanfattning | 10 |
| List of figures | 12 |
| List of Tables | 14 |
| List of Abbreviations | 15 |
| List of Papers | 16 |
| Author Contributions | 17 |
| Introduction | 19 |
| The role of Fe in marine waters | 19 |
| Rivers as Fe sources to the open sea | 20 |
| Fe in the Baltic Sea | 21 |
| Motivation of the thesis | 22 |
| Methods and implementation | 24 |
| Sampling | 24 |
| Analytical methods | 26 |
| Main findings | 30 |
| Fe speciation in river water | 30 |
| The fate of Fe at increasing salinity | 33 |
| Spatial and temporal variation of riverine Fe speciation | 34 |
| Link between Fe isotopic composition and Fe speciation | 36 |
| Colloidal size distribution and surface charge | 37 |
| Salinity effect on the colloidal size distribution and surface charge | 39 |
| Conclusion and Outlook | 40 |
| References | 42 |
| Acknowledgements | 50 |
| Paper I | 55 |
| Paper II | 75 |
| Paper III | 105 |
| Paper IV | 137 |

Popular Science Summary

Rivers are important sources of iron and other nutrients to coastal and marine waters. During the last few decades, iron concentrations in Swedish and Finnish rivers, which drain into the Baltic Sea, has increased strongly. The implications of this increase to the Baltic Sea depends on the fate of iron when it meets the saline water in the estuaries. Iron gets transported mainly in the form of small particles - colloids. Those colloids are composed either of iron oxides or organic Fe complexes. The composition of the colloids is important, because it affects how the iron behaves in the salinity gradient. If the iron-bearing particles remain in solution in the water it can reach the open waters of the Baltic Sea.

Iron is an essential nutrient for phytoplankton, since it is involved in key processes like photosynthesis and respiration. During intense algal blooms, iron can be a limiting factor for growth, especially for the potentially toxic blue-green algae, which have a particularly high iron demand. More intense blooms in the Baltic Sea have been observed during the last decades, posing a threat to the ecosystem, since they can be toxic to animals and humans. Furthermore, the blue-green algae provide a positive feedback to eutrophication, by adding nitrogen to the system through nitrogen fixation, and by causing oxygen depletion when the algal biomass is degraded. The lack of oxygen result in the release of phosphorus from sediments, and further in a loss habitat and biodiversity, habitat degradation, as well as changes in food web dynamics.

The traditional wisdom, however, is that the majority of the iron from rivers aggregate when exposed the saline conditions and consequently sink to sediment in the estuary. In the sediment iron can bind phosphorus and keep it from the water. In this way iron can instead counteract eutrophication, by acting as a phosphorus sink.

To better understand iron export from rivers into the open sea, I wanted to study what factors determine the fate of riverine iron in the estuarine mixing zone. For that purpose, 10 rivers were sampled, from the north to the south of Sweden. The composition of iron – whether it was iron oxides or organic iron complexes – was analyzed by X-ray absorption spectroscopy at synchrotron facilities.

It was found that all rivers contained a mix of organic iron complexes and iron oxides. The relative contribution of those two forms of iron varied between the rivers, but overall the fraction of organic iron complexes was surprisingly large, and it was larger during high discharge in spring than during low discharge in autumn. A very important finding was that the organic iron complexes were

much more resistant across the salinity gradient, while the Fe oxides aggregated to a large extent. This, in combination with the high prevalence of organic Fe complexes, suggest that the rising iron concentrations in rivers may result in more iron reaching the open waters of the Baltic Sea, where it could fuel algal blooms. However, even if the organic iron complexes were more prevalent than expected, the majority of the iron was in the oxide form, and can consequently enhance the phosphorus burial in coastal sediments, which may counteract eutrophication. Further studies are needed to understand the role that iron plays to the cycling of important nutrients in the Baltic Sea.

Populärvetenskaplig sammanfattning

Floder och åar är viktiga källor för järn och andra näringsämnen till Östersjön. De senaste decennierna har järnkonzentrationen i svenska och finska åar ökat kraftigt, vilket skulle kunna leda till en ökad transport av järn till Östersjön. Vilken effekt detta kan ha för Östersjön beror på vad som händer med järnet när det möter det salta vattnet i Östersjön. Järn transporteras huvudsakligen i form av små partiklar - kolloider. Dessa kolloider består antingen av järnoxider eller organiska järnkomplex. Kolloidernas kemiska sammansättning är av betydelse då det påverkar vad som händer med järnet i saltgradienten. Om de järnbärande kolloiderna stannar kvar i vattenfasen kan järnet nå de öppna vattnen i Östersjön.

Järn är ett essentiellt näringsämne växtplankton, eftersom järn är inblandat i nyckelprocesser såsom fotosyntes och respiration. Under kraftiga algbloomningar kan järn begränsa tillväxten, speciellt för de potentiellt giftiga blågrönalgerna som har särskilt stort järnbehov. Förekomsten av blågrönalgbloomningar i Östersjön har ökat de senaste decennierna, vilket är ett hot mot ekosystemet med tanke på att blågrönalger kan vara giftiga för djur och människor. Dessutom kan blågrönalger skapa en positiv feedback för övergödning, genom att tillföra kväve till systemet genom kvävefixering, och genom att ge upphov till syrebrist när algbiomassan bryts ner. Bristen på syre kan i sin tur leda till att fosfor frigörs från sedimenten, och en förlust av biodiversitet och levnadsmiljöer, samt förändringar i födoväven.

Den gängse bilden är emellertid att merparten av järnet från åar och floder aggregerar när det möter det salta vattnet och sjunker till sedimentet. I sedimentet kan järnet binda in fosfor och hålla det borta från vattnet. På så vis kan järnet i stället motverka övergödning, genom att verka som en fosforsänka.

För att bättre förstå transporten av järn från åar till öppet hav ville jag undersöka vad som händer med järnet när sötvatten från vattendragen blandas med marint saltvatten. I det syftet studerades tio åar från norra till södra Sverige. Järnets sammansättning – huruvida det var järnoxider eller organiska järnkomplex – analyserades med röntgenabsorptionsspektroskopi vid synkrotronljus-anläggningar.

Resultaten visade att alla åmynningar hade en blandning av organiska järnkomplex och järnoxider. Det relativa bidraget av de två järnformerna varierade, men överlag var andelen organiska järnkomplex oväntat stor, och den var större under höga flöden på våren än låga flöden på hösten. Ett centralt resultat var att de organiska järnkomplexen var mycket mer stabila över salinitetsgradienter än järnoxider som i stor utsträckning aggregerade. Detta,

tillsammans med den stora andelen organiska järnkomplex, indikerar att de ökande järnkonzentrationerna i många åar kan leda till att mer järn når till öppna vatten i Östersjön där de kan gynna algbloomningar. Även om andelen organiska järnkomplex var oväntat hög, så var merparten av järnet i form av järnoxider, och kan följaktligen öka inbindningen av fosfor i sedimenten, vilket kan motverka övergödning. Fler studier som belyser vilken roll järn spelar för viktiga näringscykler i Östersjön behövs.

List of figures

- Figure 1. Map of river catchments in Sweden. The rivers sampled for this thesis are shown with name and the catchment marked in blue. 25
- Figure 2. Fe remaining in suspension in response to increasing salinity for river Öre and Örekil. The squares denote the *in situ* measurements and the triangles the theoretical values. Theoretically calculated Fe concentrations are based on the loss of Fe in the artificial seawater mixing experiments and the dilution factor (From Paper II)..... 26
- Figure 3. High resolution WT modulus ($\eta = 4$, $\sigma = 2$) of EXAFS data of a river water sample. The areas representing the different Fe paths are denoted by C (Fe–C), C/O (Fe–C–C/O), and Fe (Fe–Fe). 27
- Figure 4. A selection of high resolution WT modulus ($\eta = 4$, $\sigma = 2$) of EXAFS data from river mouths, and the two upstream sites (Svineö and Biveröd) of the river Helge catchment. The samples are plotted as a function of k (Å^{-1}) on the x-axis and R (Å) on the y-axis. Data from Paper II. 30
- Figure 5. $\text{FeK}\beta_{2,5}$ X-ray emission spectra of the river mouth sample and the two upstream samples of river Helge. And the two references for Fe(II) (green) for Fe(III) (red) from Paper II. The dotted lines are included for visual guidance according to the peaks in the references. 32
- Figure 6. High resolution WT modulus ($\eta = 4$, $\sigma = 2$) of EXAFS data of an *in situ* river water sample and the corresponding salinity induced aggregates at salinity 25 from Paper I. The samples are plotted as a function of k (Å^{-1}) on the x-axis and R (Å) on the y-axis. 33
- Figure 7. The change of Fe in suspension in response to increasing salinity (0-35) of three rivers Lyckeby (A), Mörrum (B) and Örekil (C) on the left and the corresponding WT plot on the right from Paper II. 34
- Figure 8. The change in Fe in suspension in response to increasing salinity (0-35) plotted on the left from river Lyckeby. Black line denotes sampling in autumn and red line denotes sampling in spring. High resolution WT modulus ($\eta = 4$, $\sigma = 2$) of EXAFS data from the data of the according river mouth sample. 35
- Figure 9. $\delta^{56}\text{Fe}$ (‰) of three fractions - *in situ* river water, salinity-induced aggregates, and supernatant - with error bars ($\pm 2\sigma$) and the CN-ratio of river Kalix (Paper III). The discharge is shown in the background for guidance. . 37
- Figure 10. Overview of the colloidal size distribution of samples from River Lyckeby (from Paper IV). Panel A shows river water before and after

filtration. Panel B shows river water at 0 and 25 salinity, both after centrifugation..... 39

List of Tables

| | |
|---|----|
| Table 1. Basic water chemistry data and catchments information of sites considered in this study..... | 24 |
| Table 2. k^3 -weighted Fe K-edge EXAFS fits of a selection of river mouth samples and the two upstream samples Svineö and Biveröd. | 31 |
| Table 3. LCF results for river mouth samples Örekil, Lyckeby and Emån, Helge and the upstream samples Svineö and Biveröd. | 31 |

List of Abbreviations

| | |
|-------|---|
| CN | Coordination Number |
| DLS | Dynamic Light Scattering |
| EXAFS | Extended X-ray Absorption Fine Structure |
| Fe | Iron |
| Fe-OM | Organically complexed Fe |
| FeTC | Iron Transport Capacity |
| FIFFF | Flow Field-Flow Fractionation |
| HERFD | High-Energy Resolution Fluorescence Detection |
| LCF | Linear Combination Fitting |
| MS | Multiple-Scattering |
| N | Nitrogen |
| OC | Organic Carbon |
| OM | Organic Matter |
| P | Phosphorous |
| SS | Single-Scattering |
| TOC | Total Organic Carbon |
| WT | Wavelet Transforms |
| XANES | X-ray Absorption Near Edge Structure |
| XAS | X-ray Absorbance Spectroscopy |

List of Papers

This thesis is based on the following papers, referred to by their roman numerals:

- I. Herzog, S. D., P. Persson, and E. S. Kritzberg. 2017. Salinity Effects on Iron Speciation in Boreal River Waters. *Environ Sci Technol* 51:9747-9755.
- II. Herzog, S. D., P. Persson, K. Kvashnina and E. S. Kritzberg. Enhanced Iron Transport Capacity along Estuarine salinity Gradients due to Organic Iron Complexes (*in review*)
- III. Herzog, S. D., S. Conrad, J. Ingri, P. Persson, and E. S. Kritzberg. Seasonal variation in riverine Fe speciation and the fate over estuarine salinity gradients (*Manuscript*).
- IV. Herzog, S. D., L. Gentile, U. Olsson, P. Persson, and E. S. Kritzberg. Characterization of Boreal River Colloids and their Fate at high Salinity (*Manuscript*).

Author Contributions

- I. SH and EK developed the original idea and designed the study. SH carried out the fieldwork and lab work. SH, PP and KK performed the XAS analyses and subsequent data treatment. SH, PP and EK analyzed the data. SH wrote the manuscript with support from PP and EK.
- II. EK and SH conceived and designed the study. SH carried out the fieldwork and lab work. SH and PP performed the XAS analyses and subsequent data treatment. SH, PP and EK analyzed the data. SH wrote the manuscript with support from PP and EK.
- III. SH, SC, PP, JI and EK conceived and designed the study. SH and SC carried out the field- and lab work. SH and PP performed the XAS analyses and subsequent data treatment. SC performed the stable isotope analysis. SH and SC analyzed the data and wrote the manuscript with contribution from EK, JI and PP.
- IV. SH, LG, EK, UO and PP conceived the original idea. SH and LG designed the study. SH carried out the fieldwork. SH and LG conducted the experiments. SH and PP performed the XAS analyses and subsequent data treatment. LG performed the DLS and zeta potential measurements and data treatment with assistance from SH. SH, LG and EK wrote the manuscript with contribution from PP and UO.

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Introduction

The role of Fe in marine waters

Iron (Fe) is an element of pivotal importance in estuarine and marine waters, influencing the mobility, availability and biogeochemistry of numerous other elements and compounds (Tagliabue et al. 2017). For instance, Fe is a cofactor of enzymes involved in fundamental metabolic processes like photosynthesis and nitrogen assimilation, which are of particular relevance to many marine phototrophs (Boyd and Ellwood 2010, Sunda and Huntsman 2015). Exceedingly low Fe concentrations in the open ocean (0.02-0.5 nmol/L; (Buesseler and Boyd 2003), which are due to the low solubility of Fe under oxic and nonacidic conditions (Buesseler and Boyd 2003, Jickells et al. 2005), mean that phytoplankton production in about a quarter of the world's oceans are Fe limited (Raiswell and Canfield 2012). This was first postulated by John Martin's "iron hypothesis" (Martin and Fitzwater 1988, Martin 1990) and later supported by several artificial Fe enrichment experiments in ocean waters (De Baar et al. 2005, Boyd et al. 2007). Availability of Fe is thereby influencing the removal of atmospheric carbon via the ocean's biological pump (Falkowski et al. 2000).

Due to the exceptionally high surface reactivity of its mineral phases, Fe readily interacts with phosphorus (P) and organic carbon (OC) among others (Stumm and Morgan 1996). Recent findings suggest that 21 % of OC in marine and freshwater sediments are preserved from microbial mineralization by its association with reactive Fe minerals (Lalonde et al. 2012). It has also been shown that Fe is a key controller of P burial, and may act as an estuarine filter for P (Asmala et al. 2017; Lenstra et al. 2018).

These examples illustrate that Fe in direct and indirect ways affect the productivity of aquatic systems, and is intricately linked to the sequestration of carbon. Therefore, understanding the supply, removal and bioavailability of Fe is instrumental to evaluate future scenarios of global climate change (Muller et al. 2018).

Rivers as Fe sources to the open sea

Sources of Fe to marine waters are riverine inputs, atmospheric deposition, hydrothermal vents, re-suspended sediments, and sediment pore water from continental shelves (Wells et al. 1995, Jickells et al. 2005, Tagliabue et al. 2017). Typically, rivers have been viewed as insignificant sources of Fe to off-shore marine waters, since many major rivers exhibit extensive loss of Fe by aggregation and sedimentation (Jickells et al. 2005).

In freshwaters, interactions with organic matter (OM) support the stability of Fe, where it would otherwise precipitate and sediment (Shapiro 1966). Thus, in limnic systems Fe concentrations are relatively high and rarely limiting (Vrede and Tranvik 2006). The association between Fe and OM can be roughly divided into two phases: Fe (oxy)hydroxides associated with OM, and organically complexed mononuclear Fe (Fe-OM) (Hassellöv et al. 1999, Andersson et al. 2006, Breitbart et al. 2010). When riverine freshwater enters the estuary, increasing salinity and pH promote the loss of Fe by aggregation (Sholkovitz 1976, Chester and Jickells 2003, Nowostawska et al. 2008). Typically >90 % of Fe gets removed from the suspended fraction (Chester and Jickells 2003, Kritzberg et al. 2014). There are several mechanisms that may invoke aggregation and destabilization of Fe in response to increasing salinity. First, colloidal repulsion, promoted by negatively charged OM, is reduced due to neutralization of the surface charge, favoring aggregation and co-precipitation of Fe and OM (Boyle et al. 1977, Sander et al. 2004, Nowostawska et al. 2008). Neutralization of negatively charged functional groups of the OM may further weaken the interaction between colloidal Fe and OM (Turner and Millward 2002). Increasing concentrations of divalent cations (magnesium and calcium), which compete with Fe for binding sites of organic ligands, may promote the release and hydrolysis of Fe-OM (Fujii et al. 2008). Finally, salinity impacts Fe stability by the compression of water in the presence of dissolved ions, resulting in “salting out” of the organic complexes (Turner and Millward 2002, Turner et al. 2004).

Recent studies on Fe transport across estuarine salinity gradients have found that the Fe transport capacity (FeTC) – the fraction of Fe remaining in suspension at high salinity - is highly variable (1% to 55%) and that boreal rivers with high concentrations of OC and humic substances display remarkably high Fe stability (Krachler et al. 2005, Krachler et al. 2010, Kritzberg et al. 2014). It has further been suggested that the speciation of Fe is governing the variation in FeTC in the estuary, *i.e.* that the physicochemical processes in the mixing zone mainly destabilize Fe (oxy)hydroxides, while Fe-OM is less affected (Kritzberg et al. 2014, Krachler et al. 2015). Indirect assessments, based on size separation and Fe/OC ratios support such a hypothesis (Krachler et al. 2010, Kritzberg et al. 2014).

Fe in the Baltic Sea

The rivers studied in this thesis drain into the Baltic Sea (Figure 1). The Baltic Sea is one of the biggest brackish water bodies and is heavily influenced by freshwater from rivers, which represent a major source of nutrients, OM and pollutants (Agrell et al. 2001, Grimvall and Stålnacke 2001, Deutsch et al. 2012). The high riverine input of Fe and OM, in combination with the relatively low salinity, render Fe concentrations in the Baltic Sea high (15–144 nmol L⁻¹; Bothnian Sea – Baltic proper, (Gelting et al. 2010) compared to the open sea. In fact, the high Fe concentrations have been suggested as one factor contributing to the dominance of cyanobacteria during the recurrent summer blooms. Nevertheless, because phytoplankton biomass in the Baltic Sea is at times exceptionally high, and due to the particularly high Fe demand of cyanobacteria, it has been suggested that Fe can limit N fixation and growth of cyanobacteria here as well (Stal et al. 1999, Stolte et al. 2006).

Cyanobacterial blooms have increased in frequency and intensity in the Baltic Sea during the last century (Finni et al. 2001). Cyanobacterial N fixation supplies the system with new N and provides a positive feedback to eutrophication. Eutrophication enhances the downward flux of OM, which during decomposition consumes oxygen and promote hypoxia (Vahtera et al. 2007) (Conley et al. 2011).

While riverine Fe supply may potentially fuel cyanobacterial growth in the Baltic, Fe removal during estuarine mixing may act in the opposite direction, by enhancing P burial in sediments (Lenstra et al. , Lalonde et al. 2012, Asmala et al. 2017). However, during periods of hypoxia, recycling of P and Fe from sediments due to reducing conditions is enhanced, which have been shown to sustain cyanobacterial abundance (Funkey et al. 2014).

Cyanobacterial blooms and hypoxia have severe impacts on ecosystem services in the Baltic Sea through habitat degradation, as well as changes in food web dynamics, biodiversity, fishery, and aesthetic values (Vahtera et al. 2007, HELCOM 2010, Conley et al. 2011). The environmental status of the Baltic Sea has received ample attention from the scientific community, politicians and the civil society, and there is a broad consensus that efforts should be made to reduce eutrophication and cyanobacterial blooms (Zillén and Conley 2010). While management efforts have been focused on reducing N and P inputs, the role of Fe in controlling nutrient dynamics in the Baltic warrants further studies.

Motivation of the thesis

A striking trend of increasing Fe concentrations has been reported for Swedish and Finnish rivers draining into the Baltic Sea, but also for many other regions in Northern Europe and North America (Kritzberg and Ekstrom 2012, Sarkkola et al. 2013, Temnerud et al. 2014, Weyhenmeyer et al. 2014, Björnerås et al. 2017). The consequences of increasing riverine Fe for the receiving system depend first and foremost on the fate of Fe in the estuarine salinity gradient.

The overarching aim of this thesis was to gain a better understanding of what factors determine the fate of Fe from boreal rivers across estuarine salinity gradients. As mentioned previously, it has been proposed that the fate of Fe in estuarine gradients is largely dependent on the relative contribution of Fe-OM and Fe (oxy)hydroxide (Stolpe and Hassellöv 2007, Krachler et al. 2012, Kritzberg et al. 2014). The current understanding of how these two phases respond to increasing salinity relies on indirect assessments based on size separation, such as membrane filtration, ultrafiltration, and flow field fractionation coupled to ultraviolet and inductively coupled plasma-mass spectrometry detection techniques (Forsgren et al. 1996, Hassellöv et al. 1999, Stolpe and Hassellöv 2007, Krachler et al. 2010). While such studies have improved our knowledge of the physical partitioning of Fe fractions, Fe-OM and Fe (oxy)hydroxides are overlapping in size, from the nano- to the μm -range (Wilkinson and Lead 2007, Hirst et al. 2017).

Identifying the boundaries and separating macromolecules, nanoparticles, and colloids in environmental systems is highly challenging given the complex interactions among phases (Lead and Wilkinson 2006). Thus, to fully understand how the different Fe phases respond to increasing salinity, and ultimately what determines Fe stability across estuarine gradients, a direct assessment of the Fe speciation is required. For that purpose, X-ray absorbance spectroscopy (XAS), which has previously used to determine the Fe species in water samples (Sundman et al. 2014), was used. Several studies have also suggested that Fe isotopic composition reflect Fe speciation (Ingri et al. 2006, Schroth et al. 2011, Ilina et al. 2013). In addition to Fe speciation, the stability and transport of colloids depend on their size and surface charge. Thus, by combining methods that assess Fe speciation with methods that characterize colloidal properties, a more comprehensive picture can potentially be reached.

The specific research themes I address in this thesis are:

- i. Variability in the contribution of Fe-OM complexes and Fe (oxy)hydroxide in river mouths.

- ii. The link between Fe speciation and FeTC along estuarine salinity gradients.
- iii. Spatial and seasonal factors controlling variability in Fe speciation.
- iv. The link between Fe isotopic composition and Fe speciation.
- v. Colloidal size distributions in river waters and if they differ with regards to surface charge or Fe speciation.
- vi. How the colloidal size distributions are affected by increasing salinity, and how that connects to FeTC.

In this thesis, XAS was applied for a direct characterization of the Fe speciation (Papers I – IV). Paper I is focused on the comparison of Fe speciation in *in situ* river waters and aggregates formed at increasing salinity, to establish if there is preferential removal of a particular phase. Paper II is aiming to link differences in Fe speciation to variability in FeTC across salinity gradients. This was evaluated based on samples from eight river mouths, four of which were sampled at both high and low flow conditions, and two upstream samples from one of the river catchments. Based on these samples the effect of seasonal and spatial controls on Fe speciation could also be addressed. In Paper III two northern rivers were sampled from winter base-flow (pre-flood) over the spring flood and until post flood conditions. The purpose was to explore how discharge driven changes in hydrogeological pathways affect Fe speciation and FeTC. Moreover, the isotopic signature of Fe was determined to explore the links between Fe speciation and isotopic composition. Paper IV is combining XAS and dynamic light scattering (DLS) to explore Fe speciation and colloidal characteristics such as size and surface charge, and how these are affected at increasing salinity.

Methods and implementation

Sampling

For this thesis, ten rivers along the Swedish coastline (Figure 1) were considered. They were chosen to include a wide range of climate and catchment characteristics as well as Fe and organic carbon (OC) concentrations (Table 1). The size of river catchments varied between 758 and 28113 km² and forest was the dominating land cover for all catchments. Rivers in the northern part of Sweden are in the subarctic climate zone with a mean annual temperature of ~3°C and marked with seasonal temperature variations, with long cold winters and short, mild summers (Peel et al. 2007). The river catchments in the south are located in a milder climate with a mean annual temperature around 10°C with less pronounced temperature variability over the year (SMHI; <http://vattenweb.smhi.se>).

Table 1. Basic water chemistry data and catchments information of sites considered in this study.

| Site | Catchment size ^a (km ²) | Discharge ^a (m ³ /s) | Total Fe ^b (µg/L) | TOC ^b (mg/L) | pH ^b |
|------------|--|--|------------------------------|-------------------------|-----------------|
| R. Kalix | 28113 | 333 | 965 | 4.9 | 6.9 |
| R. Råne | 4207 | 55 | 1550 | 8.4 | 6.8 |
| R. Öre | 3029 | 35 | 995 | 11.8 | 6.7 |
| R. Emån | 4471 | 33 | 740 | 14.5 | 7.1 |
| R. Alster | 1525 | 10 | 665 | 14.2 | 6.9 |
| R. Ljungby | 758 | 2 | 100 | 16.8 | 6.8 |
| R. Lyckeby | 810 | 6 | 1800 | 19.9 | 6.7 |
| R. Mörrum | 3369 | 28 | 505 | 13.7 | 7.0 |
| R. Helge | 4724 | 32 | 1900 | 18.3 | 7.3 |
| Biveröd* | 28 | 1 | n.a. | 26.5 | 6.7 |
| Svineö* | 44 | <0.1 | 4200 | 29.0 | 4.4 |
| R. Örekil | 1340 | 26 | 555 | 11.7 | 6.9 |

^aData from the Swedish University of Agricultural Sciences (SLU) (<http://miljodata.slu.se/mvm/>). ^bSwedish Meteorological and Hydrological Institute (SMHI) (<http://vattenweb.se>). *upstream samples of River Helge (5 year average of discharge, total Fe, total organic carbon (TOC) and pH from 2010-2015).

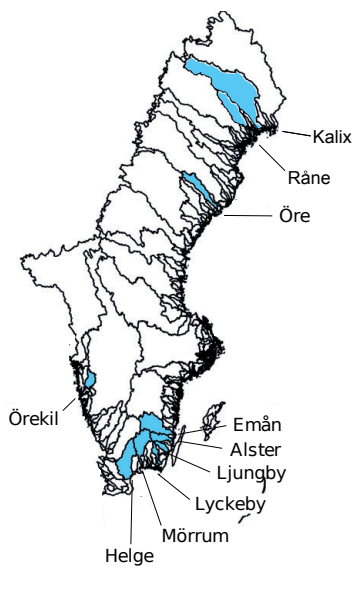


Figure 1. Map of river catchments in Sweden. The rivers sampled for this thesis are shown with name and the catchment marked in blue.

To encompass seasonal variability the river mouths of Emån, Lyckeby, Mörrum and Helge were sampled both during autumn and spring (Paper I). Moreover, the rivers Kalix and Råne were sampled from early May to mid-June, to cover base-flow condition during pre-flood, peak discharge and post-flood of the annual spring flood (Paper III). For spatial variability, the River Helge was sampled at the river mouth and two upstream sites: the 1st order stream Svineö draining a peat bog, the 2nd order stream Biveröd in a predominantly forested landscape further down the river course (Paper II). Additionally, for two rivers (Öre and Örekil), transects starting at the river mouth and extending over the estuarine salinity gradient were sampled (Paper II).

While many studies addressing Fe dynamics in aqueous systems focus on the filterable fraction, samples for this thesis were not filtered, but a 150- μm mesh was used to ensure homogenous samples free of large detritus. Filtration is motivated when a large fraction of total Fe concentrations are bound in biota, as in marine systems or turbid waters. However, in these boreal rivers Fe concentrations are exceptionally high and the contribution of Fe bound to biota is negligible. Thus, since an overarching aim of this thesis is to understand to what extent Fe survives estuarine mixing, it is imperative to include all Fe. Filtration would mean that up to 60 % of riverine Fe may not be considered (Pokrovsky and Schott (2002), and that the interactions between particulate, colloidal and dissolved Fe phases would be omitted.

Analytical methods

In artificial seawater mixing experiments, FeTC was experimentally evaluated. For this purpose river water was mixed with artificial seawater at a fixed ratio (6:1 vol:vol). The samples were placed on a shaker in darkness for 24-48h, before separating the salinity-induced aggregates by centrifugation. Total Fe concentration was measured in the supernatant and related to that of the *in situ* sample to determine the FeTC as the fraction of Fe remaining in suspension (%). A similar procedure was adopted to separate aggregates that were characterized for Fe speciation (XAS) and isotopic composition, but with a larger volume of water to acquire enough material.

The FeTC derived from the artificial seawater mixing experiments were in well aligned with the estuarine transects sampled. In Figure 2, the theoretical values for Fe along the estuarine salinity gradient, calculated based on salinity induced aggregation in the artificial seawater mixing experiments, and dilution estimated by salinity, are shown next to the measured *in situ* values. Theoretical values were only slightly lower than the *in situ* values for River Örekil, while a larger deviation was found for River Öre, especially at the lower levels of salinity. Centrifugation steps in the lab experiments may overestimate the loss of Fe, whereas in estuaries, aggregation may occur without significant sedimentation (Forsgren and Jansson 1992).

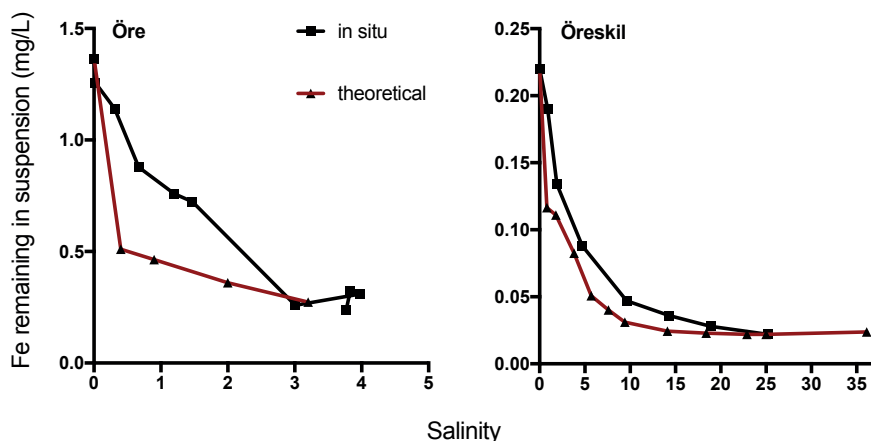


Figure 2. Fe remaining in suspension in response to increasing salinity for river Öre and Örekil. The squares denote the *in situ* measurements and the triangles the theoretical values. Theoretically calculated Fe concentrations are based on the loss of Fe in the artificial seawater mixing experiments and the dilution factor (From Paper II).

Synchrotron-based X-ray absorption spectroscopy (XAS) is a powerful method to determine the Fe speciation and oxidation state in natural samples (Vilg -Ritter et al. 1999, Karlsson et al. 2008). The basic principles behind XAS is that X-rays strike and excite core electrons of an atom, which in turn get either promoted to an unoccupied level, or ejected from the atom and consequently create a core hole. Dissociation of the electron will produce an excited ion as well as a photoelectron. The scattering of the photoelectron will modulate the absorption coefficient, and both the local transitions and the effects from the out-going photoelectron can be measured and analyzed (Newville 2004).

XAS was used in all studies of the current thesis to distinguish between Fe-OM complexes and Fe (oxy)hydroxides, and to determine the oxidation state of Fe. The analyses were done on freeze-dried samples of *in situ* river water as well as salinity induced aggregates.

The XAS data was analyzed using several methods to gain structural information. The wavelet transform (WT) method was used to qualitatively interpret the backscattering of atoms in higher coordination shells (Funke et al. 2005). The different backscattering atoms appear in different areas in the WT plot depending on their atomic number and consequently the number of electrons, as shown in an example in Figure 3. The feature representing Fe (oxy)hydroxides originates from Fe-Fe scattering paths and is indicated as Fe. Fe-OM complexes are represented by a Fe-C and a multiple Fe-C-C(O or N) scattering path, indicated as C and C/O, respectively.

The local coordination environment of Fe was further analyzed by using the extended X-ray absorption fine structure (EXAFS) region. EXAFS provides data on the local structure by quantitative modeling with input structures related to the natural samples. In our case goethite and complexed trisoxalatiron(III) were used,

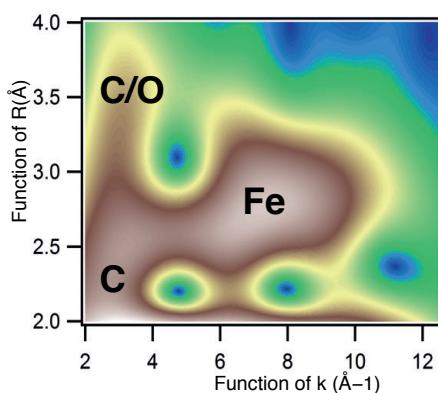


Figure 3. High resolution WT modulus ($\eta = 4$, $\sigma = 2$) of EXAFS data of a river water sample. The areas representing the different Fe paths are denoted by C (Fe-C), C/O (Fe-C-C/O), and Fe (Fe-Fe).

since they contain the relevant scattering paths (Fe–Fe, Fe–C, and Fe–C/O) allowing us to distinguish between Fe-OM complexes and Fe (oxy) hydroxides. The coordination number (CN) is gained from the EXAFS fitting and indicates the contribution of a path to the samples (Newville 2004).

To estimate the proportion of the two dominating Fe phases (Fe-OM complexes and Fe (oxy)hydroxides) in our samples, a linear combination fitting (LCF) analysis was performed on the k^3 -weighted EXAFS spectrum (Gräfe et al. 2014). As reference spectra, Fe oxides such as ferrihydrite, goethite, lepidocrocite and hematite, and Fe(III) complexed to standard Suwannee River fulvic acid were used.

Finally, based on the results from the EXAFS fitting and the LCF analysis, the relative contribution of Fe-OM complexes and Fe (oxy)hydroxides in the samples was estimated by 1) a ratio of the CN from the fitting results between the Fe-C path and the shortest (edge-sharing) Fe-Fe path (*i.e.* CN_{Fe-C}/CN_{Fe-Fe}); and 2) a ratio of the Fe-OM fraction and the sum of Fe-oxide fractions from the LCF analysis. There was agreement between the two ratios and a significant correlation between the CN ratio and the LCF ratio was observed (Paper II and III).

The average oxidation state of Fe in the samples was determined by analyzing the X-ray absorption near edge structure (XANES) (Wilke et al. 2001), $FeK\beta_{2,5}$ X-ray emission spectra (Bergmann and Glatzel 2009) and High-Energy Resolution Fluorescence Detection (HERFED). The location of the pre-edge peak as well as the intensity and centroid energy of it, provide information on the redox state and the symmetry of the Fe present in the sample.

A limitation in the use of XAS analysis was that the Fe remaining in suspension at high salinity could not be analyzed. The high concentration of salt diluted the Fe concentration in the freeze-dried samples to levels below what is required for XAS.

XAS data was collected at the beamline I811 MaxII, MaxLab Lund Sweden for Paper I and II, and at beamline 4-1, Stanford Synchrotron Radiation Lightsource (SSRL), California, USA for Paper III and IV. Further, for Paper II $FeK\beta_{2,5}$ and HERFED spectra were collected at beamline ID26 of the European Synchrotron Radiation Facility (ESRF), Grenoble, France.

Fe-isotope analysis reveals the proportion of the four stable isotopes of Fe (^{54}Fe , ^{56}Fe , ^{57}Fe and ^{58}Fe) in a given material. The relative proportion of these isotopes, in *e.g.* aqueous Fe, deviate from that in the continental crust, due to fractionation by processes that mobilize and transfer Fe. Processes that fractionate Fe isotopic composition include mineral dissolution (Bullen et al. 2001), adsorption to minerals or OM (Beard et al. 1999), oxidation (Johnson et al. 2002), organic complexation (Dideriksen et al. 2008) and precipitation (Balci et al. 2006). It was suggested by Ingri et al. (2006) that Fe isotope compositions ($\delta^{56}Fe$) can be used to distinguish between Fe-OM complexes and Fe (oxy)hydroxide in river water.

Further, $\delta^{56}\text{Fe}$ values have also been suggested to reflect the source areas, e.g. whether aqueous Fe originates from organic rich soil layers or ground waters (Escoube et al. 2015, Ingri et al. 2018). In this study $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$, which represents the deviation in per mil relative to the IRMM-014 standard, were reported. Fe isotopes were measured on *in situ* river water (freeze-dried), salinity induced aggregates (freeze-dried) and the supernatant produced at enhanced salinity after centrifugation.

Dynamic light scattering (DLS) was used to measure the colloidal size distribution in river mouth samples. This method measures the Brownian motion and Doppler shifts induced by a laser beam to determine the size and size distribution of particles in suspension (Babick et al. 2012, Xu 2015). An advantage of DLS is that it involves no perturbation, which is especially important for dynamic non-equilibrium systems, like colloids, which are sensitive to physical and chemical disturbance (Filella 2007). However, DLS data on polydisperse systems, like river water, are difficult to interpret and the results are non-quantitative. Further, colloids that dominate the scattering intensity may make other distributions hard to detect. It should be noted that colloidal size distribution in natural systems reflects a wide and continuous range of sizes. The distributions described in this study are a product of the data analysis. Therefore, the obtained result provides a model to understand colloidal distributions and their characteristics, but should not be viewed as distinctly different groups of molecules or colloids.

The zeta potential or electrokinetic potential in colloidal systems, is the potential difference between the mobile dispersion medium and the stationary layer of the medium attached to the dispersed particle (Hunter 2013). The surface charge describes to what extent the dispersion is electrostatically stabilized by inter-particle repulsion (Hassellöv et al. 2008) and consequently has a major influence on the stability and fate of colloids (Dunphy Guzman et al. 2006, Hanaor et al. 2012). Fe colloids heavily coated by OM are negatively charged due to carboxylic and phenolic functional groups of the organic molecules (Hajdú et al. 2009, Hu et al. 2010, Dickson et al. 2012), whereas Fe oxides without OM interactions usually display a positive surface charge (Baalousha 2009). The measurement of the zeta potential was limited to low salinities (\leq salinity 1).

Main findings

Fe speciation in river water

The two Fe phases previously identified by XAS in freshwaters – Fe-OM complexes and Fe (oxy)hydroxides (Sundman et al. 2014, Yu et al. 2015) – were found in all river mouth samples (Paper I – IV) and a selection is shown in the WT plots in Figure 4. The relative contribution of the two Fe phases varied widely, demonstrated for instance by the strong dominance of Fe (oxy)hydroxides in river Örekil, and dominance of Fe-OM complexes in river Lyckeby (Figure 4). This was further confirmed by the CN- and LCF- ratios, which spanned low values indicating a high contribution of Fe (oxy)hydroxides (river Örekil in Table 2 and Table 3) to high values representing a high contribution of Fe-OM complexes (river Lyckeby).

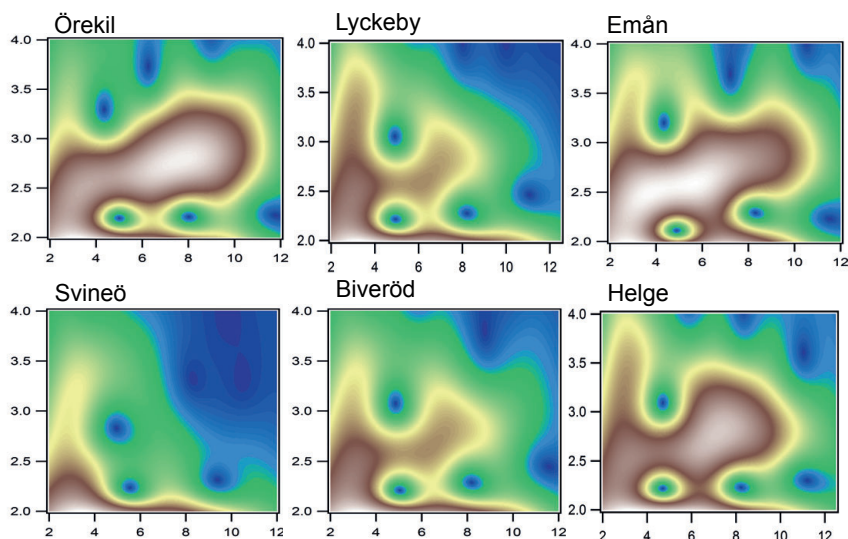


Figure 4. A selection of high resolution WT modulus ($\eta=4$, $\sigma=2$) of EXAFS data from river mouths, and the two upstream sites (Svineö and Biveröd) of the river Helge catchment. The samples are plotted as a function of k (\AA^{-1}) on the x-axis and R (\AA) on the y-axis. Data from Paper II.

Table 2. k^3 -weighted Fe K-edge EXAFS fits of a selection of river mouth samples and the two upstream samples Svineö and Biveröd.

| Site | Fe-O (SS) | | | Fe-Fe (SS) | | Fe-Fe (SS) | | Fe-C (SS) | | Fe-C/O (MS) ^a | | ΔE^b | CN-ratio ^b |
|------------|-----------|------|------------|------------|------|------------|------|-----------|------|--------------------------|------|--------------|-----------------------|
| | CN | R(Å) | σ^2 | CN | R(Å) | CN | R(Å) | CN | R(Å) | CN | R(Å) | | |
| R. Örekil | 5.9 | 2.04 | 0.0140 | 2.7 | 3.13 | 0.8 | 3.40 | 2.2 | 2.93 | 4.3 | 4.21 | 7.1 | 0.8 |
| R. Lyckeby | 6.0 | 2.03 | 0.0131 | 1.0 | 3.12 | 0.4 | 3.46 | 2.8 | 2.99 | 5.6 | 4.23 | 5.8 | 2.7 |
| R. Emån | 6.0 | 2.03 | 0.0143 | 1.5 | 3.12 | 0.5 | 3.45 | 2.5 | 2.98 | 5.1 | 4.23 | 6.3 | 1.6 |
| Svineö* | 5.4 | 2.05 | 0.0132 | - | - | - | - | 3.1 | 3.00 | 6.3 | 4.32 | 10 | - |
| Biveröd* | 6.0 | 2.01 | 0.0118 | 1.2 | 3.09 | 0.3 | 3.44 | 2.0 | 2.94 | 4.0 | 4.18 | 3.1 | 1.7 |
| R. Helge | 6.1 | 2.03 | 0.0136 | 1.4 | 3.11 | 0.7 | 3.48 | 2.3 | 3.02 | 4.6 | 4.21 | 5.9 | 1.6 |

Abbreviations were used for coordination number (CN), bond distance (R), Debye-Waller factor (σ^2), Single-Scattering (SS) and Multiple-Scattering (MS). ^aFe-C/O is correlated to CN (Fe-C) x 2. The Debye-Waller factor of Fe-C/O was correlated to σ^2 (Fe-C) x 2. The σ^2 for both Fe-Fe was 0.01, adapted from Maillot et al. (2011) and for Fe-C it was 0.0075 adapted from Sundman et al. (2014). S_0^2 was set to 0.85. ^bRatio between the CN of the first Fe-C path and the Fe-Fe path. *Svineö and Biveröd are upstream samples from river Helge

F-tests comparing EXAFS models with and without the Fe-C and Fe-C/O scattering paths confirmed their presence at the 92 % confidence level or better in all river mouth samples. The significant contribution of Fe-OM complexes in the river mouth samples is in contrast to thermodynamic modeling, which has suggested a dominance of ferrihydrite (≥ 97 %) for these systems (Wällstedt et al. 2010).

Table 3. LCF results for river mouth samples Örekil, Lyckeby and Emån, Helge and the upstream samples Svineö and Biveröd.

| Site | Fe-OM F(III) bound to Suwannee river fulvic acids | Fe-oxides | | | LCF ratio ^a (Fe-OM/ Fe-oxides) | Chi-Sq |
|------------|--|--------------|---------------|------|---|--------|
| | | Ferrihydrite | Lepidocrocite | Sum | | |
| R. Örekil | 0.27 | 0.43 | 0.13 | 0.56 | 0.47 | 62.4 |
| R. Lyckeby | 0.39 | 0.39 | 0.05 | 0.44 | 0.89 | 24.9 |
| R. Emån | 0.28 | 0.5 | 0.06 | 0.56 | 0.50 | 35.4 |
| Svineö* | 0.58 | - | - | - | - | 88.3 |
| Biveröd* | 0.42 | 0.36 | 0.06 | 0.42 | 1.00 | 9.6 |
| R. Helge | 0.27 | 0.52 | 0.07 | 0.59 | 0.46 | 24.2 |

^aratio between F(III) bound to Suwannee river fulvic acids and the sum of the Fe oxide; *upstream samples of river Helge

LCF analysis identified ferrihydrite and lepidocrocite, representing Fe (oxy)hydroxides, and Fe(III) complexed by OM, as the main components in all samples (Paper II and Paper III), but with a variable contribution (Table 3).

The Fe oxidation state in all river mouth samples was dominated by Fe(III). The XANES data suggested the presence of a mixture of amorphous Fe(III) hydroxides (ferrhydrite) and Fe-OM complexes in most samples. Moreover, some samples feature characteristics of goethite and lepidocrocite (Paper II and Paper III) (Sundman et al. 2014). The two samples taken upstream in river Helge catchment in Paper II, showed the presence of Fe(II). A gradual change from Fe(II) towards dominance of Fe(III) in the river mouth was observed (Figure 5).

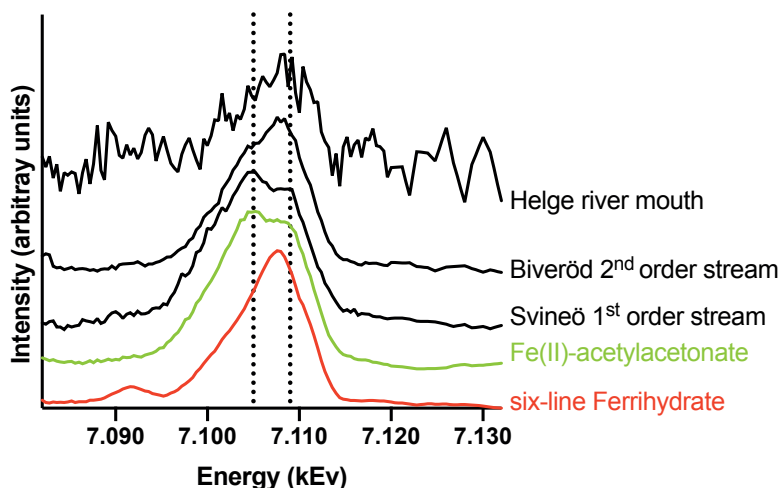


Figure 5. FeK $\beta_{2,5}$ X-ray emission spectra of the river mouth sample and the two upstream samples of river Helge. And the two references for Fe(II) (green) for Fe(III) (red) from Paper II. The dotted lines are included for visual guidance according to the peaks in the references.

The fate of Fe at increasing salinity

All artificial salt mixing experiments in this thesis demonstrated a non-conservative behavior of Fe (Figure 7, left graph), congruent with the existing literature (Sholkovitz 1976, Krachler et al. 2005, Kritzberg et al. 2014). FeTC among rivers varied, i.e. from 1 to 24 %. The high FeTC for most of the rivers studied go along with field and laboratory studies showing that high-latitude DOC-rich rivers exhibit high Fe-carrying capacity (Sholkovitz 1976, Dai and Martin 1995, Powell et al. 1996, Krachler et al. 2005). Increasing salinity had little effect on the TOC concentration as previously observed (Kritzberg et al. 2014, Linkhorst et al. 2017).

FeTC was positively correlated to the relative contribution of Fe-OM complexes (Paper I-IV), as exemplified in Figure 7, supporting that Fe stability across salinity gradients is linked to the Fe speciation and that the contribution of Fe-OM complexes are important for Fe export into the open sea (Laglera and van den Berg 2009, Batchelli et al. 2010, Krachler et al. 2010). The differences in the XANES regions between these natural Fe-OM complexes and binuclear model compounds (Blazevic et al. 2016), further suggests that the Fe-OM complexes are primarily mononuclear (Paper II).

Interestingly, the results revealed the presence of Fe-OM complexes also in the aggregates (Figure 6) illustrating that the control of Fe stability is not explained by the prevalence of the respective Fe phases alone. The loss of Fe-OM complexes could be due to high ionic strength compressing the water and consequently “salting out” of the organic complexes (Turner and Millward 2002, Turner et al. 2004). Thus factors such as colloid size and the chemical composition of the OM are likely to impact the behavior of Fe species (Krachler et al. 2015).

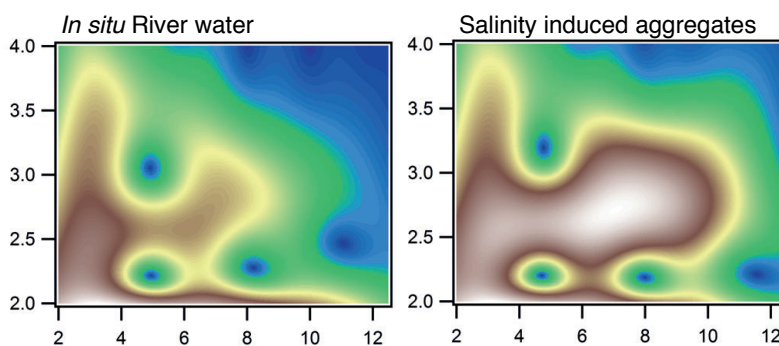


Figure 6. High resolution WT modulus ($\eta = 4$, $\sigma = 2$) of EXAFS data of an *in situ* river water sample and the corresponding salinity induced aggregates at salinity 25 from Paper I. The samples are plotted as a function of k (\AA^{-1}) on the x-axis and R (\AA) on the y-axis.

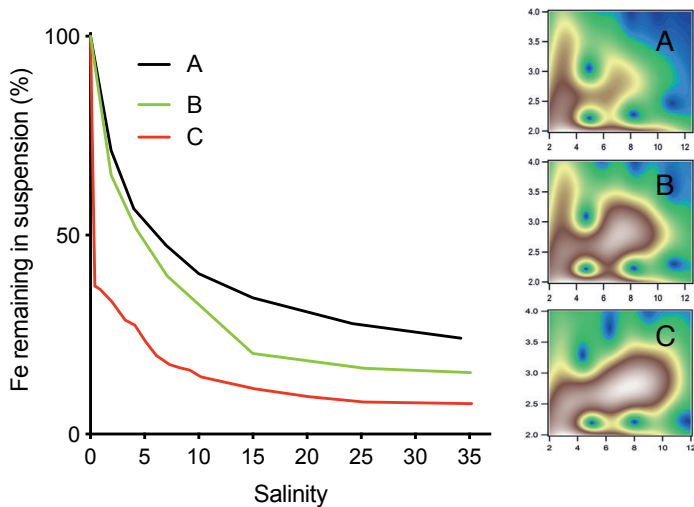


Figure 7. The change of Fe in suspension in response to increasing salinity (0-35) of three rivers Lyckeby (A), Mörrum (B) and Örekil (C) on the left and the corresponding WT plot on the right from Paper II.

Spatial and temporal variation of riverine Fe speciation

Given that there was large variability in Fe speciation across river samples, and that there was a relationship between Fe speciation and FeTC, it is imperative to understand what controls Fe speciation. Three samples along the river Helge catchment (Figure 4 and Figure 5). The sample taken most upstream (Svinö) displayed low pH and oxygen levels as well as a predominance of Fe-OM containing Fe(II). Further downstream Fe (oxy)hydroxide became more abundant with Fe(III) as the dominant oxidation state in the river mouth. The oxidation states found are in agreement with the literature, as the more soluble Fe(II) is favored under strongly reducing and highly acidic conditions (Waychunas et al. 2005, Stumm and Morgan 2012), whereas Fe(III) with a low solubility is predominating under oxic conditions at a circumneutral pH (Lofts et al. 2008). pH and OM were the main factors controlling Fe speciation in a boreal catchment according to Neubauer et al. (2013) with Fe-OM in wetland-influenced headwaters and increasing Fe (oxy)hydroxide downstream. Changing Fe speciation along the flow-path may in part be due to Fe-OM precipitating as Fe (oxy)hydroxide due to strong hydrolytic tendencies (Karlsson & Persson, 2012) as pH increases and OM declines, and also due to photo reduction of Fe(III)-OM (Waite and Morel 1984, Fujii et al. 2011, Karlsson and Persson 2012, Neubauer et al. 2013). Further, a

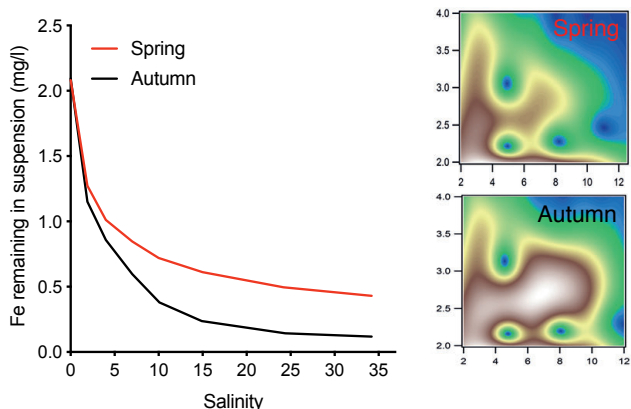


Figure 8. The change in Fe in suspension in response to increasing salinity (0-35) plotted on the left from river Lyckeby. Black line denotes sampling in autumn and red line denotes sampling in spring. High resolution WT modulus ($\eta = 4$, $\sigma = 2$) of EXAFS data from the data of the according river mouth sample.

change in the Fe source, with groundwater contribution getting more significant further downstream, supports the presence of Fe (oxy)hydroxide (Vasyukova et al. 2010). Consequently the Fe speciation present at the river mouth is determined both by the properties of the inflowing water and the chemical processing along the river flow path.

Fe speciation in the same river mouth varied seasonally, e.g. Fe-OM was contributing more to total Fe in the southern rivers during high discharge in spring than during low flow in winter (Figure 8, Paper II). In the northern rivers, Kalix and Råne, the Fe-OM contribution increased during the spring flood event (Paper III). The change in hydrogeological pathways between seasons impacts the source of Fe in the catchment and thereby the Fe speciation (Andersson et al. 2006, Neff et al. 2006, Pokrovsky et al. 2006). During winter the frozen top soil results in longer residence time of groundwater, promoting anoxic conditions and input of Fe(II) into the riparian zone, which rapidly oxidizes in stream water and precipitates to form Fe (oxy)hydroxides (Dahlqvist et al. 2007), supporting the higher contribution measured during winter. Rising water tables and surface runoff caused by higher discharge during events like heavy rain or spring flood, result in a mobilization of Fe-OM from organic-rich soil layers (Dahlqvist et al. 2007). The lower pH and higher OC concentration found in the samples during spring support a change in the Fe source.

The temporal variability in Fe speciation within rivers suggests that Fe speciation at a given time is not well predicted by catchment characteristics only. Notably however, Fe speciation (and FeTC) matched pH across the entire dataset. A high contribution of Fe-OM coincided with low pH, across river mouths, along

the flow-path of the Helge catchment, and in the spring samples compared to the autumn samples. This is probably in part due to a strong influence of pH on Fe speciation, but also a low pH may reflect strong influence on water chemistry from organic soils where Fe prevails as Fe-OM, in low order systems and under high flow conditions (Neubauer et al. 2013).

Link between Fe isotopic composition and Fe speciation

Fe isotope composition ($\delta^{56}\text{Fe}$) was measured on *in situ* river samples, in salinity-induced aggregates and in the supernatant. Aggregates formed in response to increasing salinity in the aggregation experiment separated by centrifugation. This procedure removed 78 to 93 % of *in situ* Fe, and XAS analysis showed that Fe (oxy)hydroxides were selectively removed and strongly dominating the aggregates (Paper III). Interestingly, the aggregates were consistently isotopically lighter than the *in situ* Fe, and the supernatant was consistently heavier (Figure 9). This suggests that the Fe (oxy)hydroxides, which dominated in the aggregates, were lighter and Fe-OM, which contributed more to the suspended fraction, was enriched. This is in line with recent studies that have identified ubiquitously high $\delta^{56}\text{Fe}$ values in the dissolved fraction in organic-rich rivers and lower $\delta^{56}\text{Fe}$ in the higher size fraction (Escoubé et al. 2009, Ilina et al. 2013, Escoubé et al. 2015). Moreover, the interpretation that Fe-OM complexes are isotopically heavier than Fe (oxy)hydroxides, are in line with high $\delta^{56}\text{Fe}$ found in organic soil layers, and heavier isotopic Fe signatures during increasing discharge in a first-order stream, *i.e.* closer to the source (Ingri et al. 2018).

There was also variation in the *in situ* Fe isotopic composition over the sampling period from pre-flood to post-flood conditions. XAS analyses revealed that the *in situ* Fe was strongly dominated by Fe (oxy)hydroxides over the entire period, with a tendency to higher contribution of Fe-OM at higher discharge. The Fe isotopic composition became lighter as discharge is increasing. The link between light isotope composition and dominance of Fe (oxy)hydroxides observed in the experimental separation, was not reflected in the observed *in situ* variability.

The *in situ* $\delta^{56}\text{Fe}$ correlated with OC concentrations, conductivity and oxygen isotope compositions, which suggests that the $\delta^{56}\text{Fe}$ is influenced by different source areas of Fe at varying hydrogeological conditions (Escoubé et al. 2015; Ingri et al. 2018). Thus, while there are links between Fe isotopic composition and Fe speciation, the fact that numerous processes along a river course affect and alter Fe speciation and causes isotopic fractionation, means that $\delta^{56}\text{Fe}$ values cannot be assumed to directly reflect Fe speciation at the river mouth.

The river mouth samples from Paper III showed little variation in Fe oxidation state and strong dominance of Fe(III), demonstrating that variation in

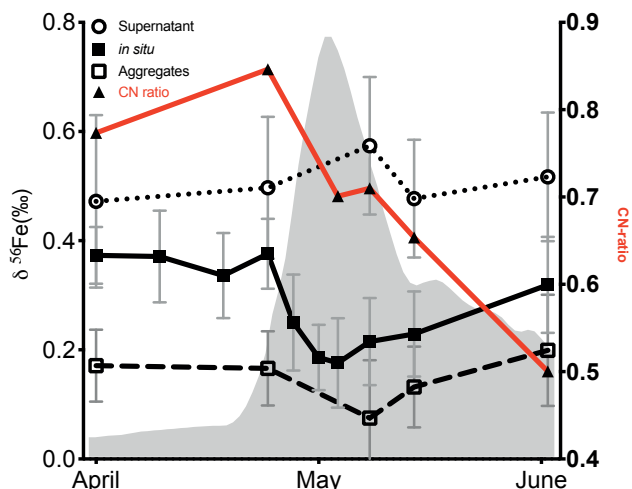


Figure 9. $\delta^{56}\text{Fe}$ (‰) of three fractions - *in situ* river water, salinity-induced aggregates, and supernatant - with error bars ($\pm 2\sigma$) and the CN-ratio of river Kalix (Paper III). The discharge is shown in the background for guidance.

$\delta^{56}\text{Fe}$ between aggregates and suspended Fe did not reflect differences in oxidation state. Previous studies have shown the presence of Fe(II) in soils and low-order streams (Sundman et al. 2014), and Ingri et al. (2018) suggested that low $\delta^{56}\text{Fe}$ values found below the groundwater table, and in stream water at winter base-flow, was due to mineral dissolution of Fe(II), which is preferential to the lighter isotope (Brantley et al. 2004). Thus, while it may be possible to infer Fe oxidation state and mobilization processes of Fe by isotopic signatures close to the source, establishing such links far down stream in the river mouth may be more challenging.

Colloidal size distribution and surface charge

Results from Paper I and II support the link between Fe speciation and FeTC, underpin the suggested role of river-derived OM complexes as carriers of Fe to marine waters. However, since Fe-OM complexes were also found in the salinity induced aggregates, it was apparent that the control of Fe stability is more complex. This implies that the division between small-sized Fe-OM complexes and larger Fe (oxy)hydroxides and how they respond to salinity may not be as distinct. Indeed, the size distribution of Fe-OM complexes and Fe (oxy)hydroxides is likely to be overlapping, and factors such as colloid size distribution and surface charge are likely to impact the behavior of Fe. To provide a more comprehensive

understanding of riverine Fe, assessments of Fe speciation and size distributions were combined.

XAS analyses showed that the *in situ* river samples contained both Fe-OM and Fe (oxy)hydroxides, and three size distributions were identified by DLS (Paper IV) (Figure 10). The largest size distribution found in the samples ranged from 300 to 900 nm and was largely removed by filtration (0.1-, 0.2-, and 0.45- μm). Filtration retained a large fraction of the Fe (29 - 62 %), around half of the absorbance at 420 nm but almost none of the organic carbon. This is in accordance with Fe being predominantly found in large size ranges, whereas OC is found in smaller colloidal size ranges (Pokrovsky and Schott (2002). The high Fe:OC ratio of the large distribution retained by filtration suggests the presence of large Fe-rich colloids dominated by Fe (oxy)hydroxides.

The filtration reduced the dominant scattering by the large size distribution, revealing a small distribution between 10 to 40 nm, (Lyckeby in Figure 10). This small distribution displayed a positive surface charge, suggesting that too was dominated by Fe (oxy)hydroxides. The positive charge indicated that the Fe oxide nanoparticles were not neutralized by surface interactions with OM. Similar sized Fe colloids without interaction with OM was identified by Hirst et al. (2017) in the Lena river. This distribution further matches an Fe-rich distribution (3-50 nm) detected by flow field-flow fractionation (FIFFF) in several studies and inferred to consist of Fe (oxy)hydroxides (Lyvén et al. 2003, Andersson et al. 2006, Dahlgqvist et al. 2007).

The third and intermediate size distribution (100-200 nm) had a negative surface charge. Based on the small contribution of OM in the other two distributions, and the negative charge, this intermediate size distribution was assumed to contain organic colloids. Moreover, since the smallest and largest distributions were dominated by Fe (oxy)hydroxides, Fe-OM should be present in the intermediate distribution.

The co-existence of positively and negatively charged colloids in the samples may seem unexpected. However, negatively charged species found are only weakly charged, which may explain the negligible interactions with the positively charged nanoparticles.

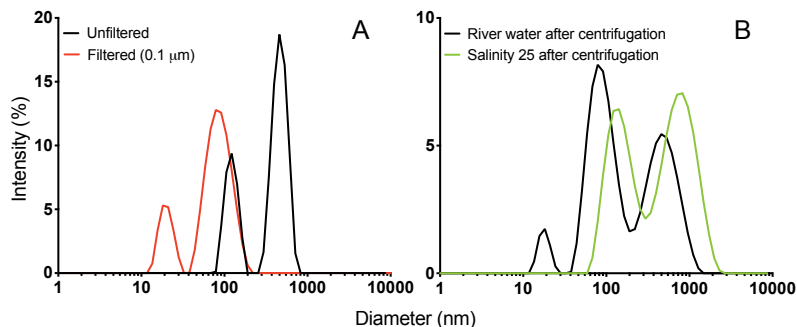


Figure 10. Overview of the colloidal size distribution of samples from River Lyckeby (from Paper IV). Panel A shows river water before and after filtration. Panel B shows river water at 0 and 25 salinity, both after centrifugation.

Salinity effect on the colloidal size distribution and surface charge

In all studies increasing salinity resulted in a major but variable loss of Fe, a selective removal of Fe (oxy)hydroxides and a minor if any loss of OM (Papers I-IV). DLS analysis made it possible to distinguish the effect of increasing salinity on different size distributions. The smallest distribution (10-40 nm) was no longer detectable at high salinity and the positive charge seen at ambient conditions decreased with increasing salinity, (Figure 10). This is in line with loss of Fe-rich colloids in the 3 to 50 nm size range at increasing salinity based on FIFFF (Stolpe and Hassellöv 2007).

Interestingly, the intermediate and largest size distributions observed in the river waters were still detected at high salinity. The intermediate size distribution is assumed to be dominated by OM and contain Fe-OM, and while these phases have been previously shown to be more stable to salinity induced aggregations, they have been assumed to be found in a much smaller size range (Stolpe and Hassellöv 2007). It is possible that such small organic complexes existed also in these systems, but were not detected by DLS. The fact that the larger distributions were still detected in response to high salinity, indicated that they were not charge stabilized, *i.e.* they did not require long range electrostatic repulsion to avoid aggregation due to van der Waal's interactions.

In all, the results obtained in Paper IV partially confirm interpretations and conclusions from previous, but at the same time suggest that our understanding of how Fe and OM respond to increasing salinity may have been biased by the focus on small size fractions, and omitted larger size fractions that may be surprisingly stable.

Conclusion and Outlook

The collective results from this thesis confirmed the existence of two riverine Fe phases – Fe-OM complexes and Fe (oxy)hydroxides. Their relative contribution varied widely among the studied rivers. The significant, sometimes dominant, contribution of Fe-OM in river mouths is especially interesting, since it is in contrast to thermodynamic modeling, which suggested a dominance of ferrihydrite ($\geq 97\%$) for these systems (Wällstedt et al. 2010).

The results further supported that Fe speciation is a key indicator when it comes to Fe export into marine waters, i.e. the occurrence of Fe-OM complexes promoted higher FeTC, and Fe (oxy)hydroxides were selectively lost at increasing salinity. Thus, the relatively high contribution of Fe-OM complexes in these boreal rivers, should facilitate Fe transport to open waters (Lenstra et al. 2018, Muller 2018). This in turn suggest that the high and rising Fe concentrations of rivers draining into the Baltic Sea (Björnerås et al. 2017) may result in more bioavailable Fe reaching open waters where it may favor cyanobacterial growth (Stal et al. 1999, Stolte et al. 2006). On the other hand, riverine Fe (oxy)hydroxides have been shown to promote P burial in coastal sediments of the Baltic (Lenstra et al. 2018), which may instead counteract eutrophication and cyanobacterial activity in the receiving system. It should be noted that this thesis explores the influence of salinity and pH gradients, and that other factors affecting the speciation and fate of Fe, such as photochemistry and biotic uptake, may come into play in the open water (Mopper and Kieber 2002, Mopper et al. 2014).

Fe speciation varied widely over both spatial and seasonal scales. This variability seemed connected to different source areas activated in different parts of the catchment and at different hydrogeological flow conditions. The contribution of Fe-OM complexes was higher in small streams than in river mouths, and higher during high discharge conditions, probably reflecting a higher influence of runoff from organic soil layers. Fe (oxy)hydroxide was more prevalent in river mouths, and during low discharge, when groundwater inflow was more significant. This suggests that riverine Fe entering saline waters during high flow conditions, such as spring flood, may be relatively more resistant to salinity-induced aggregation. Furthermore, when considering results from all studies of the thesis (I-IV), there was a tendency that the contribution of Fe-OM complexes was higher in river mouths of smaller catchments, which may reflect less “aging” of Fe-OM complexes into Fe (oxy)hydroxide. However, sampling

encompassing more spatial and temporal variability within river catchments would be required to substantiate such a hypothesis.

Separation of salinity-induced aggregates demonstrated that Fe (oxy)hydroxides were isotopically lighter than Fe-OM complexes. This difference in isotope composition could be exploited to track which Fe species survive across the estuarine salinity gradients. This would be informative since direct assessment of Fe speciation of the suspended fraction could not be assessed by XAS. Temporal variation of in situ $\delta^{56}\text{Fe}$ in river mouths could not be simply linked to Fe speciation. However, it would be interesting to combine XAS and isotopic analysis of Fe in soil water, riparian zones and first order streams, to see if it is possible to infer Fe speciation and mobilization processes from isotopic composition close to the source. This could further clarify how the different source areas of Fe impact the Fe speciation and isotopic composition found at the river mouth.

Three colloidal size distributions with different characteristics were detected in river waters. Fe (oxy)hydroxides were found both in a small distribution without organic matter interactions, and in a larger distribution associated with chromophoric OM. An intermediate size distribution was organically dominated and inferred to contain Fe-OM complexes. This confirms that the two Fe phases are not distinctly separated between “small” and “large” molecular sizes. In response to increasing salinity, the small Fe (oxy)hydroxide nanoparticles were rapidly lost, while both the larger distributions were still detected and seemingly more stable. Moreover, the presence of larger colloids as well as both Fe-OM complexes and Fe (oxy)hydroxides at higher salinity has important implications when considering nutrient and trace metal export into the open Sea.

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