IRON:
SPECIATION AND BIOAVAILABILITY IN THE BALTIC SEA

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Doctor Dissertation

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Für meinen Vater, meinen Bruder, meine Schwestern
und in Gedenken an meine Mum

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LIST OF ABBREVIATIONS

AS	Aaland Sea
BB	Bornholm Bay
BoB	Bothnian Bay
BS	Bornholm Sea
Chl a	Chlorophyll a
CTD	Conductivity Temperature Depth
ρ	Density
DFe	Dissolved iron fraction
DIN	Dissolved inorganic nitrogen (NO_2+NO_3)
DIP	Dissolved inorganic phosphorus
DOM	Dissolved organic matter
D_{VFE}	Upward turbulent diffusive transport of dissolved iron
EGB	Eastern Gotland Basin
FeSPM	Particulate iron
Total Fe	Total iron (DFe + FeSPM)
FIA	Flow Injection Analysis
g	Universal gravity constant
GFAAS	Graphite Furnance Atomic Absorption Spectrometry
HELCOM	Helsinki commission
HDPE	High density polyethylene
HNLC	High nutrient low chlorophyll areas
Ka	Kattegat
LDPE	Low density polyethylene
Luminol	5-Amino-2,3-dihydrophthalazine-1,4-dione

N^2	Buoyancy frequency
PMT	Photo multiplier tube
POC	Particulate organic carbon
PTFE	Polytetrafluorethylene
QUASIMEME	Quality Assurance of Information for Marine Environmental Monitoring in Europe
RV	Research vessel
S_{Fe}	Downward flux of particulate iron
Sk	Skagerrak
WGB	Western gotland basin

ZUSAMMENFASSUNG

Die Rolle des Eisens als Mikronährstoff sowie seine Spezifikationen im Meerwasser der zentralen Ostsee wurde über einen Zeitraum von zwei Jahren untersucht. Eine Annahme der Studie ist, dass Eisen als limitierender oder begünstigender Faktor die Ausbildung sommerlicher diazotropher Cyanobakterienblüten in der Ostsee steuert. Zwischen 2008 und 2009 wurden drei Forschungsreisen durchgeführt, während derer Oberflächenwasserproben entlang der verschiedenen Becken der Ostsee und die Wassersäule an drei charakteristischen Stationen (Gotland Tief, Landsort Tief, Ålands-See) beprobt wurden. Wasserproben aus oxischem und anoxischem Milieu wurden hinsichtlich ihres Gehaltes an löslichem Fe(II), gelöstem Eisen (DFe), partikulärem Eisen (FeSPM), sowie ihrer Konzentrationen an gelösten Makronährstoffen (N und P), Sauerstoff und Chlorophyll analysiert. Die höchsten Werte für Fe (II) (~ 39 nmol L^{-1}), DFe (~ 600 nmol kg^{-1}) und von FeSPM (~ 250 nmol L^{-1}) im Oberflächenwasser wurden im Sommer 2008 im Bottnischen Meerbusen gemessen; diese Region nimmt fast 50 % des gesamten Süßwasserzuflusses der Ostsee auf. Diese Beobachtung unterstützt die Annahme, dass die Einträge durch Flüsse die wichtigste Quelle für Makro- und Mikronährstoffen in der zentralen Ostsee sind. Typischerweise sind im Sommer, nach der Frühjahrsblüte und der Ausbildung einer Sprungschicht, die Makronährstoffe im Oberflächenwasser der Ostsee abgereichert. Wasserprofile im Gotland Tief erlaubten es, den vertikalen Fluss von partikulärem Eisen (SFe) und den nach oben gerichteten turbulenten diffusiven Transport von gelöstem Eisen (DVFe) durch die Redoxkline (~ 120 m), die das oxische Oberflächenwasser vom darunterliegenden anoxischen Wassermassen trennt, zu berechnen. Die an Profile der Brunt-Väisälä-Frequenz (Auftriebsfrequenz) gekoppelten Mittelwerte des SFe = 16 pmol m^{-2} d^{-1} und DVFe = 42 pmol m^{-2} d^{-1} bestätigen, dass der bioverfügbare gelöste Fe (II)-Pool im tieferen anoxischem Wasser nur schwer die Redoxkline überwinden kann und kaum das oxische Oberflächenwasser erreicht. Bezüglich des gelösten Fe (II) im Oberflächenwasser, betonen die Differenzen zwischen der theoretischen (~ 2 min) und der empirischen (35 min) Halbwertszeit (im Sommer und im Winter) die Bedeutung der photochemischen Prozesse und das Vorhandensein organischer komplexbildner Verbindungen (biogenen oder terrigenen Ursprungs), welche die Eisen-Ionen im oxischen Milieu stabilisieren.

Die potentielle Biomasse-Produktion wurde basierend auf hochauflösenden CO_2-Partialdruckdaten, Fe (II)-Konzentration (theoretisch bioverfügbare Fe-Spezies) im Oberflächenwasser und einem C:Fe Verhältnis von 100.000-500.000:1 berechnet. Das Ergebnis war deutlich höher (> 1000 pmol L^{-1} C) als der berechnete Wert, welcher auf Daten der Stickstoff-Fixierung in der Ostsee basiert und schließt damit eine mögliche limitierende Rolle von Fe für Cyanobakterienblüten in der Ostsee aus. Chlorophyll-Konzentrationen, Veränderungen der partikulären Eisen-Fraktion und des partikulären organischen Kohlenstoffs im Sommer 2008 und 2009 zeigen eine deutliche Aufnahme von Eisen durch verschiedene diazotrophe Bakterien während der Sommerblüte. Dies bestätigt die Hypothese, dass Fe ein fördernder Faktor für die Cyanobakterien in der Ostsee ist.

ABSTRACT

The role of iron as micronutrient and its speciation have been investigated for two years based on the hypothesis of iron as possible limiting or promoting factor of the summer cyanobacteria blooms in the Baltic Sea. Three research cruises between 2008 and 2009 were carried out with the target of sampling the surface along the different basins of the Baltic Sea and the water column of three characteristical stations (Gotland Deep, Landsort Deep and Aaland Sea). Measurements covered the determination of dissolvable Fe (II), dissolved iron (DFe) and particulate iron (FeSPM) both in oxic and anoxic waters together with dissolved macronutrients (N and P), oxygen and chlorophyll a analysis. Highest surface values of Fe (II) (~ 39 nmol L^{-1}), DFe (~ 600 nmol Kg^{-1}) and FeSPM (~250 nmol L^{-1}) were recorded in summer 2008 in the Gulf of Bothnia; the region where almost 50 % of the total freshwater in the Baltic Sea is discharged. These data support the idea that river inflow is one of the major sources of macro- and micronutrients for the surface waters of the Baltic Sea. After the spring bloom and the development of a seasonal thermocline, the common state of the Baltic Proper during summer is the depletion of macronutrients in the surface waters. Vertical profiles carried out at the main station of Gotland Deep allowed to calculate the downward flux of particulate iron (S_{Fe}) and the upward turbulent diffusive transport of dissolved iron (D_{VFe}) through the redoxcline (~ 120 m) that separates the oxic surface waters from the anoxic deep waters. Mean values of S_{Fe} = 16 µmol m^{-2} d^{-1} and D_{VFe} = 42 µmol m^{-2} d^{-1} coupled to buoyancy frequency profiles corroborate that the bioavailable dissolved iron pool (free and complexed Fe (II)) below the redoxcline hardly could reach the oxic surface waters. Related to dissolve Fe (II) in surface waters, discrepancies between theoretical (~ 2 min) and empirical (35 min) half-time for Fe (II) both in summer and winter emphasize the importance of photochemical processes and the presence of organic complexing compounds (biological or terrigenic origin), which stabilize the ferrous ions in oxygenated environments. An hypothetical biomass production was calculated based on Fe (II) concentrations (theoretically most bioavailable Fe species) in surface waters, high-resolution CO_2 partial pressure data and C:Fe (100.000-500.000:1) ratio from literature. The result was much higher (> 1000 µmol L^{-1} C) than the calculated biomass production based on nitrogen fixation data excluding iron as a possible limiting factor for cyanobacteria blooms in the Baltic Sea. Chlorophyll values and changes both in the particulate iron fraction and particulate organic carbon concentrations in reference to the summer blooms in 2008 and 2009 show an important uptake of dissolved iron by different diazotrophs. This confirms the hypothesis that Fe is a promoting factor for the cyanobacteria blooms in the Baltic Sea.

To summarise, the aims of the study are:

(1) To characterise and quantify the Fe (II), Fe (dissolved) and Fe (particulate) distribution in the surface- and deep water of the Baltic Sea as function of oxygen and salinity.

(2) To characterise and quantify the vertical turbulent diffusive dissolved Fe (II) transport from the anoxic deep water to the euphotic zone as this could be potentially, responsible for the fertilisation and the intensification of cyanobacteria blooms.

(3) To understand and quantify the relationship between Fe (II) and Fe (III) speciation in relation to the total Fe in the water column and to the annual growth of cyanobacteria in the Baltic Sea.

CHAPTER 1 – INTRODUCTION

1.1. Iron in seawater: Sources and its biological role

Since the planet formation, the role of iron and oxygen balance together with carbon has been a key point for the development of life on earth and the evolution from a primordial reducing atmosphere (~ 98 % CO_2) to the oxygenated atmosphere nowadays (Turner et al. 2001). Iron is the fourth most abundant element in the earth's crust and the most abundant one of the heavy metals. Iron is present in a large number of minerals (pyrite, goethite, rhodonite...) and ores (hematite, limonite, taconite…), being used for different industrial purposes. Despite its abundance on earth and its multiple applications, the dissolved iron content in seawater is at a very low level ranging from 20 pM to 1 nM (Bowie et al. 1998, Bowie et al. 2003). The concept of dissolved iron is operatively defined. In this study and commonly accepted, the dissolved iron is the fraction passing through a 0.4 µm pore size filter. The fraction of iron retained in such filter is defined as particulate iron. Along the text the abbreviations "DFe" and "FeSPM" will be used to name the dissolved and particulate iron fraction, respectively.

The low content of dissolved iron in surface waters of the world oceans is intimately related to the oxygen concentration. Iron enters the ocean via dissolved and suspended river-borne solids resulting from rock weathering, acid volatiles emanating from volcanically active areas and atmospheric input. Rivers and hydrothermal input with iron fluxes 625-962 Tg y^{-1} and 14 Tg y^{-1} respectively are together with atmospheric input (30 Tg y^{-1}) the main sources of iron in seawater (Haese 2006). The influence of the different iron sources varies along the world geography presenting seasonality changes in the fluxes discharged. Atmospheric input can be used as example for this regional profile. High deposition regions as the equatorial Atlantic and the west Pacific with fluxes up to 100 mg m^{-2} y^{-1} with North Africa desert and Asia as major sources, contrast with low deposition rates in areas as the Southern Ocean with values close to 1 mg m^{-2} y^{-1} (Haese 2006; Brust and Waniek, 2010). Sinking particles are mainly constituted by ferric hydroxides that are very insoluble and largely confined to particulate phases counting only a 10 % of the total atmospheric iron deposited as dissolved iron (Duce et al. 1991; Kuss and Kremling, 1999). Glacial input is one of the most obvious examples for seasonal sources of iron in seawater. In remote areas as the east Antarctic, ice melting contribution to the total flux of iron in surface waters can rise up to values of the 70 % (Lannuzel et al. 2007). The concentrations in freshwaters and ground waters of iron are in the order of micromolar (Pozdniakova et al. 1997; Staden and Kluever, 1998; Kawakubo et al. 1999; Hirata et al. 1999). In estuarine areas, where the river runoff is mixed with the seawater the dissolved iron fraction undergoes the main transformations. The most of the dissolved iron in river waters is present as hydrolysed Fe (III) ions surrounded by humic acids. The mixing with seawater cations neutralizes these colloids providing the coagulation of Fe-oxyhydroxides and humic acids finishing with the removal up to 80 % of the dissolved iron from the surface waters.

The oxidation state of the different iron species and thus, the metal speciation vary as a function of temperature, redox potential, pH, salinity, dissolved oxygen concentration and the presence of organic matter (Millero 1998; Liu and Millero, 2002). Iron is classified as a depleted element in seawater with a short residence time (Whitfield and Jagner, 1982) and the distribution of dissolved iron is dominated by its input pattern (Measures et al. 1995). Iron prensents values of residence time up to several days under different supply conditions (e.g. high aeolian input from Saharan dust; Croot et al. 2004).

The most common oxidation states in seawater are Fe (II) and Fe (III), being Fe (II) species thermodynamically unstable in oxic conditions. Thus its concentrations are much lower than Fe (III) species due to rapid oxidation by O_2 and H_2O_2 in the surface waters. To understand the speciation of iron in different aquatic environments many studies were focused on the different iron species and their interaction with the major components of natural waters and the different organic compounds under different physical and chemical conditions (i.e: temperature, pH, salinity and oxygen concentration). First studies in the eighties were focused on the effect of the ionic interactions from the major components of natural waters on the oxidation metals in natural waters, paying special attention to the oxidation of Cu (I) and Fe (II) ions (Millero 1985; Millero et al. 1987; Millero 1989; Millero and Sotolongo, 1989; Millero and Izaguirre, 1989). Following the oxidation mechanism proposed by Haber-Weiss (1934), the determining oxidation steps are

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^- \qquad [1]$$

$$Fe(OH)^+ + O_2 \rightarrow Fe(OH)^{2+} + O_2^- \qquad [2]$$

$$Fe(OH)_2 + O_2 \rightarrow Fe(OH)_2^+ + O_2^- \qquad [3]$$

being the third equation the determining step for the oxidation. With a pH interval 5-8 and a wide range of temperature and ionic strength, the oxidation rate at the presence of oxygen is second order with respect to H^+ or OH^-. The oxidation rate equation is given by

$$-d[Fe(II)]/dt = k[Fe(II)][OH^-]^2[O_2] \qquad [4]$$

The effect of various anions present in natural waters and seawater on the oxidation of Fe (II) has been determined in NaCl and NaX solutions at a constant ionic strength. The overall order of the rate constants is $HCO_3^- >> Br^- > NO_3^- > ClO_4^- > Cl^- >> SO_4^{2-} >> B(OH)_4^-$. At pH > 9 the oxidation rate increases largely attributed to the formation of $FeCO_3$ which has a faster oxidation rate than $Fe(OH)_2$. The formation of ion pairs with Cl^- and specially with SO_4^- and $B(OH)_4^-$ decreases the oxidation rate, reflecting slightly lower oxidation rate in the measurements carried out for seawater samples than the ones realised for fresh waters and synthetic media (NaCl, NaX) (Millero 1989; Millero 1992; Millero and Hawke, 1992).

Special attention deserves the work elaborated by Moffet and Zika (1987) about the kinetics of the Fe (II) oxidation by H_2O_2 process in seawater. The work suggests the process as source of OH increasing the oxidation rate and hydrogen peroxide as dominant oxidant of Fe (II) in sea surface waters. The accepted mechanism is the revised version proposed by Barb et al. (1951) (Millero and Sotolongo, 1989) given as

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^- \qquad [5]$$

$$Fe(OH)^+ + O_2 \rightarrow Fe^{3+} + OH^- \qquad [6]$$

$$OH + H_2O_2 \rightarrow OH_2 + H_2O \qquad [7]$$

$$Fe^{2+} + HO_2 \rightarrow Fe^{3+} + HO_2^- \qquad [8]$$

$$Fe^{3+} + O_2^- \rightarrow Fe^{2+} + O_2 \qquad [9]$$

Unlike with oxygen, the oxidation with H_2O_2 follows a first order rate in respect to H^+ or OH^-:

$$-d[Fe(II)]/dt = k_2[Fe(II)][OH^-][H_2O_2] \qquad [10]$$

Where $k_2 = k/ [OH^-] = k [H^+] / K_w^*$ and K_w^* is the dissociation product for water. For oxygen as oxidant of Fe (II), $Fe(OH)_2$ is the most reactive species in seawater. In the case of H_2O_2, $FeOH^+$ is the most reactive species and its oxidation rates are not affected by ionic interactions with Mg^{2+} and SO_4^{2-}. At high pH the presence of HCO_3^- and CO_3^{2-} produces an increase in the rate of both oxidation mechanism with oxygen and hydrogen peroxide theoretically due to the formation of $FeCO_3$ that is more reactive than $Fe(OH)_2$ and $FeOH^+$ (Millero and Sotolongo, 1989). At Fe (II) concentrations in the order of nanomolar, the hydrogen peroxide present in natural waters can compete with the oxygen for the oxidation of the different species of Fe (II). Remarkable is the case of coastal surface waters, where H_2O_2 concentrations are in the order of 200 nM, being able to control Fe (II) oxidation by hydrogen peroxide even at high pH (Santana-Casiano et al. 2006).

A further study of ionic interactions of Fe (II) and Fe (III) with minor anions present in seawater was performance by Millero et al (1995) focused on the speciation of Fe (II) and Fe (III) in seawater. The work was based on the application of the specific interaction and the ion pairing models known as the Pitzer equations (Millero et al. 1995). The estimation of the different activity coefficient related to the free iron and different anions species and the complexes they constitute are carried out in artificial media of NaCl and $NaClO_4$ solutions at different ionic strength and composition applying the Pitzer's equations. The access to reliable coefficient activities allows the calculation of the different association and dissociation constants (pK_{HX} and pK_{mX}) and the stability constants for the different ion pairs ((pK_{HX}^* and pK_{mX}^*) determining together with the values of the concentrations of the different free anions ($([X_i])_F$) the speciation of the metal ($[M]_F$ and $[MX_i]$) (Millero 1992; Millero et al. 1995). At pH 8, almost 76 % of the Fe (II) is free, 23 % belongs to ion pair or complex form as $FeCO_3$ and less than 1 % correspond to the first hydrolysis form "$FeOH^+$". In the case of Fe (III), its speciation in seawater is ruled by the hydrolysis of the free metal. The predominant specie with 92 % is $Fe(OH)_3$ that is quite insoluble, followed by the complexes $FeOH^{2+}$ and $Fe(OH)_4^-$ remaining less than 5 % and 3 %; respectively (Millero 1998; Liu and Millero, 2002).

The speciation of Fe (III) and Fe (II) is highly influenced by organic matter. Gledhill and Van den Berg (1994) calculated for seawater samples with 10 nM of Fe (III) and 4 nM of organic ligands that more than 27 % of the iron belonged to the formation of organic complexes. Fe (II) and Fe (III) are sensitive to form complexes with organic compounds as function of the media's pH and the stabilisation constants of the different ligands. Such complex formation can increase the rate of Fe (II) oxidation or decrease it due to the high stability of the organic compound (Santana et al. 2000). The presence of these organic compounds in the euphotic layer can generate reduction processes due to photochemically induced electron transfer from complexing organic ligands to oxidized metals. The important role of organic matter increasing the solubility of iron was contrasted by Rue and Bruland (1995) pointing out an organic complexation up to the 99 % of the total dissolved iron in North Pacific waters. The organic ligands bound to iron come from different origins (e.g. biogenic, atmospheric, fluvial) and exist at concentrations in excess of the dissolved metal itself (Rue and Bruland, 1995; Wu and Luther, 1995).

Understanding the iron cycle in seawater and the speciation in different aquatic environments (coastal waters, open seas, estuaries…) is the first step to estimate the impact and the role of the metal in marine systems. Relate to biota, iron is an important micronutrient during photosynthesis, nitrate reduction, nitrogen fixation and other type of oxidations. The lack of iron in a cell inhibits growth, nitrogen fixation and enzymatic processes, and also leads to the modification of the synthetic pigment composition (Wilhem et al. 1996; Paczuska and Kosakowska, 2003). Iron is an obligating micronutrient during diazotrophic cyanobacterial growth (Kustka et al. 2002; Berman-Frank et al. 2007). Depletion of cellular iron inhibits growth by promoting oxidative stress, targeting cellular redox reactions, and resulting in reduced rates of acquisition and assimilation of nitrogen, including nitrogen fixation (Raven 1988; Kustka et al. 2002). For diazotrophy in particular, the process requires between 10-20 times more quantities of iron than the uptake of dissolved nitrate from the water column (Kustka et al. 2002; Kustka et al. 2003) due to the iron demand for the synthesis of enzymes used during nitrogen fixation. To precise, the structural requirement for iron occurs in both subunits of nitrogenase and in providing reductant via ferredoxin. Characterisation of the iron bioavailable species of iron has been the subject of many studies (van den Berg 1995; Kuma et al. 1999; Wu et al. 2001; Breitbarth et al. 2009). Fe (II) is more soluble than Fe (III), and therefore is considered more labile and bioavailable. The transition across the lipid membrane of the cell involves the reduction of Fe (IIII), thus the acquisition of Fe (II) from the different phytoplankton does not require energetically costly uptake systems (Shaked et al. 2005; Morel et al. 2008).

The last step in the biological uptake of iron by the different marine organisms is the interphase marine environment-cell. The transport is carried out through the impermeable to charge or polar dissolved species lipid-bilayer membrane-by-membrane transport proteins. Two major iron transport mechanisms are known in cells (Sunda 2001). The main mechanism is based on ferrous or ferric ion membrane transporters by binding external Fe (II) or Fe (III) following a ligand exchange with labile iron species (Fig. 1). A second mechanism is carried out by an important class of organic ligands released by aquatic organisms, whose affinity for metals range from that of simple amino acids (major organic compounds class with sizable complexation affinity for metals) up to strong artificial chelating agents such as Ethylenediaminetetraacetic acid “EDTA” (Santana–Casiano et al. 2000). Special Fe complexing organic ligands increasing the bioavailability of Fe for biological uptake by enhancing its solubility under Fe-repleted conditions are compiled under the register of “siderophores” (Macrellis et al. 2001; Sunda 2001) (Fig. 2). Kuma et al. (1992) reported that during algal blooms in an estuarine environment 15 – 20 % of the total dissolved Fe was Fe (II) owing to the reduction by organic substances of phytoplanktonic origin. A study in the Gulf of Gdansk located in the Baltic Sea proved the presence of such organic ligands produced by local phytoplankton (Mucha et al. 1999) (Appendix I).

The increasing interest in connecting the iron speciation and its biological role started with different projects carried out in three specific areas of the world oceans defined as “High Nutrient, Low- Chlorophyll” (HNLC) where iron is considered one of the most important limiting factors in phytoplankton growth, which may have important implications for the global carbon cycle (Boyd et al. 2007). Those three specific areas are located in the subarctic Pacific, equatorial Pacific and the Southern Ocean characterised by the year round presence of macronutrients phosphate and nitrate at the surface. These three areas are upwelling zones but with differentiable features such as high seasonality of temperature and light (Southern Ocean) or shallow mixed surface layer (equatorial Pacific) (Watson 2001).

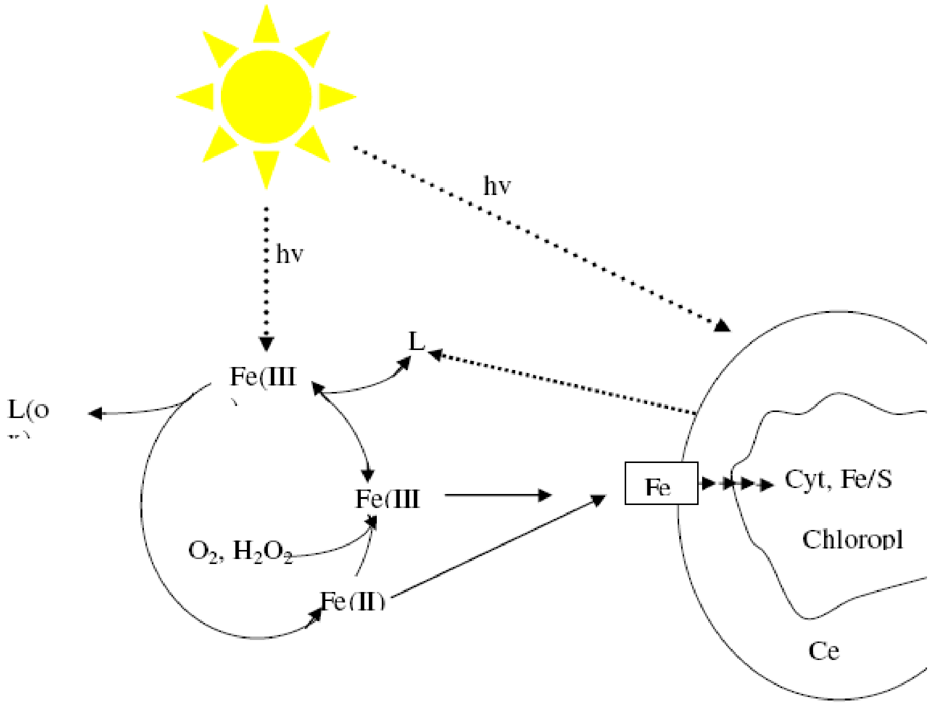

Figure 1.1. Ferrous and ferric ion membrane transporters bind with external Fe(II) and Fe(III). Extracted from Turner and Hunter, 2001.

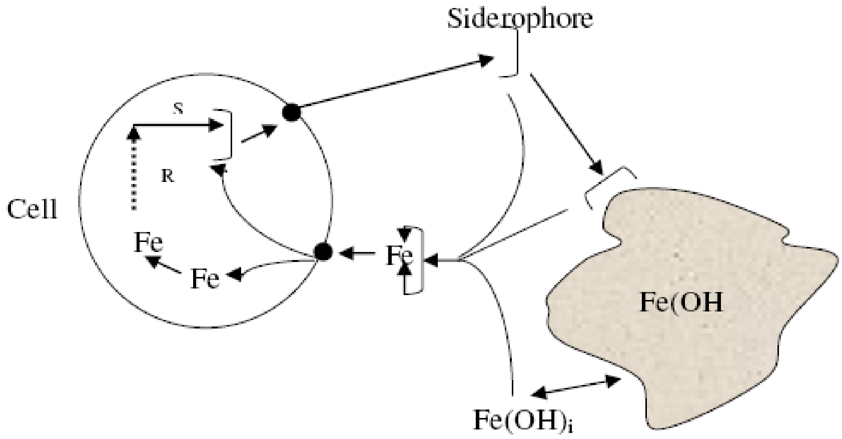

Figure 1.2. Siderophores systems in which cells excrete strong Fe (III) binding chelators. Extracted from Turner and Hunter, 2001.

The HNLC areas have different iron sources; upwelling is the main source both for the Antarctic and for equatorial Pacific where the atmospheric deposition makes a non-negligible contribution. Atmospheric input is the dominant source in the subarctic Pacific, but the soluble fraction of the atmospheric iron is considered to be lower than 10 % (close to 2 %) (Jickels and Spokes, 2001). Three main iron fertilisation experiments carried out in the eastern equatorial Pacific and in the polar Southern Ocean provided contrasted results regarding in the role of iron as co-limiting factor (Croot et al. 2001; Maldonado et al. 2001). The experiments IRONEX I and II carried out in an surface area close to 10 km in size of the equatorial Pacific and using a ferrous sulphate revealed some common features as a decay of the dissolved iron concentrations of the order of 1/e lifetime just one day after the artificial additions, increases of the quantum efficiencies of the phytoplankton and the increase of chlorophyll a that triplicate the initial concentration during the first three days. The addition of iron stimulated the growth of diatoms, which are responsible for nearly entirely new production and therefore affecting the “carbon pump” in surface waters. Similar results were obtained by the SOIREE mesoscale iron enrichment experiment carried out in the Southern Ocean, where an addition of iron induced a bloom dominated by diatoms slower but of higher extension that the one carried out in the IONEX II experiment. At both experiments IRONEX II and SOIREE, iron was co-limiting factor together with silicate limitation and light conditions respectively in the development of the different phytoplankton blooms (Watson 2001).

The real impact on the carbon cycle is hard to estimate based on such short artificial fertilisation experiments. The observation of natural iron enrichment in the Southern Ocean revealed that the efficiency of fertilization, defined as the ratio of the carbon export to the amount of iron supplied, was at least ten times higher than previous estimates from short term blooms. This leads to the assumption that iron has a significant effect in reduction of the atmospheric carbon dioxide concentration (Blain et al. 2007; Boyd et al. 2007). Over the last decade it has been assumed, that the high Fe-concentrations should be sufficient in the Baltic Sea because of the terrigenic-, atmospheric-, and riverine inputs. Thus, it has been assumed that limiting conditions like in the HNLC regions not occurre (Pohl et al. 2004; Pohl and Hennings, 2005). Iron is present at higher concentrations relative to the average of the iron concentrations in the world oceans waters but until now it is unknown what percentage of the dissolved fraction is bioavailable and what are the main features of the iron cycle in the Baltic Sea.

1.2. The hydrology of the Baltic Sea

Located in the Northern Europe, the Baltic Sea is a brackish water mass connected to the North Sea through the Kattegat with limited water exchange and a positive water balance (Fig. 1.3). Divided in different regions, it is stratified into a lower saline surface and a higher saline deep-water body, both separated by a permanent halocline located between 60 m (Bornholm Basin) and 80 m (Gotland Deep and Landsort Deep) depth. During spring due to the surface warming a thermocline develops between 10-20 m depth.

Annually the fresh water supply into the Baltic Sea is around 481 km^3, being almost equal to the volume of saline water inflow from the North Sea. The evaporation and precipitation rate are in the same order making the Baltic Sea together with the freshwater supply a positive estuary. The freshwater balance provides an estuarine circulation model. The excess of fresh water coming into the Baltic Sea generates a pressure gradient due to the slight elevation of the mean sea level in comparison with the level of the Kattegat (Lass and Matthäus, 2009). This gradient leads to a barotropic outflow of brackish water at surface, balancing the freshwater excess.

This barotropic pressure is compensated by baroclinic pressure created by the huge difference in salinity between the Kattegat (~ 30) and the Arkona Sea (~ 8). The salinity in the Baltic Sea surface layers is controlled by runoff, with around 70 % of fresh water discharged into the Gulfs of Finland, Bothnia and Riga. Positive water balance regulates several hydrographic properties as the estuarine circulation, deep-water formation and ventilation, stratification and nutrient balance (Matthäus et al. 2009). The limited water exchange leads to long stagnation periods of the deep waters resulting in a residence time between 20-25 years of the Baltic Sea waters (Lass and Matthäus, 2009).

The transformation of water masses occurs mainly in the Belt Sea restricted by the Baltic Sea topography due to the dimensions of the entrance channel and the subdivision of the Baltic Sea into several basins separated by submarine sills. These conditions are also responsible for a reduced mixing of this penetrating water with the ambient water along the path into the central Baltic Sea (Matthäus et al. 2009). The transition area of the Belt Sea and the Baltic Proper are separated by two sills being the Darss Sill of 18 m depth and the Drogden sill of 7 m both preventing the continuous inflow of highly haline and oxygen rich water into the Baltic Sea. The main transport route of inflowing water from the sills into the central basins follows the deepest parts of the Baltic Proper via the Arkona Basin into the Bornholm Basin. From there the inflowing water propagates through the Slupsk Channel and counterclockwise around the Island of Gotland and into the Gulf of Finland (Jakobsen 1995) (Fig. 1.4). Thermal convection during winter, the permanent halocline and the inflow water from the Danish Sound are the main factors controlling the oxygen distribution. During winter due to the thermal convection the oxygen is partly refilled reaching undersaturated values in the water column. The permanent halocline is an effective boundary and prevents the convection to reach down to the deep water layer. The inflow of water from the Danish Sound through the bottom of the different basins takes several months until the water body arrives at the central Baltic Proper. Thus, part of the oxygen is already depleted (Lass and Matthäus, 2009). Special meteorological conditions related to wind and pressure fields generate such major inflows of saline water, which are a key factor for the renewal of the bottom water in the Baltic Sea basins changing the redox conditions in the deep basins of the Baltic Proper (Voipio 1981). The last two larger inflow events providing the Baltic Proper with highly saline and oxygen rich deep water were registered in 1993 and 2003.

Figure 1.3. Map of the Baltic Sea topography.

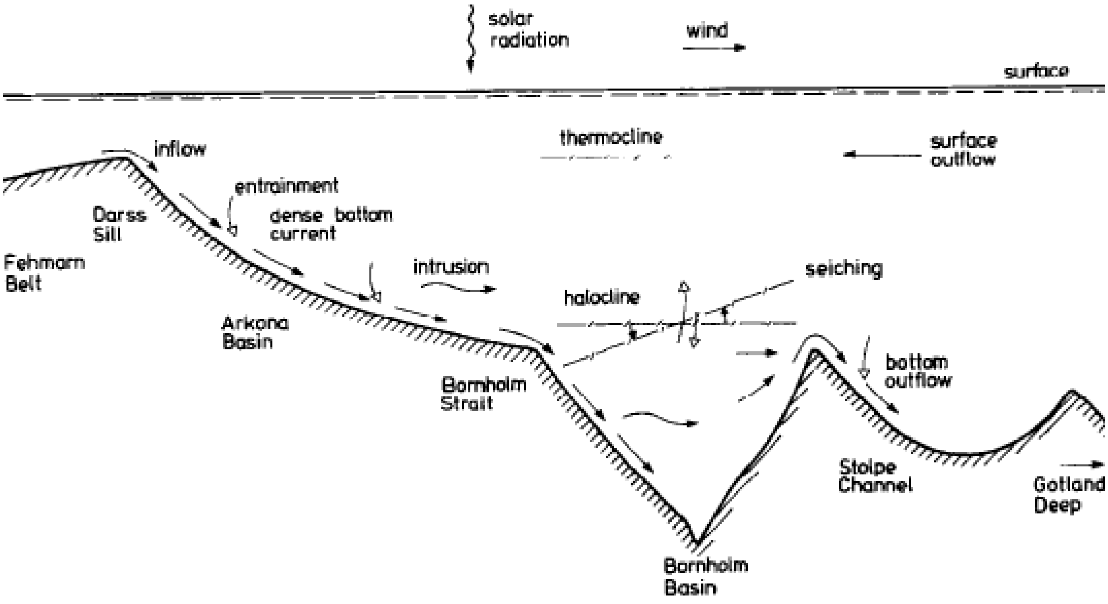

Figure 1.4. Route of inflowing water between the North Sea and the Baltic Sea (Jakobsen, 1995).

1.3. Cyanobacterial blooms in the Baltic Sea

Eutrophication remains a major challenge to the ecological integrity of the Baltic Sea. Arguably, its most obvious manifestation is the annual appearance of diazotrophic cyanobacteria blooms, especially in the central Baltic Proper (Larsson et al. 1985; Finni et al. 2001; Reissmann et al. 2009), which have increased in intensity, frequency and area in the Baltic Sea in recent decades (Kahru et al. 1994; Stal et al. 2003). Cyanobacteria are one of the major components of the phytoplankton population present in the Baltic Sea together with diatoms and dinoflagelates, leading the main bloom events in the Baltic Sea along the year. These summer cyanobacteria blooms in the Baltic Sea reported from the last part of the 19th century are considered a natural phenomenon. The presence of cyanobacteria fossil in sediment cores collected in the northwestern part of the Baltic Sea showed that cyanobacteria blooms occurrence is old as the brackish state of the Baltic Sea waters and previous to the increased anthropogenic inputs of the 20th century (Bianchi et al. 2000). Large blooms of diazotrophic filamentous cyanobacteria; mostly *Nodularia spumigena* and *Aphanziomenon spec*. accumulate in the surface water between July and August in the central Baltic Sea. This happens on non-periodical yearly time scales as demonstrated by satellite images registered by Kahru et al. (1994), who developed a methodology to get some correlations between those blooms and different factors like wind speed, surface temperature, solar irradiance, salinity, oxygen and nutrients distribution (Kahru et al. 2007). However, the causal factors for the increased cyanobacteria blooms in the last decade are still not clear. The major inflows of high saline waters from the North Sea and the phosphorus pool in sediments can promote those blooms reaching unexpected regions as the western Gulf of Finland (Kahru et al. 2000). In the Baltic Sea, optimum physico-chemical conditions (low wind speeds, warm surface temperatures and many hours of light) often combine in mid-summer to estimulate the growth of diazotrophic cyanobacteria. The spatial distribution of cyanobacteria blooms is restricted to a salinity range in surface waters of 3.8 to 11.5 constituting practically the whole Baltic Proper and water temperatures of 16 to 22 °C (Wasmund 1997).

Considering chemical requirements, diazotroph growth is foremost promoted under low molar ratios of dissolved macronutrients N:P, a condition that occurs annually in the Baltic during summer (Granéli et al. 1990; Nausch et al. 2008). A low N:P ratio is not enough to trigger a bloom itself, it is rather considered as prerequisite. In environments with high N:P ratio other phytoplankton species would compete for the nutrients uptake preventing a nitrogen-fixing cyanobacteria bloom (Stal et al. 1999). Beyond the N:P ratio, the excess of phosphate in summer surface waters is the real requirement for the development of cyanobacteria blooms under certain weather conditions during the summer period (Wasmund 1997). The excess of dissolved inorganic phosphorus is defined as the quantity of phosphorus present in the surface water less the phosphorus required for nutrient uptake by phytoplankton (Janssen et al. 2004, Nausch et al. 2004). In turn, the phosphate excess depends on the winter conditions in the Baltic Sea driving the vertical mixing. Strong winters allow the vertical mixing in the upper part of the water column to reach the nutriclines (40 - 60 m) migrating upwards water masses rich in nutrients. Between 1985 and 1988 nearly no cyanobacteria blooms have been observed in the Baltic Sea surface waters. The data registered from the wintertime in that period revealed that the mixed layer only sporadically exceeded the 50 m depth reducing the amount of phosphate transported upward (Wasmund and Heerkloss, 1993; Wasmund 1997; Janssen et al. 2004). The excess of phosphate in surface waters provides a potential scenario for cyanobacterial blooms in summer, as function of the summer sea surface temperature. Beyond the sea surface temperature different factors are involved such as thermocline depth; wind induced mixing, solar radiation and turbidity of the surface layer (Vahtera et al. 2005; Breitbarth et al. 2008). To summarize, sunny calm summer are the perfect media for the development of large cyanobacteria aggregates in surface waters of the Baltic Proper (Robarts and Zohary, 1987; Wasmund 1997).

Trace metals such as copper, molybdenum cobalt or iron are essential for different living organisms. Such elements are co-factors for several enzymes and are involved in different physiological processes (Raven 1988). Iron is an essential micronutrient for diazotrophic cyanobateria involved in different processes such as photosynthesis, nitrogen fixation and irradiance protection

(Literature). Stal et al. (1999) and Paczuska and Kosakowka (2003) pointed out the possible role of iron as limiting factor in the development of cyanobacteria blooms. Different microcosm experiments based on the collection of biological material of cyanobacteria blooms from different regions of the Baltic Sea confirmed that the adition of dissolved iron estimulate the primary production (Stolte et al. 2006, Schubert et al. 2008).

CHAPTER 2 – MATERIAL AND METHODS

2.1. Review of iron determination in seawater

Iron is not a conservative element in seawater. Involved in different physical, chemical and biological processes its speciation is function of the features of the studied environment. Such features cover metal input sources, physico-chemical conditions (temperature, salinity and oxygen content) and biological activity (Fig. 2.1). For decades many scientist studied the iron cycle connected to those features in the different seas and oceans of the world (e.g.: Geider and La Roche, 1994; Millero 1998; Vassiliev et al. 2001; Yakushev et al. 2007; Shaked 2008; Turnewitsch and Pohl, 2010). The complexity of the iron cycle implied the development of different sampling and analysis techniques and strategies. An evolution counting on the redox characteristics of iron and its reactivity that demand a special care in the sampling strategy and the analysis procedure (Croot and Hunter, 2000; Croot and Laan, 2002). Long time periods between sampling and analysis, the addition of acids or filtration of the sample can adulterate the original iron speciation (Bowie et al. 2002). Especially in former times and beyond possible redox changes in the iron speciation external iron contamination during sampling, sample storage, or analytical procedures are considered the main concerning issues in the determination of iron in seawater. An important aspect is to unify the different concepts and protocols related to the element in marine research. The lack of general establishments for different term definitions appointed in published data as dissolved, particulate, colloidal or dissolvable iron fraction hampers the comparison among different studies (Bowie et al. 2006). Procedures for clean trace metal facilities have been developed in the last two decades based on the use of special labware (Such as low density polyethylene “LDPE” bottles and Teflon caps), cleaning routines (use of micro detergent and ultraclean acids) and special isolating equipment (laminar flow and clean benches) (Bowie et al. 1998; 2002; 2003). In the 80´s the first accurate measurements of dissolved iron based on preconcentration steps and subsequent measurement using graphite furnace atomic absorption spectrometry (GFAAS) were achieved (Danielsson et al. 1978; Landing and Bruland 1987, Bowie et al. 2006). This technique still in use in nowadays became an accurate instrument for the determination of the total particulate and dissolved iron fraction (Grasshof et al. 1999; Pohl et al. 2004, Pohl and Hennings, 2005). The main disadvantages of this kind of methods are the use of large sample volumes and the impossibility of carrying out the measurements on board. Other important disadvantage is the impossibility of carrying out detailed speciation studies because of the lag of time between sampling and analysis. In the middle of the 90´s the importance of the organic fraction in the speciation of the metal was discovered. In surface waters, especially in coastal areas or areas of high biological activity the organic complexes of terrestrial or biological origin affect the thermodynamic solubility, the rates of redox processes and the interaction of iron with organisms (Millero et al. 1995, Macrellis et al. 2001, Liu and Millero, 2002). Techniques as differential pulse anodic stripping voltammetry and catodic stripping voltammetry were used with the purpose of an accurate characterisation of the dissolved iron fraction and the identification of the different organic iron ligands in seawater (Gledhill and van den Berg, 1994; Rue and Bruland, 1995; Wu and Luther III, 1995; Croot and Johansson, 2000). Many efforts were made to develop an analytical methodology providing accurate and rapid iron determination at the levels of iron in seawater on board of a research vessel. Research studies trying to clarify the iron speciation in seawater were carried out coupling flow injection analysis systems (F.I.A) to different detection instruments. Few examples of these systems are the direct current amperometric detection (allowing determination of both Fe (II) and Fe (III)), the combination of spectrophotometry and atomic absorption spectrometry or F.I.A systems coupled to Chemiluminescence methods (Elrod et al. 1991, Obata et al. 1993; Mulaudzi et al. 2002). F.I.A. systems provide a great versatility in the in situ analysis of different iron species (Bowie et al. 2007). Accurate measurements under a wide range of different physical and biogeochemical conditions and iron concentrations allow the use of the instruments in the most areas of the ocean (King et al. 1991; Bowie et al. 1998; Breitbarth et al. 2009). Hence, a flow injection system coupled to chemiluminesce analysis was the tool deployed for carrying out the analysis of dissolvable Fe (II) in this study. In parallel, total dissolved iron (DFe) and particulate iron samples were analysed by Dr. C. Pohl and U. Hennings with a methodology based on a GFAAS detection contrasted by decades of experience and tested in several QUASIMEME studies (Pohl 1997, Pohl et al. 2001).

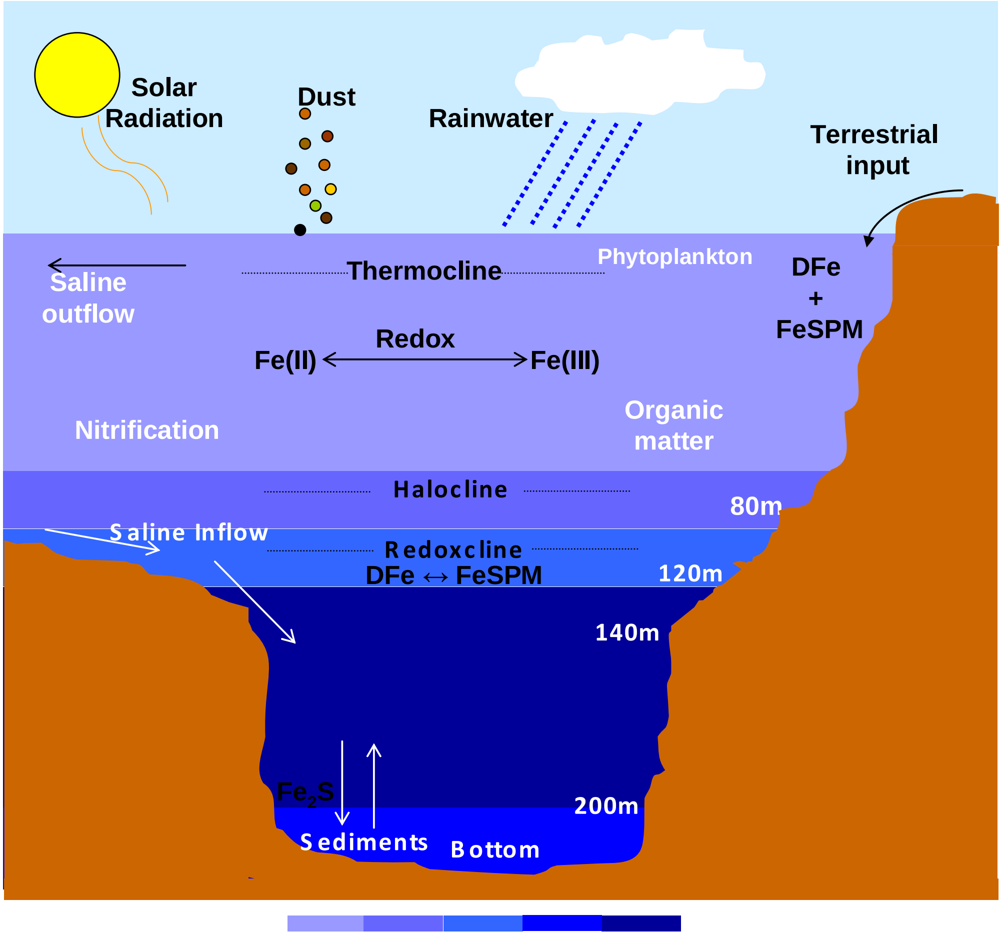

Figure 2.1. Diagram of the iron cycle in seawater based on the results obtained in the Gotland Deep and described widely detailed in following sections.

2.2. Sampling

The sampling of the surface waters for the analysis of DFe, Fe (II) and FeSPM was accommodated by underway collection using the metal-clean “Kieler” pump system for the cruises (Schüβler and Kremling 1993). The system is appropriate for the collection of particulate and dissolved trace element samples in open ocean and continental shelf surface waters. A hollow stainless steel shaft, a membrane pump, an air compressor and polyethylene tubing (HDPE, 1.4 mm i.d.) constitute the main parts of the system. The steel shaft is deployed below the ship through a “moon hole” located in the base of the hull. Hence, the water is pumped from below the ship’s hull at 9 m depth that is the sum of the ship’s draught and the length of the shaft (1.7 m). The inlet head is based on a Teflon cap that is connected to the HDPE tubing mounted inside the hollow shaft. This tubing crosses the moon hole and goes directly into the laboratory where the samples are taken. The double membrane pump employed presents Teflon flow tubes and thus the sample along the system is in contact only with inert materials avoiding contamination (Fig. 2.2). The system is characterised by a maximum flow rate 1.2 m^{-3} h^{-1} and a residence time about 15 – 25 s (Schüssler and Kremling 1993). The sample integrity with this sampling methodology for the analysis of trace metals; for both particulate and dissolved fraction were tested with the analysis of reference material and comparing it with other sampling strategies by Schüssler and Kremling (1993). To avoid external influence, the system is rinsed for several hours with seawater when is set up on board and the sampling is carried out when the ship is steaming to avoid ship’s hull contamination.

Sampling at the process stations combined CTD casts with deployment of a metal-clean Pump-CTD (Strady et al. 2008) (Fig. 2.3). During sampling of distinct depth horizons, the pumped water flows through a metal-clean nylon hose, which is plumbed directly into a clean bench in the laboratory minimizing possible sample contamination.

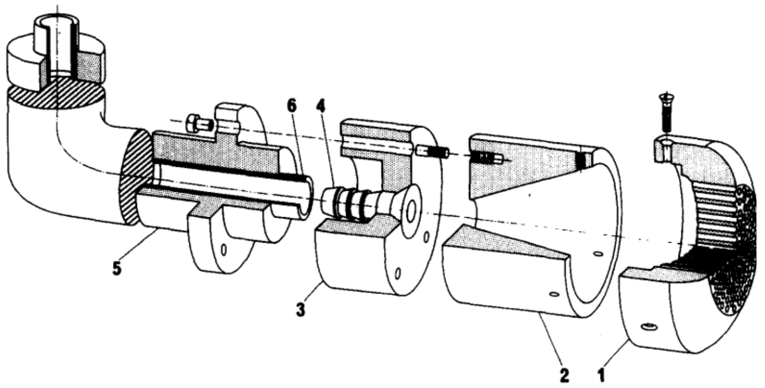

Figure 2.2. Snorkel system designed by Schüβler and Kremling (1993): Inlet head. (1) Sieve cap (Teflon) with PE screws; (2) cone shaped sieve cap adaptor (Teflon); (3) main connecting unit (Teflon); (4) tube adaptor (HDPE); (5) termination of hollow steel shaft with stainless steel bolts; (6) suction tube (HDPE) inside the shaft.

The samples for DFe and FeSPM were collected in 2 L LDPE (Low Density Polyethylene) bottles and immediately filtered through a 0.45 µm precleaned and weighed Nucleopore filters separating the dissolved and the particulate fraction according to the methods described by Grasshoff et al. (1999).

Figure 2.3. Pump–CTD-System attached to CTD–bottle–Rosette, with Free-FLO bottles (Strady et al. 2008).

After the filtration step DFe samples were stored in 500 ml LDPE and acidified to a pH of 2 with the addition of sub-boiled nitric acid under a Laminar flow bench. The samples storage for DFe were analysed following the cruise according to the method of Danielsson et al. (1978) by Dr. Christa Pohl and Ursula Hennings (IOW). Prior to DFe analysis by graphite furnace atomic adsorption spectrometry, the dissolved metal was extracted from the matrix of the sample by freon-dithiocarbamate extraction. On board, after the filtration the FeSPM filters were rinsed with Mili-Q water and stored in cleaned petri boxes at –20 ºC. FeSPM filters analysis implies pressure wet washing digestion with nitric (sub-boiled) and hydrofluoric acid (suprapure) for 2 h at 180 °C, evaporated to dryness and dissolved in 1 cm^3 of nitric acid (Danielsson et al. 1983; Pohl et al. 1998). Finally, these acidic solutions were analysed in the same way as DFe samples by using a Perkin-Elmer AA spectrophotometer combined with graphite furnace and an autosampler. For trace metals, our laboratory takes part regularly and successfully in the QUASIMEME studies for quality assurance (Pohl 1997, Pohl et al. 2001).

Dissolvable Fe (II) measurements were carried out through the analysis of unfiltered samples by a chemilumenescence flow injection analysis system (FIA) described below.

Sampling strategies and the analysis methods selected were employed to get the main data used for this study during three cruises carried out between summer 2008 and summer 2009 in the Baltic Sea:

R.V. Maria S. Merian: 18 th June – 14 th July 2008.

What are the main sources of iron in the Baltic Sea? How is the iron speciation along the central Baltic Proper during summer? How the Baltic hydrographical conditions interact with the metal (profile of iron through the different clines and redox changes sensitivity) through the different basins? How is the state of the cyanobacteria bloom in the Baltic Proper related to the DFe:FeSPM ratio in the moment of sampling? These are the first questions to answer in this study and the subject of this cruise. The survey took place on board the research vessel (RV) Maria S. Merian. The collection and analysis of surface water samples from Baltic surface and deep waters was carried out in the main basins of the Baltic Sea from the Skagerrak to the Gulfs of Finland and Bothnia passing by the Baltic Proper (Fig. 2.4) in combination with CTD casts each 30 nm and high resolution sampling at process stations in the western Baltic Proper (Landsort Deep), Gotland Deep, Kattegat and Skagerrak.

R.V. Alkor: 30 th January – 14 th February 2009. It is suggested that certain winter conditions rule out the development of the summer blooms (Janssen et al. 2004). Estimating the seasonal changes of iron speciation in the Baltic Sea and the way that changes in the river runoff (volume and type of matter discharged) affects the iron content in surface waters were the next steps of the study. During winter, ice covered the most part of the Northern Baltic Sea; therefore the cruise was focused in the western and central Baltic Proper surrounding the Gotland Island until reach the Landsort Deep station (Fig. 2.4). It was not possible to use the “Kieler” pump at this cruise and therefore the sampling of the surface and the depth profiles at the main stations of Landsort and Gotland Deep were carried out employing normal CTD casts. This fact increased the sampling time and the lag phase between the capture of the sample and the measurement of soluble Fe (II) on board but it was not taken in account for possible recalculation of the soluble Fe (II) concentrations.

*RV Alkor: 11 th – 18 th July 2009*A second cruise in summer allowed to compare the distribution of Fe and the development of the cyanobacteria bloom regarding the same parameters measured the year before in the Baltic Proper. Such comparison helps to clarify which is the bioavailable fraction of Fe in the Baltic Sea and to estimate the uptake of the metal. The cruise started from the Gotland Island on the second week of July. Special sampling was made at the eastern part of the island with the purpose of locate possible upwelling events. As the summer before, the depth profiles were obtained using the P-CTD carrying out three depth profiles in the stations of Gotland Deep, Landsort Deep and Bornhom Basin.

2.3. Fe (II) measurements on board

Fe (II) analyses were carried out using a “Flow Injection System” (Waterville Analytical) following the chemiluminescence method of King and Farlow (2000) and Croot and Laan (2002) based on the chemilumenescence properties of Luminol. In aqueous solutions, Luminol is the most commonly used chemiluminescent species. This compound reacts with a potent oxidizing agent (e.g. H_2O_2) in the presence of a catalyst (generally a metal or metal-containing compound or an enzyme) in alkaline solution to yield 3-aminophthalate in an excited electronic state, which returns to ground state emiting light (Rose and Waite, 2001). The samples were retained at room temperature during the analysis. Each analysis consumed a volume lower than 10 ml over a period of 5 minutes. On board, the cleaning procedure is based on 1 M Nitric acid solution flushing the system for one hour before and after one measurement session with a solution of 10% subboiled nitric acid. Each solution (carrier solution, Luminol and buffer solution) was prepared in Milli-Q water and stored in LDPE bottles. The samples and the different reagents are pumped through the whole FIA system by a “Gilson Minipuls 3” 8 channels peristaltic pump equipped with 2 - stops Tygon tubes. 0,3M hydrochloric acid solution was used as carrier eluting the column after the load phase. Milli-Q water is introduced between the loading and eluting phases removing the salt content from the column.

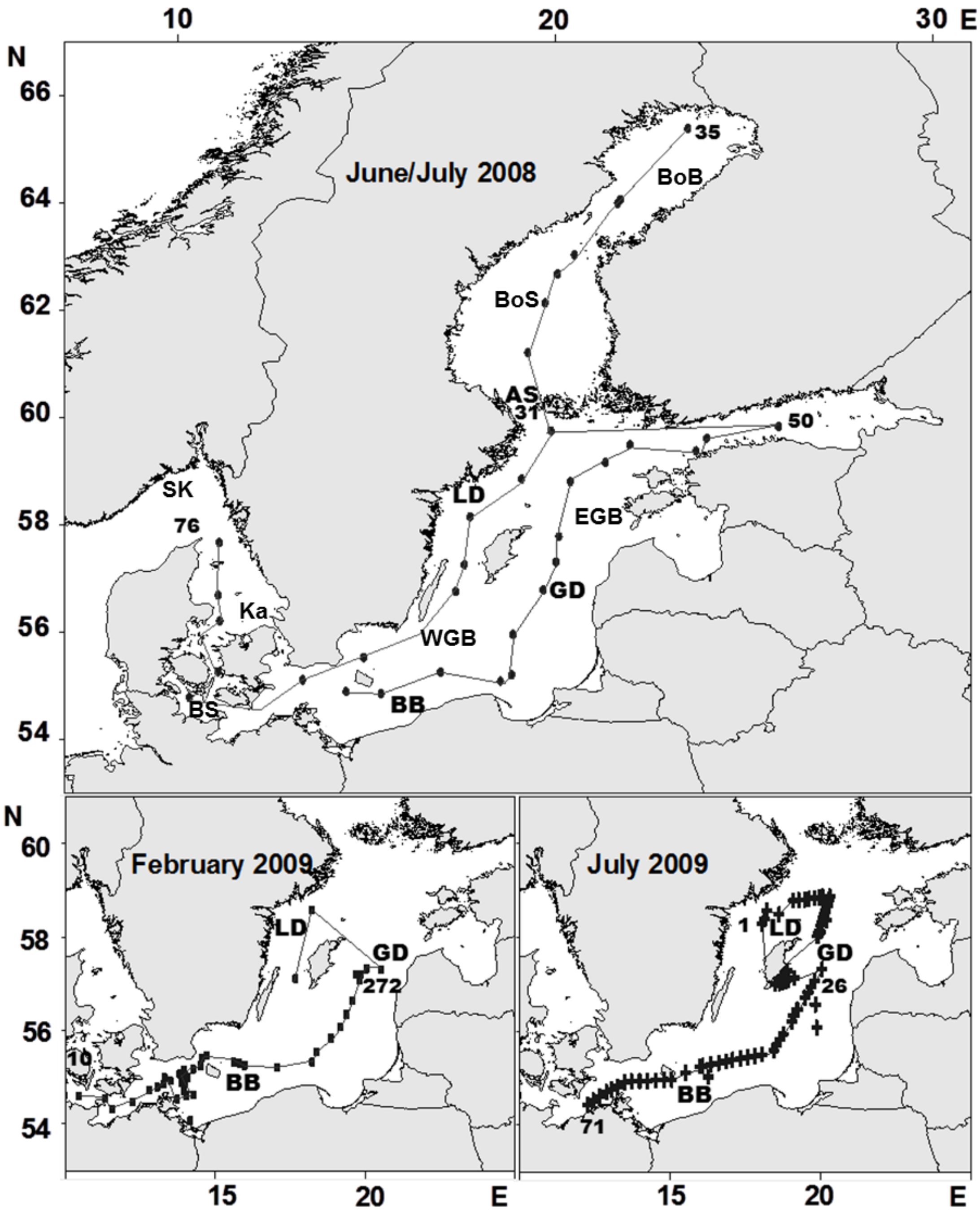

Figure 2.4. Sampling locations and transects of the three cruises carried out in the Baltic Sea in 2008-2009.

The buffer solution is used reaching the accurate pH to load the iron (II) into the column (pH 5.5). Depending on the range of concentration a preconcentration step was introduced and adapted. For the preconcentration step a 1 cm long column (Global FIA, 1 cm length no metal frits minicolumn) was used packed with 8-hydroxyquinoline resin immobilised on a Toyopearl gel HW65C according to the method of Landing et al. (1986). The resin was prepared before the cruise. The set up and the procedure without preconcentration step is the same, and a PTFE coil with a volume of 83 µl replaces the minicolumn. The acidified not buffered sample goes directly through the coil into the reaction cell. The acquisition system is based on a photo multiplier tube (PMT) and a Plexiglas flow cell (58 mm x 52 mm x 15 mm) (Fig. 2.5).

Measurement protocol:

Samples for soluble Fe (II) were immediately acidified with hydrochloric acid and analysed within 2 minutes after collection to avoid oxidation in the first survey of the Baltic Sea. In the other two cruises the acidification step was abolished to avoid possible reduction of ferric iron. In the load phase the buffered sample goes through the column by retaining the iron (II) ions. Then, the automatic multivave (10 ports multivalve VALCO microvalve) changes to position B and the acid carrier elutes the samples carrying the sample to the acquisition cell. In the cell the sample is mixed with the Luminol reagent. This Luminol reagent is prepared on a 1 M ammonia solution reaching the optimum pH (10-11) for the reaction with Luminol (Fig. 2.5). The computer software Labview 7.1 from National Instruments operates the PMT and the microvalve by Bluetooth remote control.

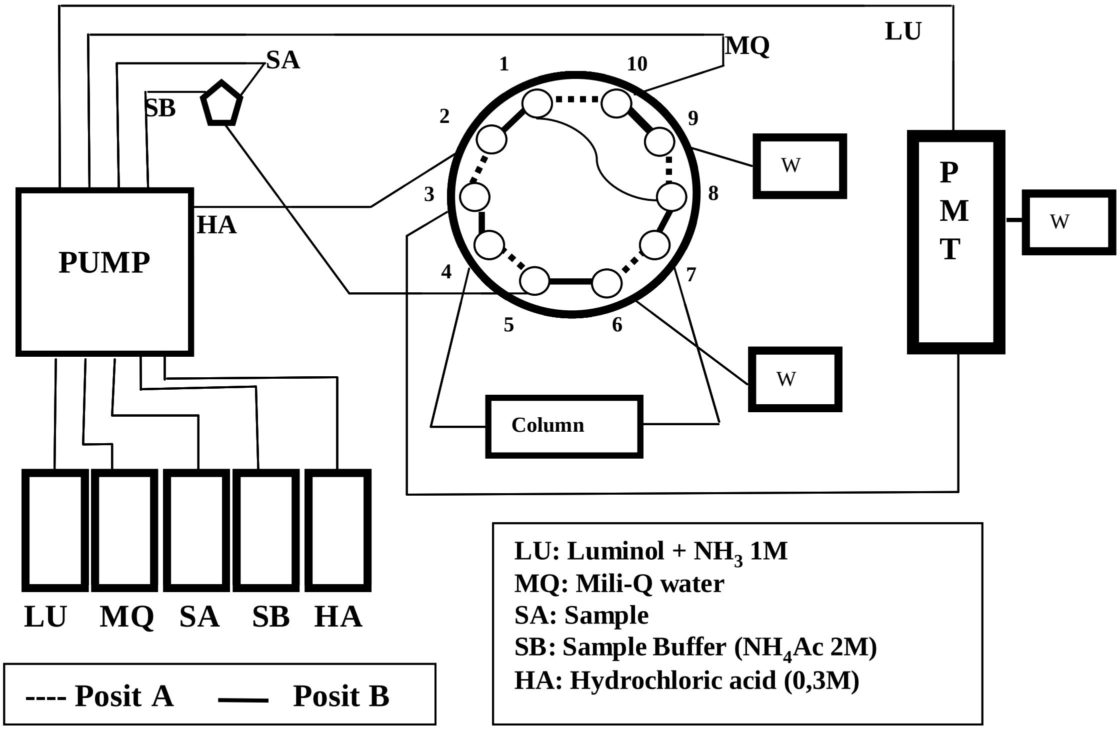

Figure 2.5. Manifold of the Flow Injection System including a preconcentration step.

Calibration:

A solution of 0.01 M of Fe (II) in “ultrapure water” Milli-Q water was prepared using ammonium Fe (II) sulphate each day of analysis. It was used as stock solution for the preparation of the different standards of the calibration curve and kept in a fridge at 4 °C. The stock solution and the standards for the calibration curve were acidified to a pH of 2 with commercial suprapur HCl and prepared in dark volumetric flask of 250 ml. The glassware was cleaned with a solution of 10 % of nitric acid and rinsed with Milli-Q water 12 hours before each round of analysis. Standards were prepared daily in Milli-Q water for a concentration range between 0.2 nM and 20 nM. Calibration was performed daily before and after analysing the samples. Three replicates of each standard and sample were measured injecting the blank (acidified Milli-Q water) between each solution (standard or sample) to avoid memory effects.

The data treatment was carried out based on the average of the signal (Fig. 2.6). The catalysed reaction (oxidation of Luminol) is adjusted to a second order polynomial. The ”Limit of Detection” (LOD) (n = 10) was calculated for the system with and without column providing a result of 146 and 155 pM, respectively. This is in agreement with Croot and Land (Croot and Laan, 2002) carrying out Fe (II) oxidation measurements by achieving a detection limit of 100 pM without a preconcentration step.

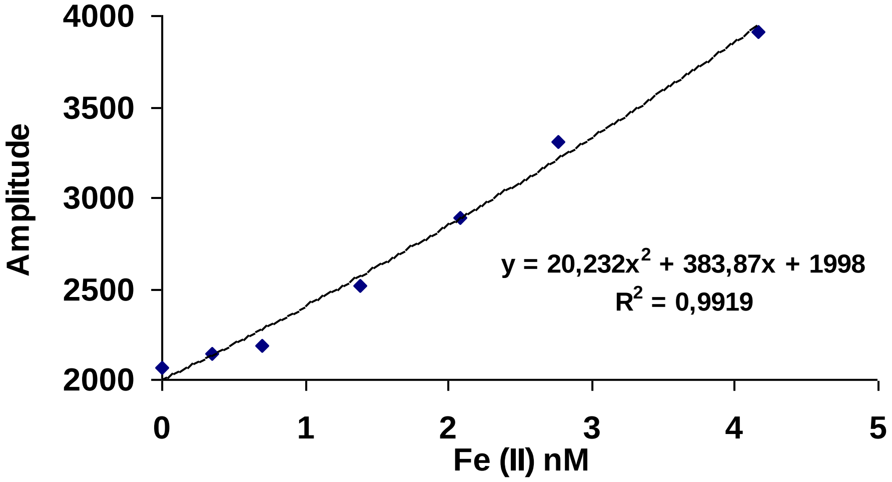

Figure 2.6. Calibration curve carried out on board of the R.V. Alkor on the 12th of July 2008.

2.4. Additional measurements

Data for salinity and oxygen were taken from CTD rosette sampler with 5 L free flow bottles equipped with sensors for conductivity, temperature, depth and for chlorophyll a.

Nutrients data was provided by Dr. G. Nausch (IOW). Inorganic nutrient concentrations were measured by colorimetric methods using the autoanalyzer system "Evolution III" on GF/F filtered water samples (Rohde and Nehring, 1979; Nausch et al. 2008).

POC and Chl a data was provided by Dr. M. Nausch (IOW). Samples were filtered onto pre-combusted Whatman GF/F-filters and analysed in a CHN analyser for the determination of particulate organic carbon (POC) (Nausch et al. 2008).

Chlorophyll *a* (Chl *a*) was extracted using ethanol from seston collected on GF/F filters, followed by fluorescence detection. Phytoplankton species composition and bio-volumes were determined according to the HELCOM guidelines (1988). The cell counts were converted to wet weight phytoplankton biomass (mg m^{-3}) (Nausch et al. 2008).

CHAPTER 3 – RESULTS

3.1. Iron distribution in the Baltic in July 2008

The cruise on board of the research vessel M.S. Merian in summer 2008 covered different areas of the Baltic Sea including the transition area to the North Sea (Skagerrak, Kattegat and Belt Sea), the Baltic Proper and the Gulfs of Bothnia and Finland. This part of the chapter shows how special topographic (subdivision in different basin, sills and rims) and hydrographical features (limited saline inflow, river discharge, atmospheric deposition and deep water formation) define the Baltic Sea as a complex system divided into different interconnected compartments. The main aim is to relate the iron distribution to different physical and chemical parameters such as temperature, salinity, oxygen concentrations and distribution of nutrients in the different compartments.

Hydrography

The natural barrier constituted by the shallow basins of the Kattegat and the Kiel Bight between the North Sea and the Baltic Sea reflects the low water exchange capacity showed in the decrease of surface salinity from 30 to 13 (Fig. 3.1 a). Mixing of high saline water inflow and outflow of brackish Baltic Sea water leads to a water body not stratified in the transition area. The mixing with colder North Sea waters also influence the surface temperature with a difference of 2-3°C between the Skagerrak and the Kiel Bight where the highest temperatures of 18 °C were found. The presence of a thermocline in the first 10 – 15 m of the water column separates the warmer and lower saline surface water from the colder and higher saline deep waters with gradients close to 10 °C during summer. Major fluctuations in temperature and salinity in the Baltic proper occur in coastal proximities. Samples taken along the Swedish coast reflected higher temperature in comparison with the stations occupied in the center of the basins (Fig. 3.1 a).

Below the thermocline, the deep waters become anoxic with depth as they penetrate into the central Baltic Proper. The Gotland Deep in the Baltic Proper is characterised by the permanent halocline at ~ 75 m. Oxygen depletion starts below 100 m with the development of a redoxcline at ~ 110 m. In the Gotland

Deep the thermocline remains at a temperature around 14.5°C down to the depth of 17 m (Fig. 3.2 a).

The Landsort Deep is the deepest part of the Baltic Sea and is located in the Northern part of the Baltic Proper close to the Swedish coast. Presumably, the degradation of organic matter controls oxygen depletion in the Landsort Deep. Depletion starts above 90 m overlaying the redoxcline and the halocline. This affects the distribution of dissolved inorganic nutrients and the different species of iron as it is described in following sections (Fig. 3.3 a).

The Baltic Proper and the Gulf of Bothnia are separated by the Aaland- or Archipelago Sea; one of the narrowest areas of the Baltic Sea characterised by thousands of islands and rocks. In comparison to Gotland- and Landsort, this region is well mixed and contains oxygen throughout the whole water column. The salinity is less influenced by the outflow of lower salinity waters from the Gulf of Bothnia (Fig. 3.4 a).

The shallow Bothnian Bay presents the coldest and lowest saline waters in the upper north of the Baltic Sea (Fig. 3.1 a). The Gulf of Bothnia receives the input of surface water from the central Baltic Sea through the narrow channel of the Aaland Sea where it is mixed with the river runoff of the surrounding landmass. In contrast to the central Baltic, stratification does not occur below the thermocline. Salinity and temperature in the surface waters decrease from 5 and 13 °C in the Aaland Sea to a minimum of 3 and 8 °C respectively, in the Bothnian Bay.

In constrast to this enclosed gulf, the entrance of the Gulf of Finland is wider and the water exchange is favoured. Compared to the other regions in the Baltic Sea, the surface temperature remains constant at 15 °C in the Gulf of Finland. The influence of freshwater input in the Finnish Gulf is lower than in the Bothnian Bay based on the temperature profile and salinity of 5 - 7 at the surface (Fig. 3.1 a). The water column has lower stability according to the buoyancy frequency favouring the vertical mixing and the consequent arrival transport of nutrients as phosphate into the euphotic zone.

Dissolved Macronutrients

After the spring bloom of diatoms nitrate and phosphate are mostly depleted from the surface. In relation to the growth of phytoplankton, the Baltic Sea changes from phosphate to nitrate limitation between winter and summer.

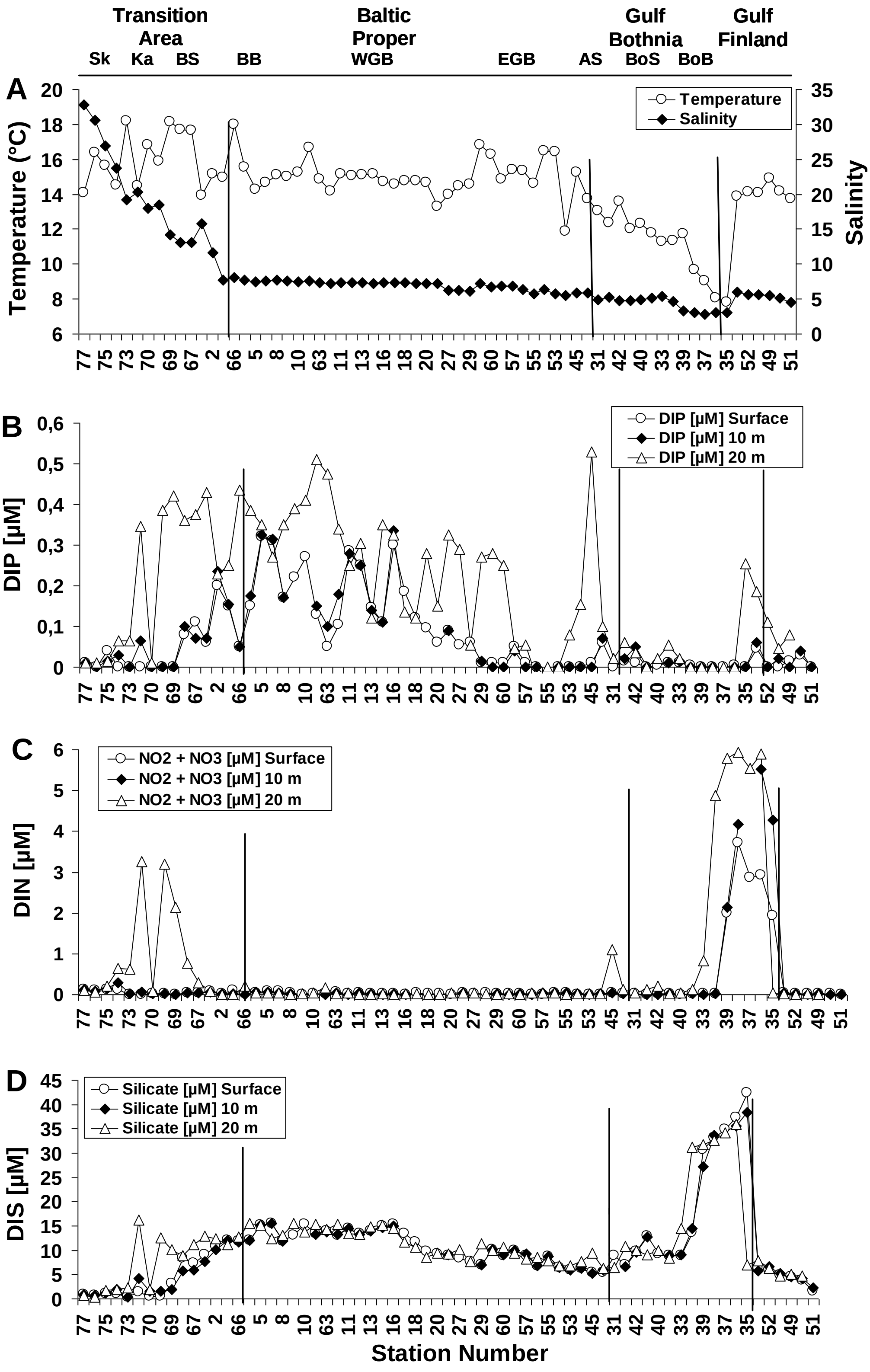

Figure 3.1. Salinity, temperature (A) and dissolved inorganic nutrients (B,C and D) surface profiles along an entire Baltic Sea transect in July 2008. The stations were set up from west to east and the values from T and S were selected from 10 m CTD data. DIN: Dissolved Inorganic Nitrogen, DIP: Dissolved Inorganic Phosphorus, DIS: Dissolved Inorganic Silicate. Nutrients data provided by Dr. G. Nausch (IOW).

In the whole western part of the Baltic Proper, dissolved inorganic phosphate (DIP) remains in the first 10 m along the profile. Maximum surface phosphate concentrations of 0.35 µmol L^{-1} were observed in the Arkona and Bornholm Basin and in the southeastern part of the Gotland Basin (Fig. 3.1 b). Below the thermocline, pool of phosphate was found in the whole Baltic Proper. Highest concentrations were registered below the redoxcline at ~ 125 m in the Gotland Deep (Fig. 3.2 c). Dissolved inorganic nitrate (DIN) has a similar distribution being nearly depleted in the surface water of the whole Baltic Proper. One exception was identified with slightly increasing concentrations of DIN in the 20 m depth horizon in the Kattegat, which is possibly influenced by inflowing waters from the North Sea (Rosenberg et al. 1996). Also in the Bothnian Bay, highest nitrate concentrations were found reaching a maximum of 4.5 µmol L^{-1} due to high freshwater input (Fig. 3.1 c). A reservoir of DIN was also observed in deep waters of the Baltic Proper but restricted to the oxic basins of Arkona and Bornholm. In anoxic conditions nitrates and nitrites are reduced to ammonia. A maximum DIN concentration of ~ 7 µM is located in the 75 m depth horizon close to the halocline in the Gotland Deep, while in the Landsort Deep the shift of the redoxcline to an upper depth leads to the depletion of nitrate in the entire water column (reduction to ammonia) (Fig. 3.2 b & 3.3 b). Lowest silicate concentrations close to 0.5 µM were observed in the transition area of the Skagerrak. The maximum concentration up to 45 µM was found in the upper part of the Bothnian Bay. In the Baltic Proper silicate concentrations vary between 5 and 20 µM. The distribution of silicate along the transect shows no big differences between concentrations of the samples collected at surface, 10 m or below the thermocline (20 m) (Fig. 3.1d).

Iron speciation at the surface along an entire Baltic Sea transect

The speciation of iron in the Baltic Sea is highly influenced by its hydrological and topographic properties. Further on, it is controlled by the deep-water stagnation periods, mixing processes and external sources as river runoff, dust input, ground waters and lixiviation. High concentrations for the different Fe species were found in surface waters in proximity to specific regions in the Baltic Sea, which are characterised by a shallow topography (Fig. 3.5 & Fig. 3.6).

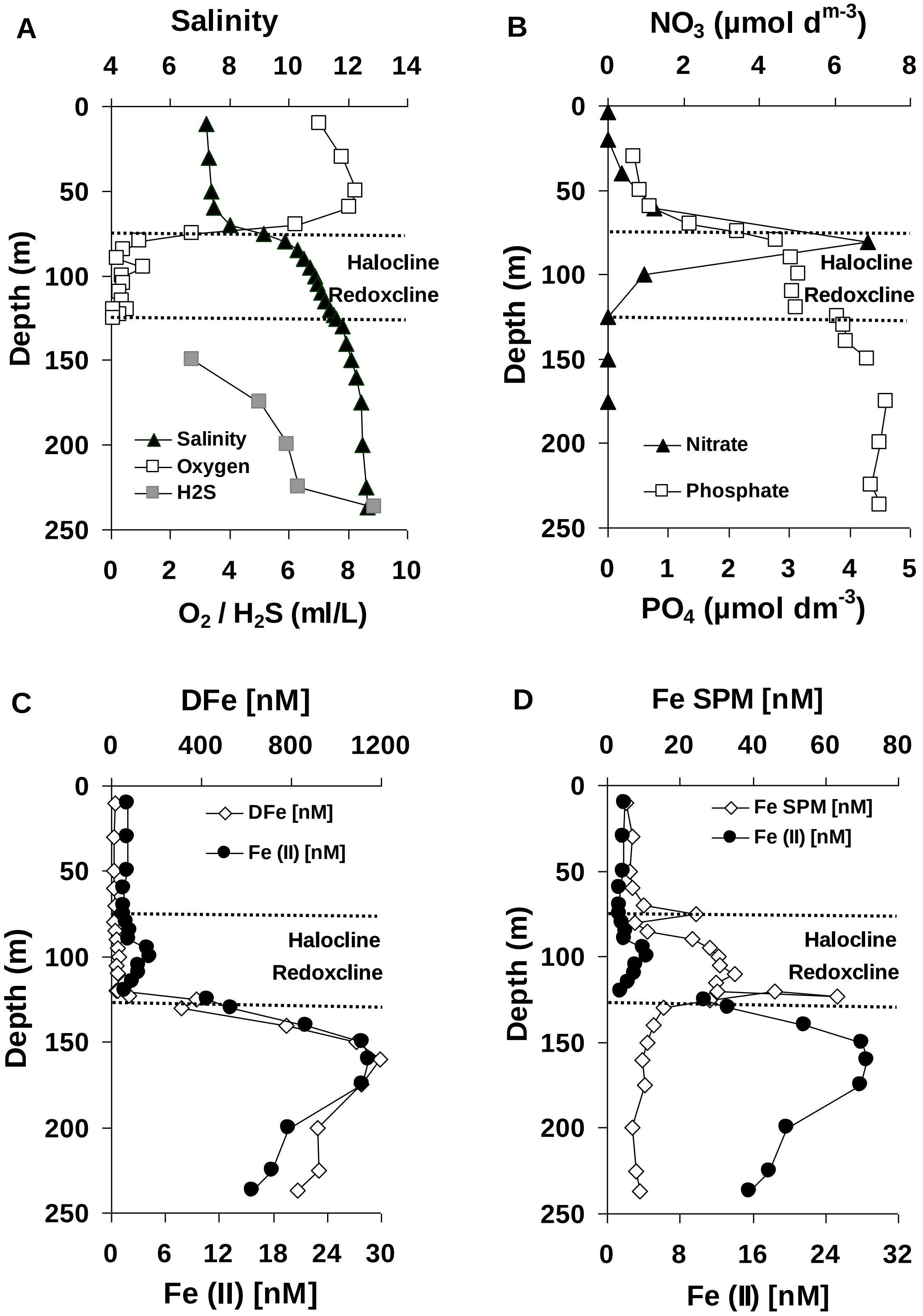

Figure 3.2. Vertical profiles of salinity, oxygen (A), dissolved inorganic nutrients (B) and Fe speciation (C & D) at the Gotland Deep in July 2008. Nutrients data provided by Dr. G. Nausch. FeSPM and DFe data provided by Dr. C. Pohl and U. Hennings.

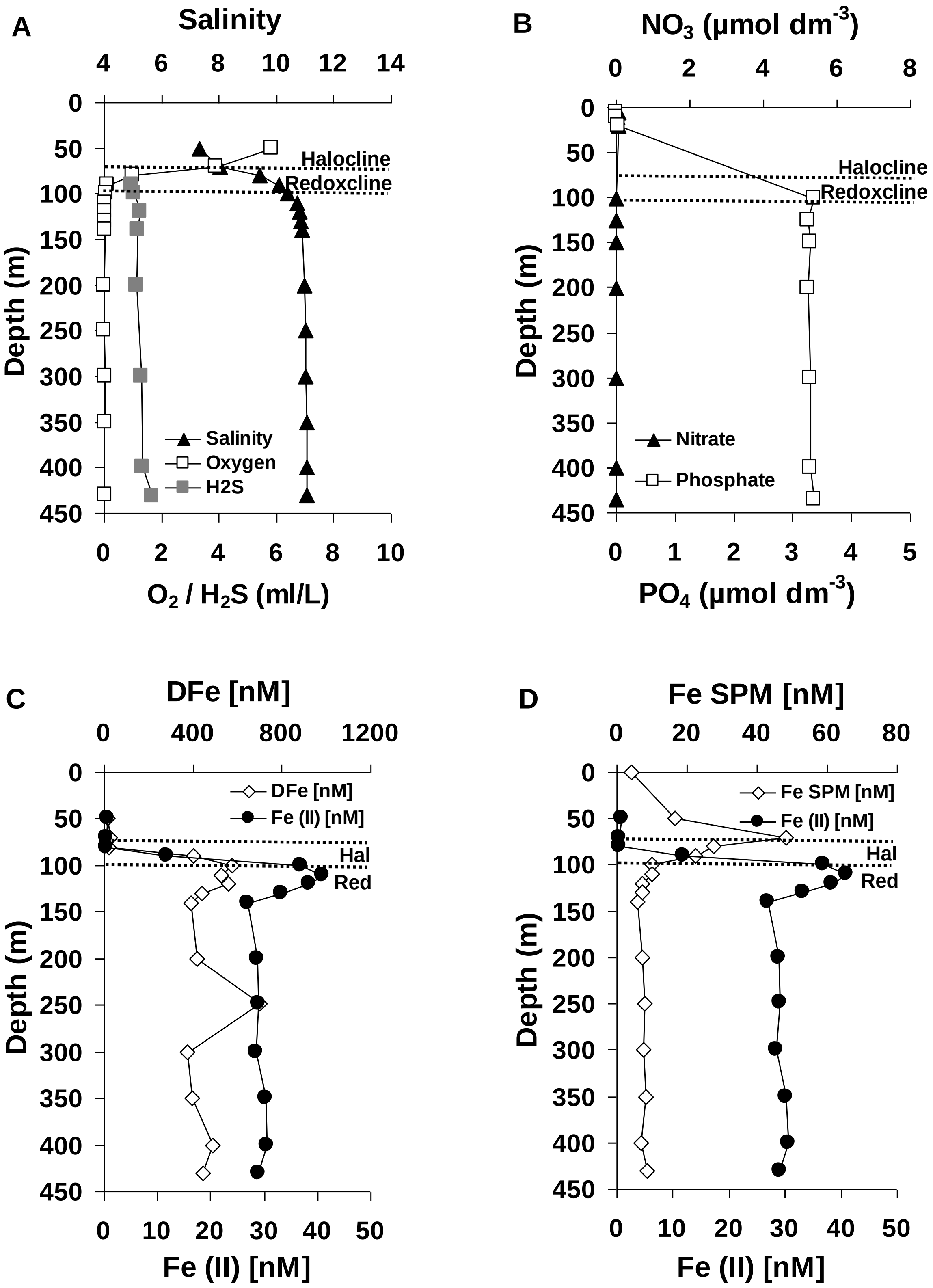

Figure 3.3. Vertical profiles of salinity (A), oxygen (A), dissolved inorganic nutrients (B) and Fe speciation (C & D) at the Landsort Deep in July 2008. Nutrients data provided by Dr. G. Nausch. FeSPM and DFe data provided by Dr. C. Pohl and U. Hennings.

In Skagerrak, DFe values from 7 nM were found. The contribution of Fe (II) to the dissolved fraction reached values close to 5 nM; this is about 45 % of the total dissolved Fe fraction in this region. Skagerrak, with low primary production and minor seasonal variations in deep waters, is mainly characterised by the inflow of refractory organic matter and low nutrient fluxes through the sediment-water interface. Slomp et al. 1997 revealed a contribution of iron oxides in the organic decomposition (Fe reduction) of about 19% in the Skagerrak sediments. Concentrations around 180 µM of Fe (II) were found in the porewater of the Skagerrak sediments. It is suggested that most part of this Fe (II) is reoxidized in the interface. However, a small fraction can escape to the water column.
DFe concentrations increase up to values of 35 nM in the Kiel Bight in the transition area while the Fe (II) dissolved fraction decreases to values around 2 nM (Fig. 3.5). This increase in DFe is typical for shallow regions with mixing processes occurring near the bottom and higher input of fresh organic matter, resulting in anoxic sediments, which lead to an input of Fe (II) from these reduced sediments (Pakhomova et al. 2007).

DFe and Fe (II) dissolved fraction fluctuate along the Baltic Proper with concentrations below 65 and 5 nM, respectively. Lowest values in the Fe (II) fraction were found in the area of the Arkona Basin (Stat. 5) and Bornholm Sea (Stat. 9). These low concentrations could be related to biological activity. During summer, the Baltic Sea surface waters are characterised by a limitation of nitrate and a surplus of phosphate, which supports the diazotrophic growth of cyanobacteria. The diazotrophic, nitrogen fixation requires between 10 - 20 times more iron than the uptake of dissolved nitrate from the water column (Kustka et al. 2002; 2003). This owes to the structural requirement for iron in both subunits of nitrogenase and provides reductant via ferredoxin. Net probes reveal the predominance of *Aphanizomenon sp* and *Nodularia spumigena* cyanobacteria species in the western Baltic Proper. In general, this biological activity could be a possible explanation for the decrease of Fe (II) and DFe in surface waters coupled to an increase of the particulate fraction (cells and excretion products).

For the stations located in the Skagerrak, in the Baltic Proper and the surroundings of the Gulf of Finland and Bothnia, the values of Fe (II) accounted for 10 up to 40 % of the DFe fraction (Fig. 3.5). Highest concentrations of Fe (II) and DFe were found in the Gulf of Bothnia reaching values of 39 and 590 nM, respectively (<10 % of the dissolved fraction in the reduced form of Fe (II) species). FeSPM shows the same distribution in the Baltic Sea as DFe with high values up to 47 nmol dm^{-3} observed in the shallow areas of the Kattegat and near to the Swedish coast. Highest concentrations of FeSPM (244 nmol dm^{-3}) were measured in the north of the Bothnian Bay. In this area, the high Fe concentrations of all three species considered in this study are attributed to the freshwater input of the Kemijoki river, discharging one of the largest watersheds with a basin area of 52452 km^2 into the Baltic. 76 % of this area includes forests and the river runoff is most likely to be enriched in organic matter and humic substances. Therefore it is assumed that most of the Fe, delivered by the Kemijoki river is associated with organic matter, increasing also the solubility of iron in brackish water (Liu and Millero, 2002).

3.2. Vertical distribution of Fe species at the characteristic stations of the Baltic Sea

Vertical iron profiles are strongly related to the hydrographical conditions in the water column of the Baltic Sea. Iron speciation is strongly controlled by the content of oxygen and the redox potential of the water column, since it affects the distribution of the particulate and dissolved iron.

In the Gotland Deep the Fe profile is clearly divided into three different parts separated by the salinity interface at ~ 75 m and the oxic-anoxic interface at ~110 m. In the upper water column including the surface waters, DFe concentrations are ranging between (9 - 30 nM) and Fe (II) (1 – 2 nM) fraction oscillates between 5 - 20 % of the total dissolved fraction (Fig. 3.4). Due to microbial degradation of organic matter most of the oxygen is consumed and starts the formation of hydrogen sulphide between the halocline and the redoxcline (80 - 110 m). At this depth interval a first increase of Fe (II) was observed with maximum concentrations up to 4 nM. Below the redox interface maximum concentrations were registered for Fe (II) and DFe with 28 nM and 1200 nM, respectively down to the depth of 160 m.

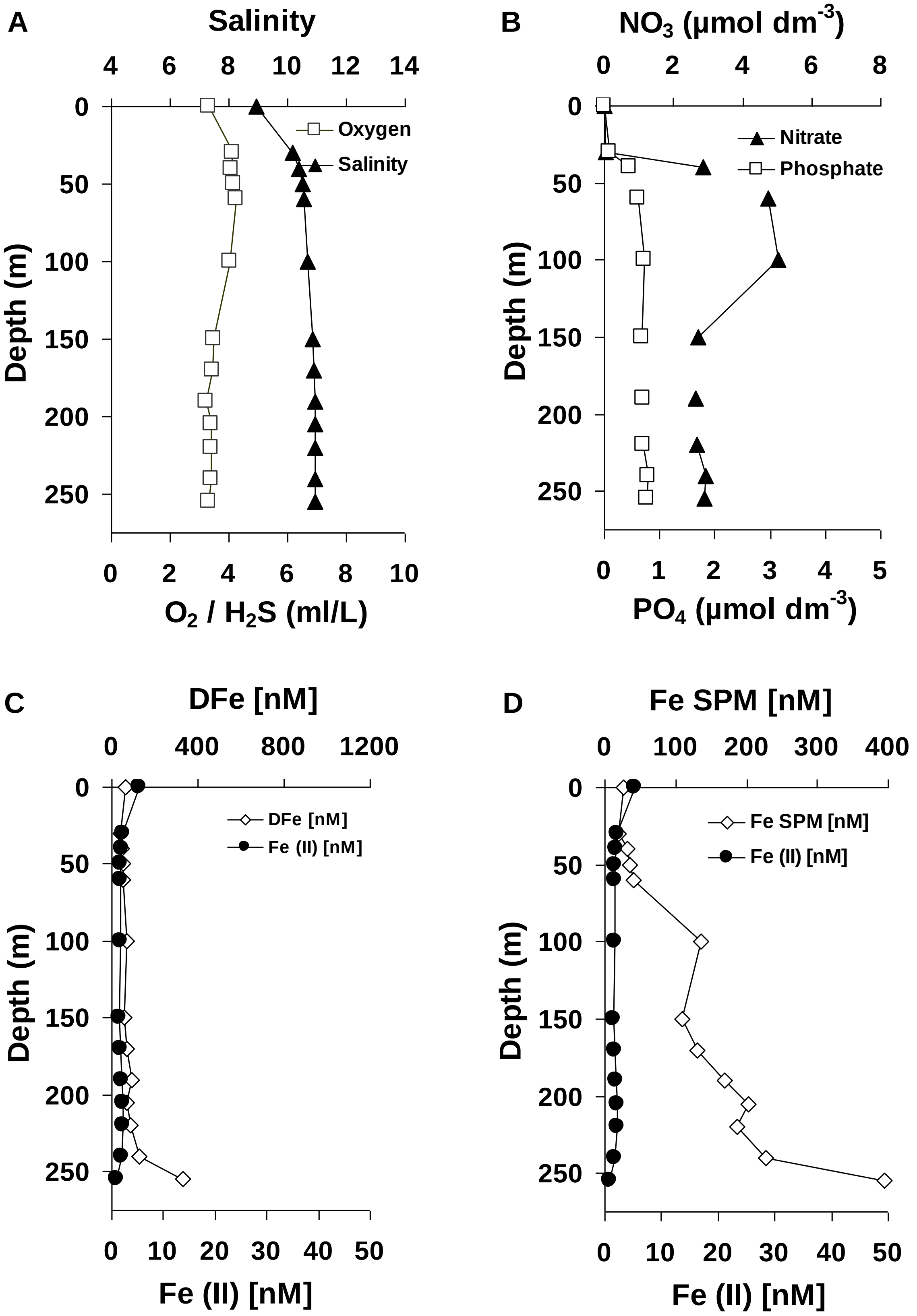

Figure 3.4. Vertical profiles of salinity, oxygen (A), dissolved inorganic nutrients (B) and Fe (C & D) speciation at the Aaland Deep (Station 31) in July 2008. Nutrients data provided by Dr. G. Nausch. FeSPM and DFe data provided by Dr. C. Pohl and U. Hennings.

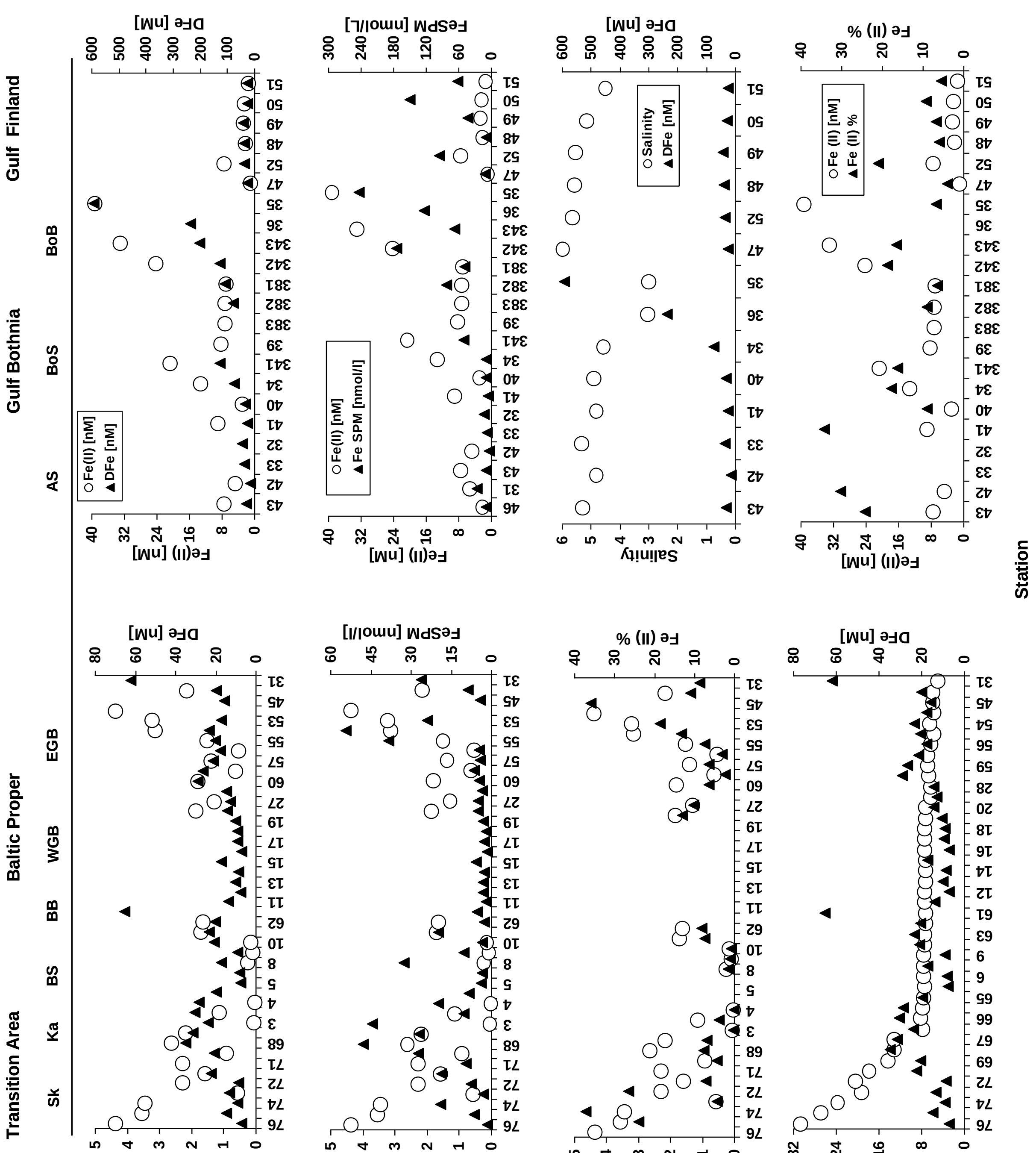

Figure 3.5. DFe, Fe (II) dissolved fraction and FeSPM in the different areas of the Baltic Sea reflecting the influence of river runoff. FeSPM and DFe data provided by Dr. C. Pohl and U. Hennings.

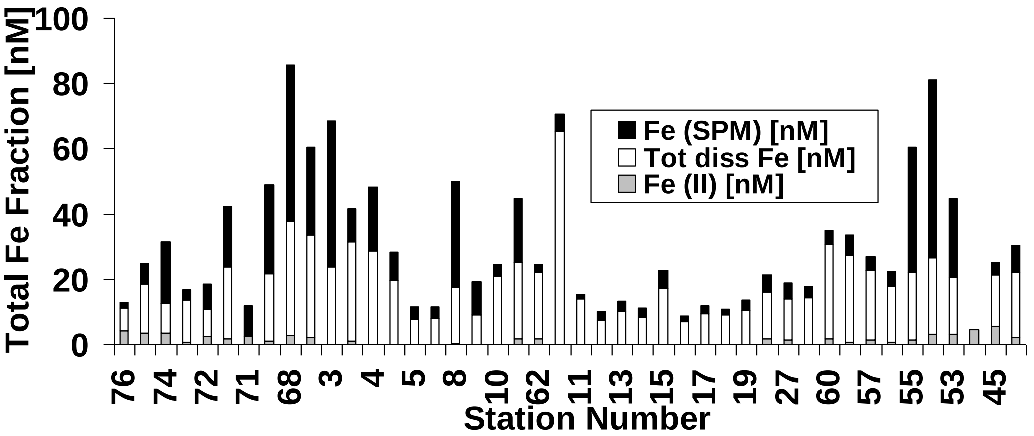

Figure 3.6. Overview of the iron content (Fe SPM + DFe) in the transition area and Baltic Proper in July 2008. From station 11 to station 19 Fe (II) measurements are not available. At station 3 and 5 the dissolved fraction of Fe (II) was below the detection limit.

Surprsingly, the results reflected than less than 3 % of the dissolved fraction occurred as reduced free Fe (II) below the redoxcline. Thus, the next question is focused on the remaining 97 % of Fe dissolved species. Because of this high content it is assumed that the major fraction of the dissolved Fe is associated and / or complexed with organic material. Also bisulfide complexes can bind up to 70 % of Fe in anoxic waters, which coincides with an increase in solubility of 1 - 6 orders of magnitude (Kersten et al. 1998).

Fe (II) concentrations are increasing down to 160 m due to the reduction of Fe (III) compounds e.g. Fe phosphates and Fe hydroxides. Below 160 m Fe (II) and total dissolved Fe concentrations are decreasing due to the formation of insoluble FeS.

Evaluating the possibility of Fe (II) transport from anoxic waters across the redoxcline, turbulent diffusive fluxes have been calculated. Pohl and Hennings (2005) calculated a mean DFe flux of 12.4 µmol m^{-2} day^{-1} across the oxic/anoxic interface using a turbulent diffusion coefficient from Lass et al. (2003) of K_D = 5.5 x 10^{-6} m^2 s^{-1}. Applying the same calculations, mean fluxes of 10.1 µmol m^{-2} day^{-1} for DFe and 0.3 µmol m^{-2} day^{-1} for Fe (II) were obtained by using a reviewed turbulent diffusion coefficient of K_D = 6 x 10^{-6} m^2 s^{-1} (Reissmann et al. 2009).

The overlap of the halocline and redoxcline at the Landsort Deep station divides the profile in two parts with the rise of the dissolved fraction and Fe (II) reaching a maximum below the redoxcline (~ 100 m) of 576 nM and 40 nM respectively.

Below the maximum, the concentrations remain rather uniform down to the bottom with concentrations around 400 nM and 30 nM. A lower content in H_2S compared to the Gotland Deep controls the formation of FeS particles. Therefore, the decrease of concentrations close to the bottom is imperceptible (Fig. 3.3). The FeSPM distribution at both stations characterized by anoxic deep water is related to the position of the redoxcline. In the Landsort Deep, a maximum of 48 nmol L^{-1} in the 70 m depth horizon was observed. In the Gotland Deep two maxima of 30 nmol L^{-1} at 75 m and of ~ 60 nmol L^{-1} in the 123 m depth horizon were registered.

Solid aggregates of Mn-Fe-P dominate the transition between oxic and anoxic conditions in relation to the geochemical cycles of these three elements. It should be mentioned, that Turnewitsch and Pohl (2010) estimated the dissolved inorganic phosphate (DIP) trapping efficiency. They calculated that at least 40% up to 60 % of the DIP that is mixed downward across the redoxcline would be scavenged by precipitating Fe- and Mn oxyhydroxides just below the redoxcline. This Mn-Fe-P-shuttle plays an important role in the phosphate transport throughout the water column and thus impacts primary production at least over longer time scales (Dellwig et al. 2010).

The Aaland Sea presents the highest values of DFe of the three stations in the first 70 m of the profile presumably due to the influence of the outflow of lower saline water from the Bothnian Bay. DFe double the concentration near the bottom. This increase coincides with the increase in the FeSPM and high values of turbidity (Fig. 3.6). As mentioned before oxic conditions and the influence of Kemijoki river are responsible for the existence of compounds like Fe (III) hydroxides and Fe (III) bound to humic substances. In several past investigations (not published) a “nepheloid layer” of 5 - 10 m thickness was observed, enriched in particulate Mn oxo-hydroxo complexes in the southern area of the Gulf of Bothnia. This could be an explanation of the increasing turbidity close to the bottom in that area. An accidental contact of the P-CTD with the bottom and a resuspension of particles from the sediments can be neglected. The Pump-CTD is additionally equipped with a camera and such event was not recorded.

3.3. Seasonal changes in iron speciation: Oxic/Anoxic transition and biological uptake

The in-situ monitoring of the iron distribution in different seasons and years was the strategy selected for a better understanding of the iron cycle in the Baltic Sea. Three cruises were carried out to stimate how changing conditions in the Baltic Sea throughout the year influences the iron speciation.

Furthermore comparisons of the blooms in both summer seasons with the profiles of Fe, nutrients and physical conditions (wind and temperature) appear at the end of this section. As seen in the first part of this chapter, Fe is not a conservative element in the Baltic Sea. The iron introduced by different sources (terrestrial, aeolian or recycling from the sediments) in the complex system of the Baltic Sea is transported by water circulation and transformed due to water properties (temperature, salinity, pH, organic content and redox conditions) and the biological activity of the different sub-basins. The cruises covered the winter of 2009 and the summer periods of 2008 and 2009.

The temperature increase in spring culminates with the development of a thermocline interrupting the vertical mixing separating the surface water layers from the water layers immediately located below the thermocline. Due to mixing restriction, biological activity depletes the nutrients resources available at the surface, as the layers immediately below the thermocline are rich in nutrients. Hence, meteorological conditions in winter (temperature, wind speed and direction) and the river runoff after the melting of the ice rule the spread of the spring bloom. At the same time the extension of this bloom will condition the availability of nutrients of surface waters in summer. Surface temperature profiles and satellite images obtained during the sampling periods show stable temperatures in 2008 (Fig. 3.1 & 3.7). The satellite images in winter are compromised by the presence of heavy clouds; however a winter with warmer temperatures in the central Baltic Proper and the area of Skagerrak of the order of 4 ºC can be recognized (Fig. 3.7).

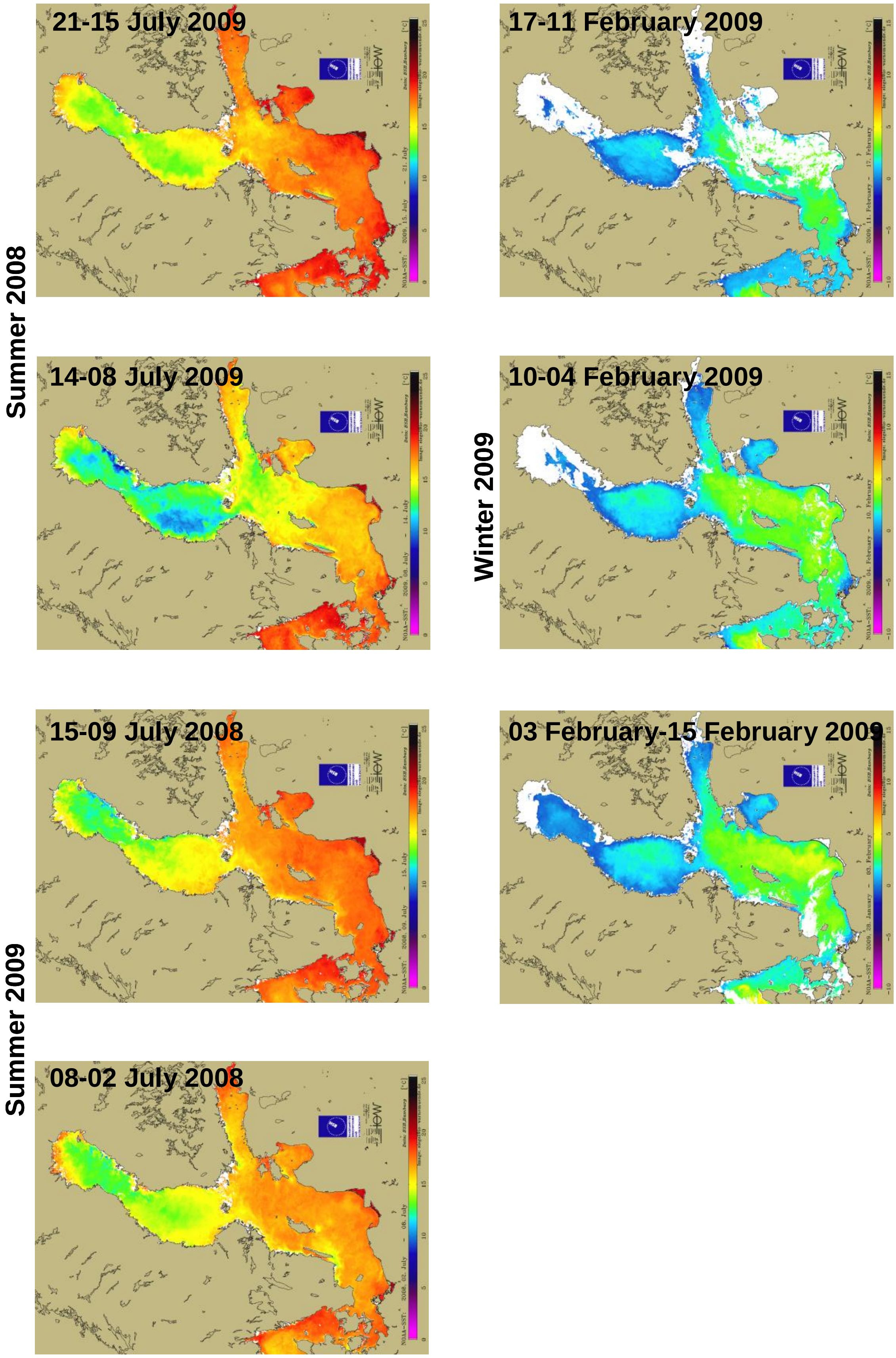

Fig.3.7. Satellite images of temperature distribution in surface waters of the Baltic Sea during the sampling periods in 2008 and 2009. The images are provided by Dr. H. Siegel and P. Wlost (IOW).

The first step to interpret the data collected is based on the development of four maps related to the iron content in the Baltic Sea and the distribution of the different fractions (particulate and dissolved). These maps condense the different stations and sampling points of the three cruises related to a concentration range of the different iron species in surface waters (Fig. 3.8 - 3.11). The data base for the maps cover the different areas of the Kattegat, Belt Sea, Arkona Basin, Bornholm Sea and the central Baltic Proper including the main stations of Landsort Deep and Gotland Deep. As the concentrations cover different intervals, the accurate concentration of the different species for each cruise together with other relevant information for each sampling point used in the maps are given in the appendix (Appendix 2 - 4).

The first map shows the distribution of total iron in the central Baltic Proper and the transition area. The iron concentration is expressed as a sum of the dissolved and particulate fraction (Fig. 3.10). No big seasonal variations in the iron content in the central Baltic Proper were observed. The main seasonal changes take place in the shallow areas of the Baltic Sea, especially in the area of the Belt Sea.

Referred to the dissolved fraction, three quarter of all samples collected in both years for DFe present values lower than 25 nM (Fig. 3.9). A common trend for the three transects is an increase of concentrations in the narrow area of the Belt Sea up to 40 nM. Highest concentrations both in summer and winter were found at stations close to the coasts of Germany and Poland. The “ob boje “ station with salinity of 7.9 influenced by river runoff sampled in winter shows the highest concentration of the profile with a DFe concentration of 250 nM. Both summer periods present higher concentrations than winter in the west part of the Arkona Basin and the surroundings of the Bornholm Island (Fig 3.10).

The lack of sampling along the transect between Landsort Deep and Öland Island in 2009 (winter and summer) can not corroborate if the increase of DFe in July 2008 in that area is a common fact in that area due to terrestrial input or a punctual phenomenon due to vertical mixing events. Sporadic high values in the central Baltic Proper during winter 2009 can be the result of a mixed water column (Fig. 3.10). The evaluation of the water column stability later on provides a better idea of the different pathways of DFe in such areas.

Inside the dissolved fraction, the Fe (II) presents small differences related to the total dissolved fraction. 75 % of all samples collected among the three cruises are in a range of concentrations below 5 nM. Higher concentrations were not restricted to shallow areas of the transition area. Concentrations up to 6 - 7nM were measured in front of the east coast of the Gotland Island and in the open sea areas of the south Baltic Proper (Fig. 3.9). It seems that most of the dissolved iron of terrigenic origin corresponds to non-labile hydroxides compounds of Fe (III). Higher concentrations during summer periods than winter suggest that photochemical processes and biological activities regulate the presence of Fe (II) in the surface waters of the Baltic above possible vertical transport from deeper layers or external sources.

FeSPM presents similar trend to DFe with the highest concentrations in the area of the Belt Sea and Arkona Basin and low values of the order of 10 nM in the open sea areas of the central Baltic Proper. The content of FeSPM in the surface waters of the Baltic Sea is higher during winter than in the summer periods; accumulation of iron particulate matter in the interface of the halocline together with a well mixed water column down to the halocline favours the upwards flux of particulate matter towards the surface (Fig. 3.11).

The distributions of the dissolved and particulate iron fractions show similar patterns for both summer periods, but present some differences compared to the winter distribution in 2009. A look on the DFe:FeSPM ratio (Fig. 3.12 and Appendix 2 – 4) for the different stations provides an idea how the iron speciation changes between the seasons. DFe:FeSPM ratio in winter is lower and more regular than in the summer seasons and always ranging from 2 to 4 (except “ob boje” station). Furthermore of the positive effect of the temperature in the solubility of iron oxyhydroxides, the contribution of the melting ice from the Gulfs during the early spring should be reflected in an increase of the iron content (mainly in the dissolved fraction) in the Baltic Proper. The melting of ice causing an outflow of lower saline water together with the characteristic weak counter-clockwise circulation of the surface waters of the Baltic Sea can explain the increase of DFe concentrations along the Swedish coast in summer. The low values in particulate iron in that area suggest that most part of the particulate material discharged sinks along the Gulf of Bothnia before it reaches the central Baltic Proper.

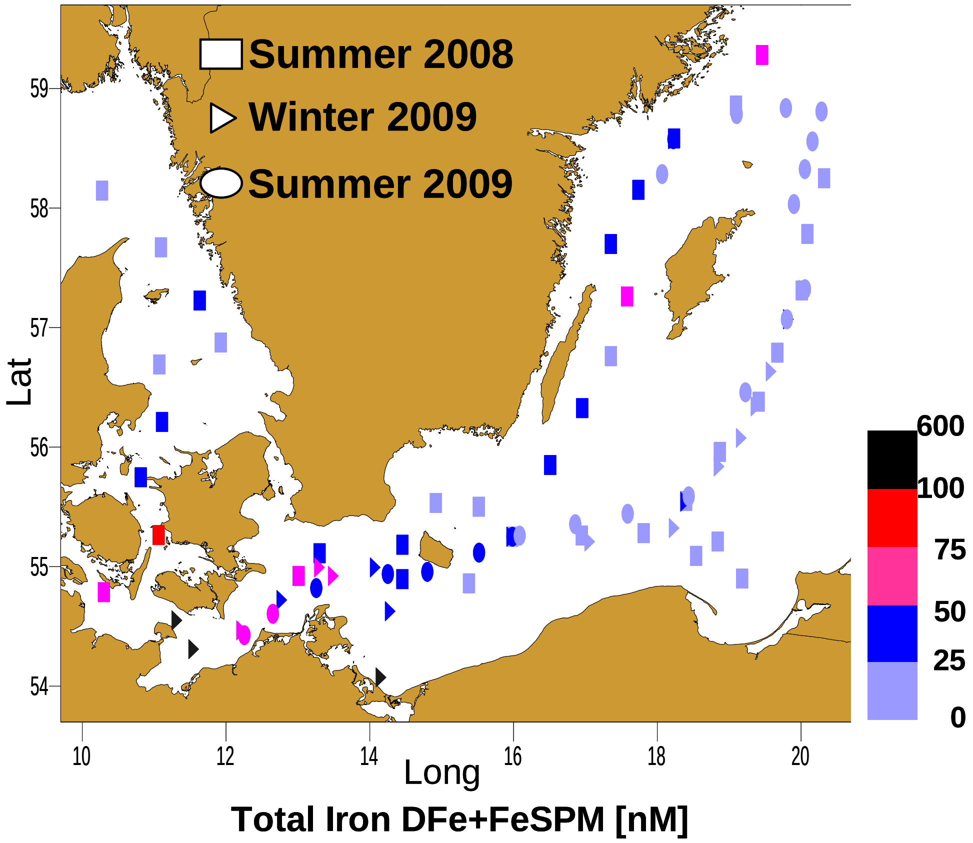

Figure 3.8. Total Fe distribution in surface waters of the Baltic Sea in winter 2009 and the summers 2008 and 2009.

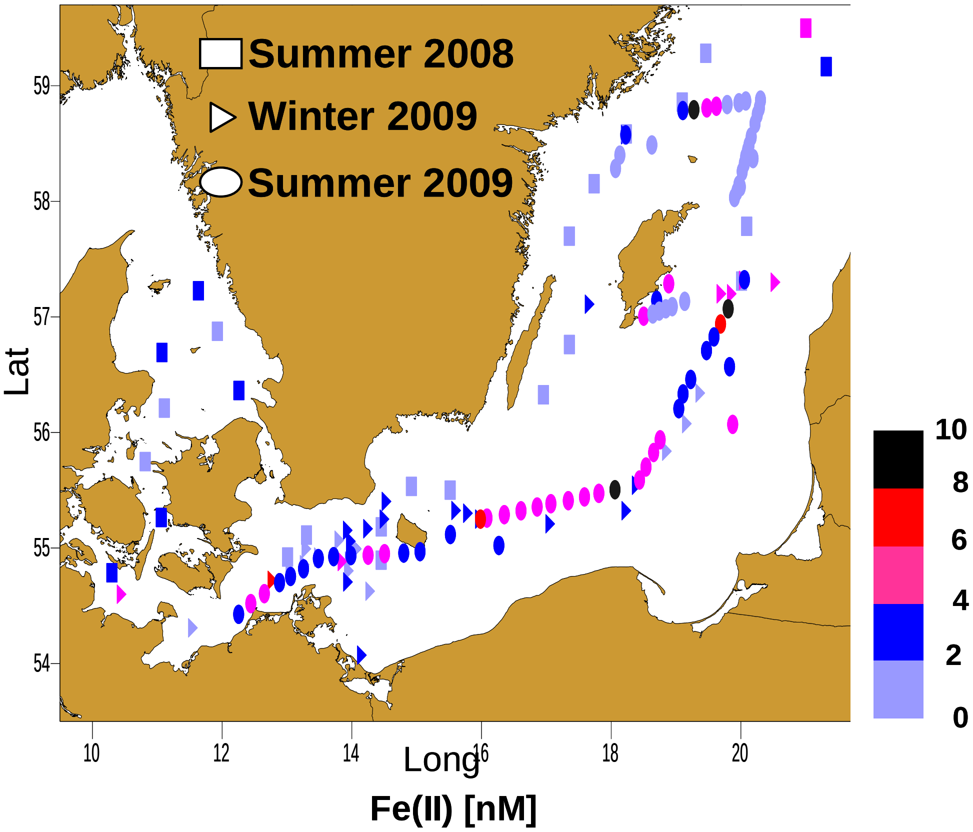

Figure 3.9. Surface Fe (II) distribution in the Baltic Sea.

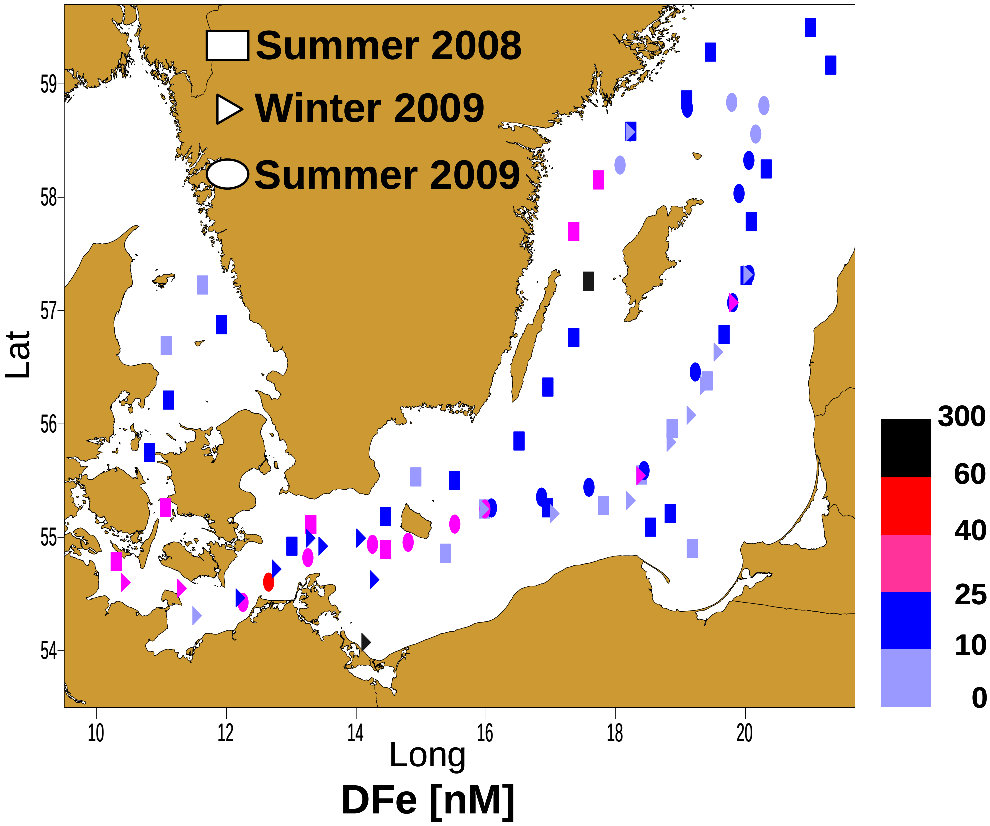

Figure 3.10. DFe distribution in the surface waters of the Baltic Sea between summer 2008 and summer 2009. Data provided by Dr. C. Pohl and U. Hennings.

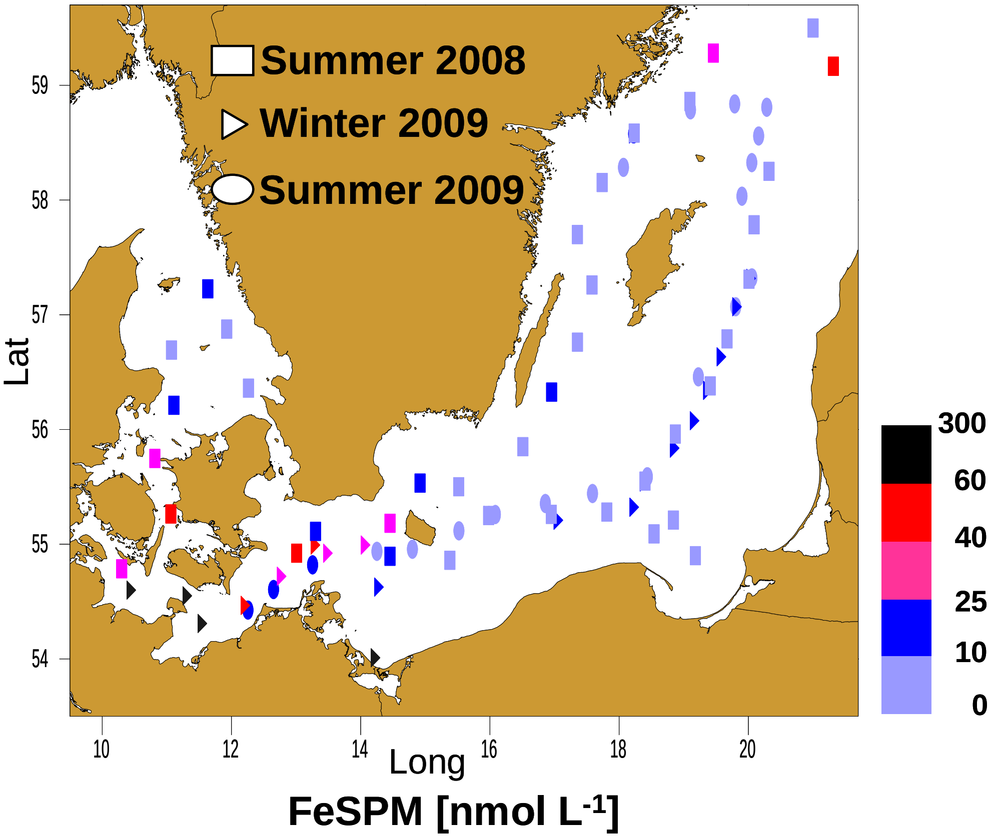

Figure 3.11. The FeSPM content in the Baltic Sea. Data provided by Dr. C. Pohl and U. Hennings

The next step is to connect the distributions of the different fractions of iron along the different sampling periods with the depth profiles recorded at the stations of Gotland Deep, Landsort Deep and Bornholm Basin in 2008 and 2009.

Gotland Deep

Salinity and dissolved oxygen profiles show a smoother interface of the halocline in July 2009, being the profiles for summer 2008 and winter 2009 more similar below 30 m. The thermal stratification and melting ice from the gulfs lead to a decrease of salinity in the surface waters in the summer periods compared to the winter. The decrease of oxygen in summer 2009 between 40 and 70 m could be related to a localised increase in mineralisation processes such as nitrification; however this cannot be proved by the dissolved nitrogen profile recorded (Fig. 3.13).

The profiles of nutrients show clearly depletion of both dissolved inorganic phosphate and nitrogen after the spring bloom for both summer cruises. Otherwise, during winter DIN and DIP in the first 50 m of the profiles had concentrations close to 3.5 µM and 0.7 µM, respectively. Maximum concentrations for DIN were recorded at the depth of 80 m during the three sampling periods coinciding with the halocline interface (Fig. 3.14) and the main mineralisation activities.

In summer the phosphacline is located around the 30 – 40 m depth that is 10 to 20 m above the nitrocline. This fact can be related to changes between seasons in the N:P ratio at the surface favouring the cyanobacteria blooms in summer. In the water layer located between both interfaces (halocline and redoxcline) the inorganic phosphorus is higher in winter than in summer. This will be discussed in the next section in relation to the formation of Mn-Fe-PO_4 aggregates.

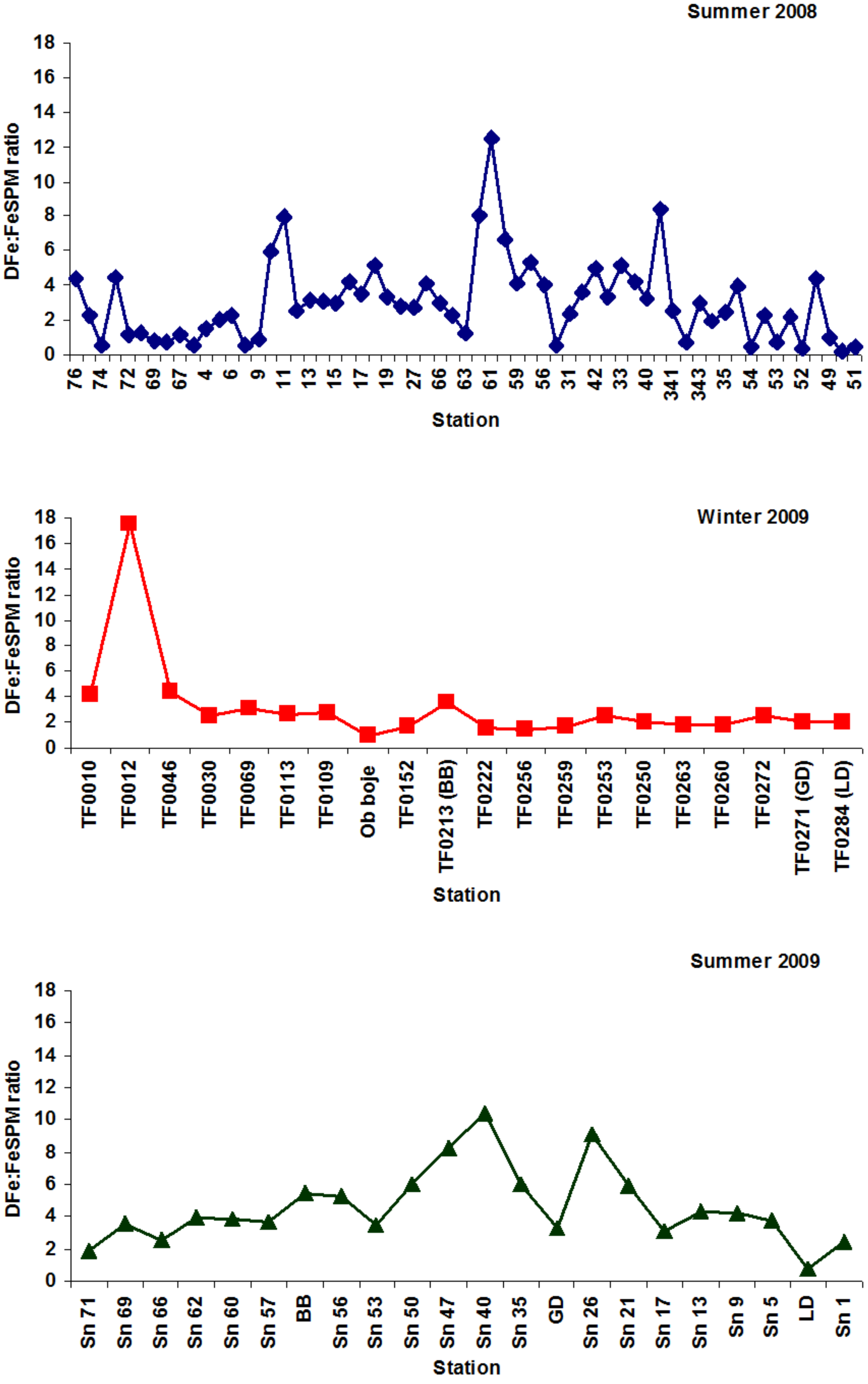

Figure 3.12. DFe : FeSPM ratio for the three cruises: The sampling points of the different cruises are distributed in the graphs from West to East and from South to North.

DFe concentrations during winter remain stable around 10 nM in the first 80 m of the profile. The decrease in oxygen content (60-65 m) coincides with the maximum above the halocline of DFe of 40 nM in July 2009 (Fig. 3.15). Similar distribution was observed in 2008 but around 10 m below and with a concentration of 30 nM. The decrease of oxygen is a consequence of the degradation of organic matter in summer after the decay of the spring bloom releasing DFe. In the next chapter it will be discussed the biological requirements of Fe in the Baltic Sea paying attention to the Redfield ratio. Below the redoxcline the content of DFe increases with a maximum concentrations higher than 1 µM between 150 and 175 m. Higher concentrations in winter than in summer and the change in location of the maximum below the redoxcline could be related to small inflows of higher saline waters and the appearance of H_2S in the deeper part of the basin. As DFe, the Fe (II) fraction is higher above the halocline in July 2009 compared to the other two sampling periods influenced by the content of oxygen. Below the redoxcline the winter shows higher concentrations of free Fe (II). The lower fraction of H_2S in wintertime affects the presence of FeS complexes and therefore the content of the free ion is higher (Fig. 3.16).

In the profiles of particulate iron; the main aspect is the difference in the concentrations around 60 m depth between both summers. Those values represent content 10 times higher in particulate Fe compared to the summer before. Below the redoxcline the highest content of H_2S occurs in July 2009 providing the highest concentrations of FeS particulate at the bottom of the Gotland basin (Fig. 3.15).

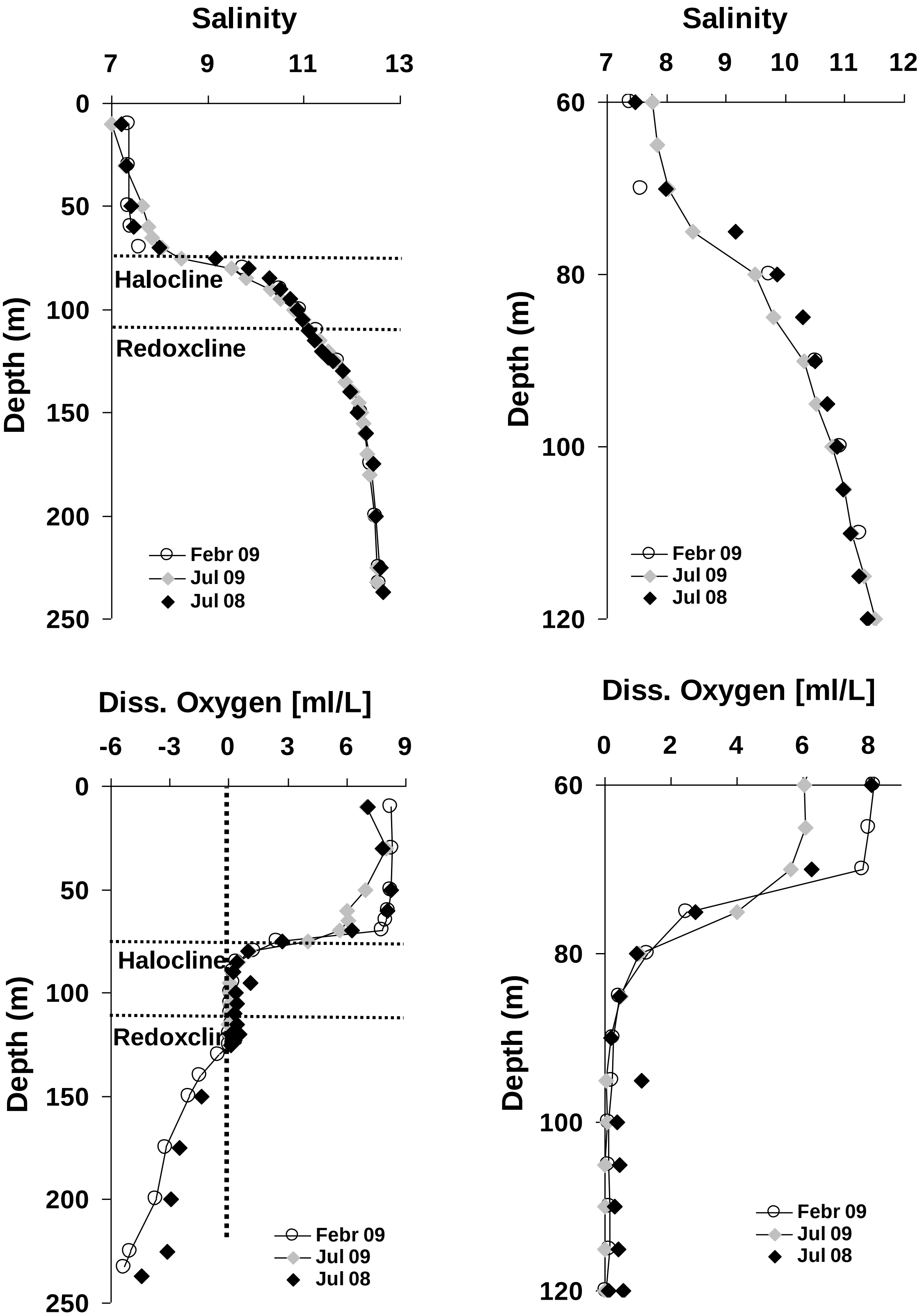

Figure 3.13. Salinity and dissolved oxygen profiles in the Gotland basin in 2008 and 2009. A emphasize to the first 100 m of the water column was made to distinguish better the processes occurring between the interfaces of halocline and redoxcline.

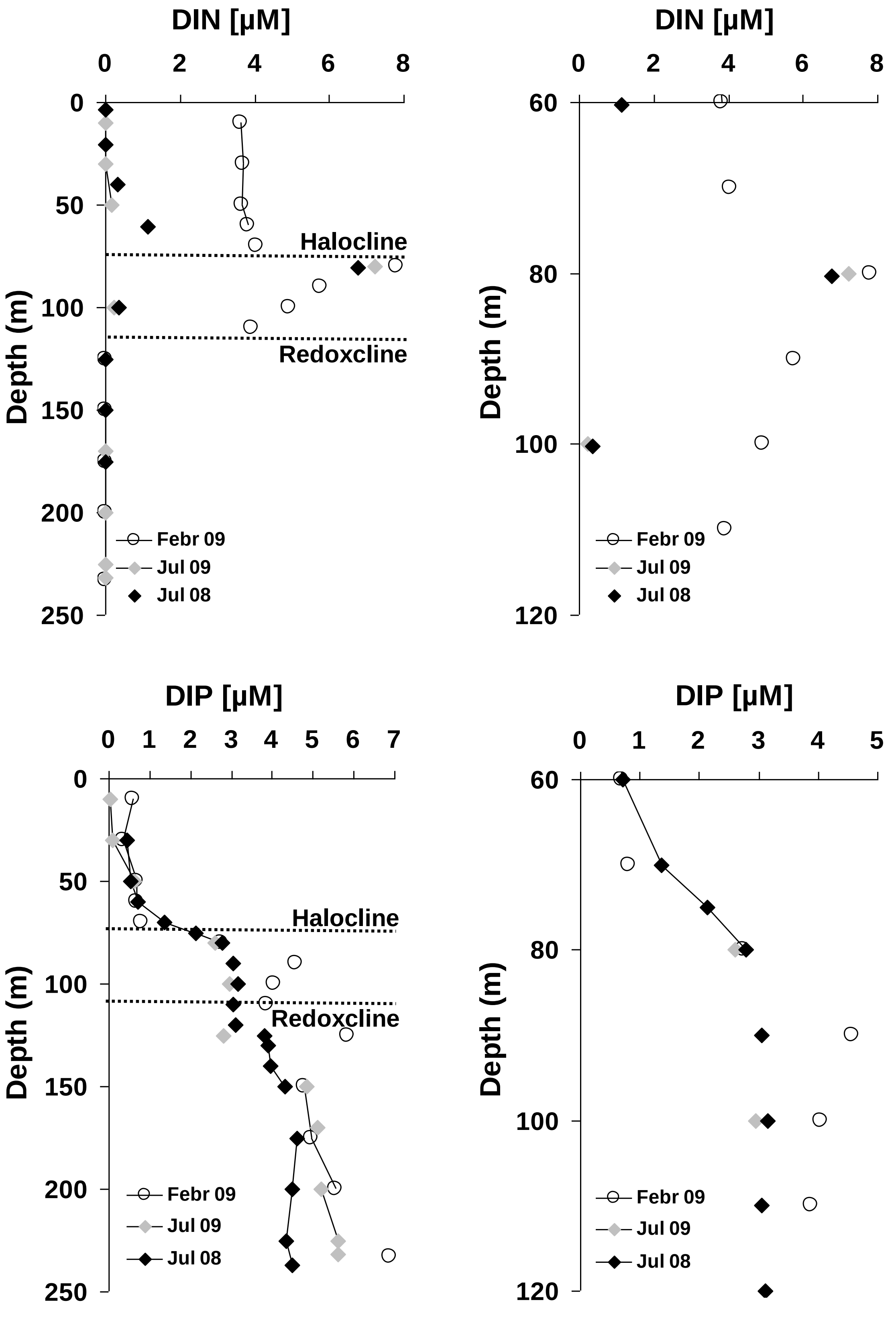

Figure 3.14. Dissolved nutrients distributions of the Gotland basin in 2008 and 2009 (DIN = NO_3 + NO_2). Data provided by Dr. G. Nausch (IOW).

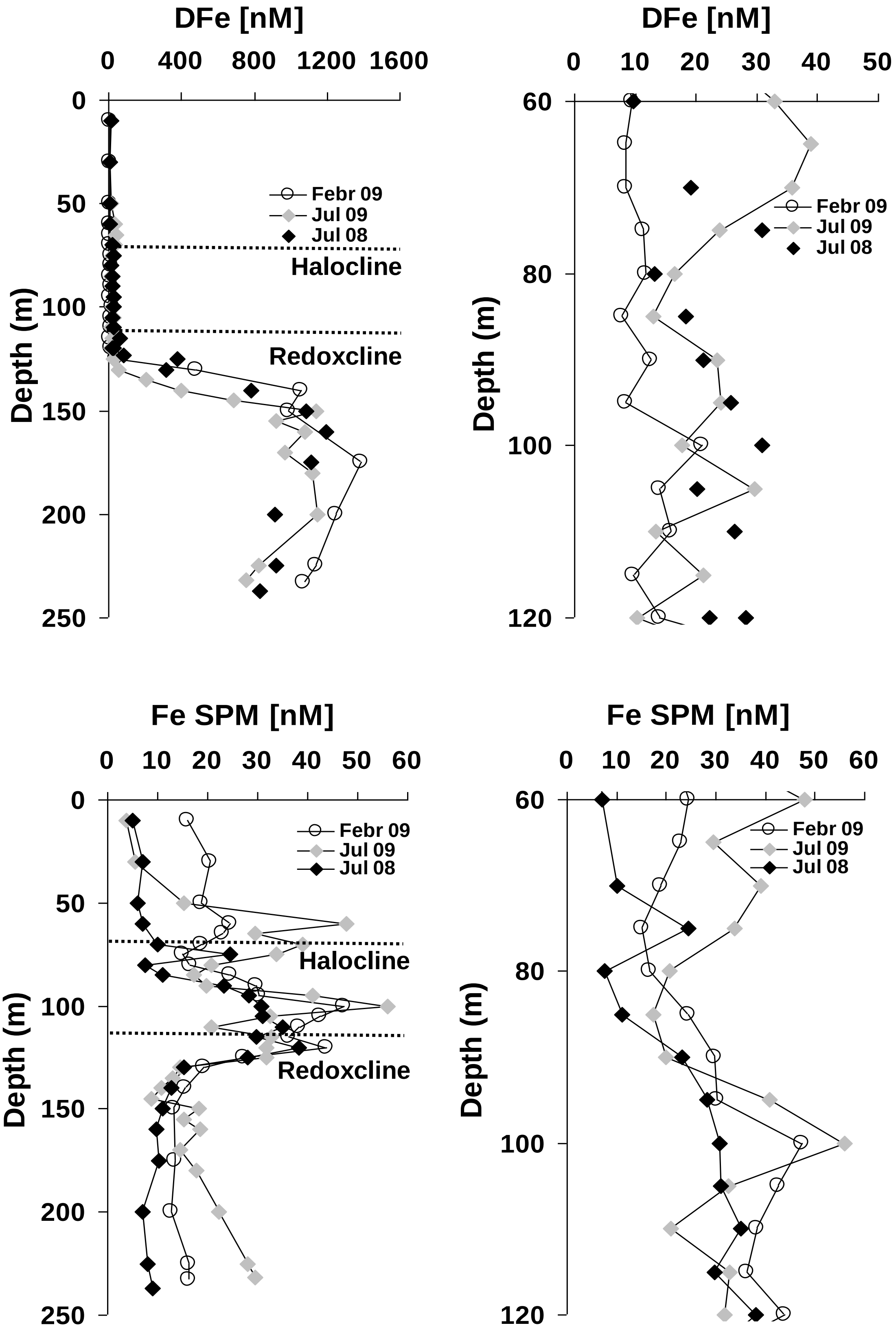

Figure 3.15. DFe and Fe SPM profiles at the Gotland basin in 2008 and 2009. Data provided by Dr. C. Pohl and U. Hennings.

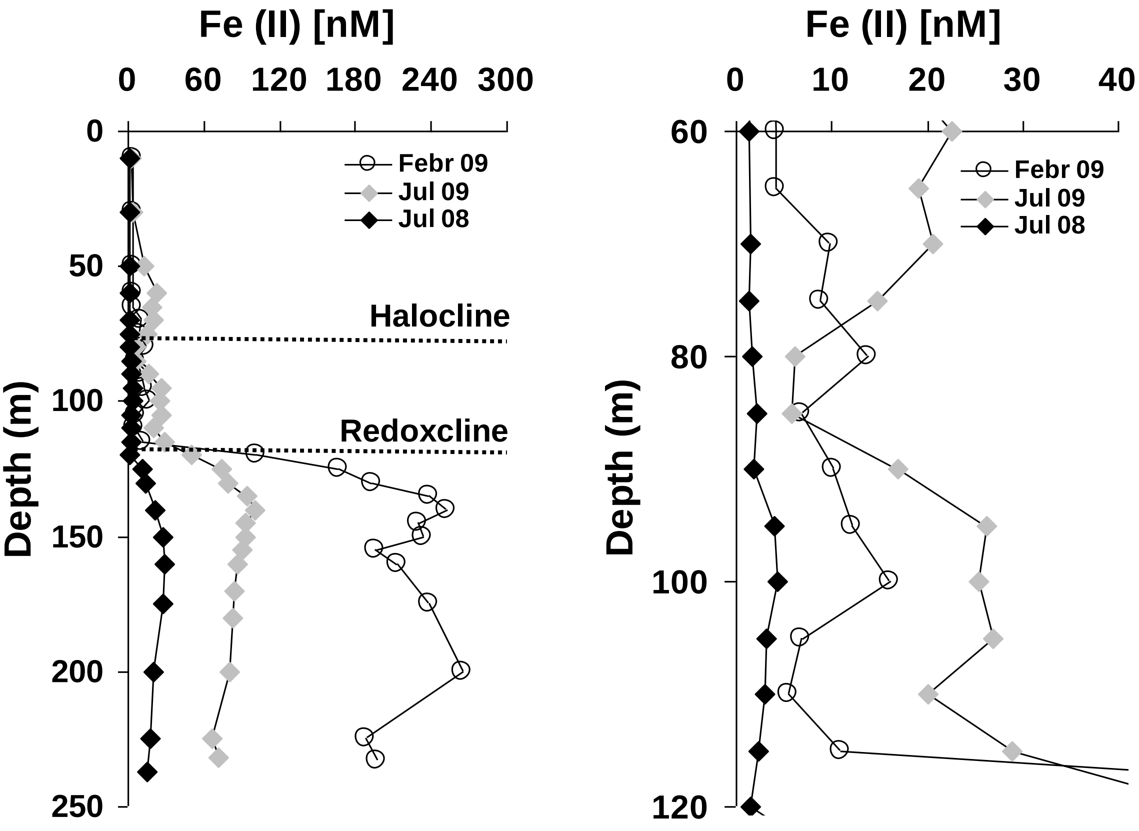

Figure 3.16. Fe (II) profiles at the Gotland basin in 2008 and 2009.

Landsort Deep

The difference in salinity between summer and winter in the surface waters is around 2, much higher than in the central Baltic Sea. This confirms the direct influence of the gulfs onto the hydrology of this area. In summer 2009 the redoxcline is located 10 m higher than during the summer before presenting an anoxic state around 75 m depth. A faster depletion of the oxygen content in the water column during summer 2009 could be related to a higher degradation of organic matter (higher biological activity) respect the summer before, contrasting with the winter period where vertical mixing allows that oxic conditions remain up to 90 m in the water column (Fig. 3.17).

The summer surface waters both in 2008 and 2009 were depleted of dissolved inorganic nutrients. The concentrations of DIN and DIP are slightly lower than in the Gotland Deep but present the same distribution along the water column. In July 2009, the depletion of oxygen in the first 75 m of the profile led in a lower content of nitrate (converted in ammonia under anoxic conditions) than during the other two sampling periods (Fig. 3.18).

The phosphacline is located higher than in the Gotland Deep at around 30 m depth. Upwelling events are common along the Swedish coast. This allows easier the vertical transport of rich phosphate water masses in the proximities of the Landsort Deep than in the open sea area of the Gotland Deep. Below the 40 m the distribution of DIP is similar in the three periods of sampling. This suggests that thermal stratification and biological activity are the only processes with a seasonal character that influence the DIP concentration (Fig. 3.18).

The dissolved iron fraction presents the most interesting profiles. Despite the Gotland Deep and their clear division in three well-distinguished parts, the proximity between both clines diffuses the area between the salinity gradient and the change in redox potential (Fig. 3.19). Dividing the profiles in two parts based on the oxygen content, differences among the three sampling periods are marked by its rate of penetration in the water column. Summer 2008 and the following winter are characterised by an abrupt rise of the dissolved fraction with the oxygen depletion reaching a maximum around 120 m.

Below that maximum the concentration decreases in an order of 200 nM in summer, whereas in winter the concentration of DFe remains in the order of the maximum value down to the bottom. The transition between oxic and anoxic layer related to the DFe is smoother presenting a gradient around 300 nM from 50 m to 150 m depth.

Below this depth, the concentrations for both summer periods are in the same range (Fig. 3.19). The processes occurring in the transitions between oxic and anoxic conditions and the difference in DFe content in the deep waters of the main stations of Landsort and Gotland Deep (2 - 3 times higher in Gotland) will be discussed in the first two sections of the discussion chapter.

Regarding FeSPM in the Landsort Deep, especially significant is the difference between both summer periods in the first 50 m of the profile. Summer 2009 provides the highest concentrations in surface waters with values up to 20 nM. The FeSPM content in July 2009 is more than 4 times higher than the year before and 20 % higher than the values registered during the winter of 2009 five months ago (Fig. 3.19).

Beyond biological activity, one hypothesis could be related to the depth of the oxygen minimum zone and the highest concentrations of DFe in upper layers of the water column. Located in an upper zone of the water column the flux upwards to surface waters of high quantity of DFe is more plausible. Part of this DFe could form aggregates of iron hydroxides in the oxic surface waters. This particulate matter formed at the surface would sink and taking part in the iron turnover at the anoxic/oxic interface again. As expected, inside the dissolved fraction, the Fe (II) has the same trend as DFe in the water column with rising concentrations as the water column turns anoxic. Of special interest is the slight decrease around 125 m that involves a consumption of free Fe (II) ions under anoxic conditions (Fig. 3.20).

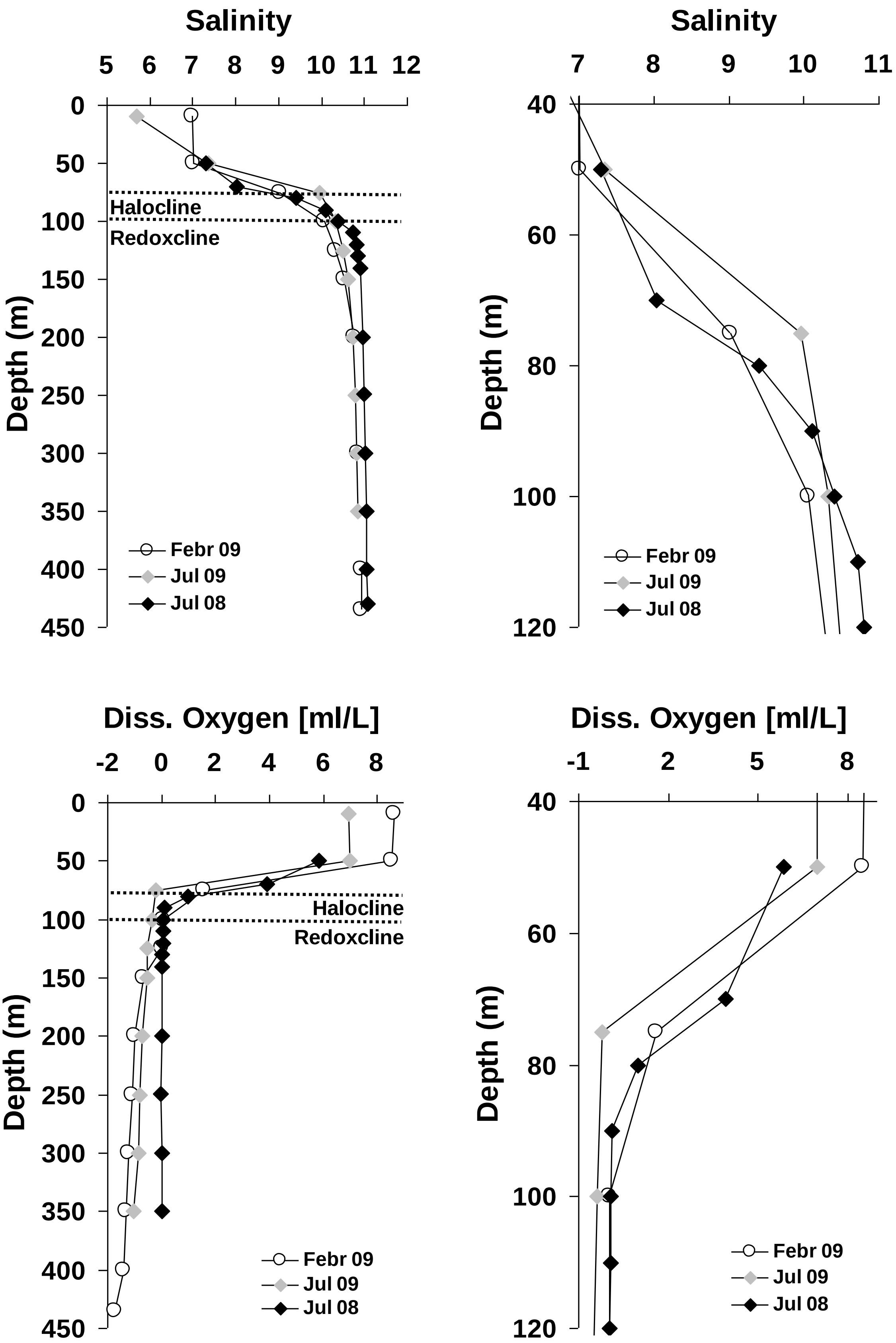

Figure 3.17. Salinity and dissolved oxygen profiles at the Landsort Deep in 2008 and 2009. An emphasis to the first 150 m of the water column was made to distinguish the processes occurring between the interfaces of the halocline and the redoxcline.

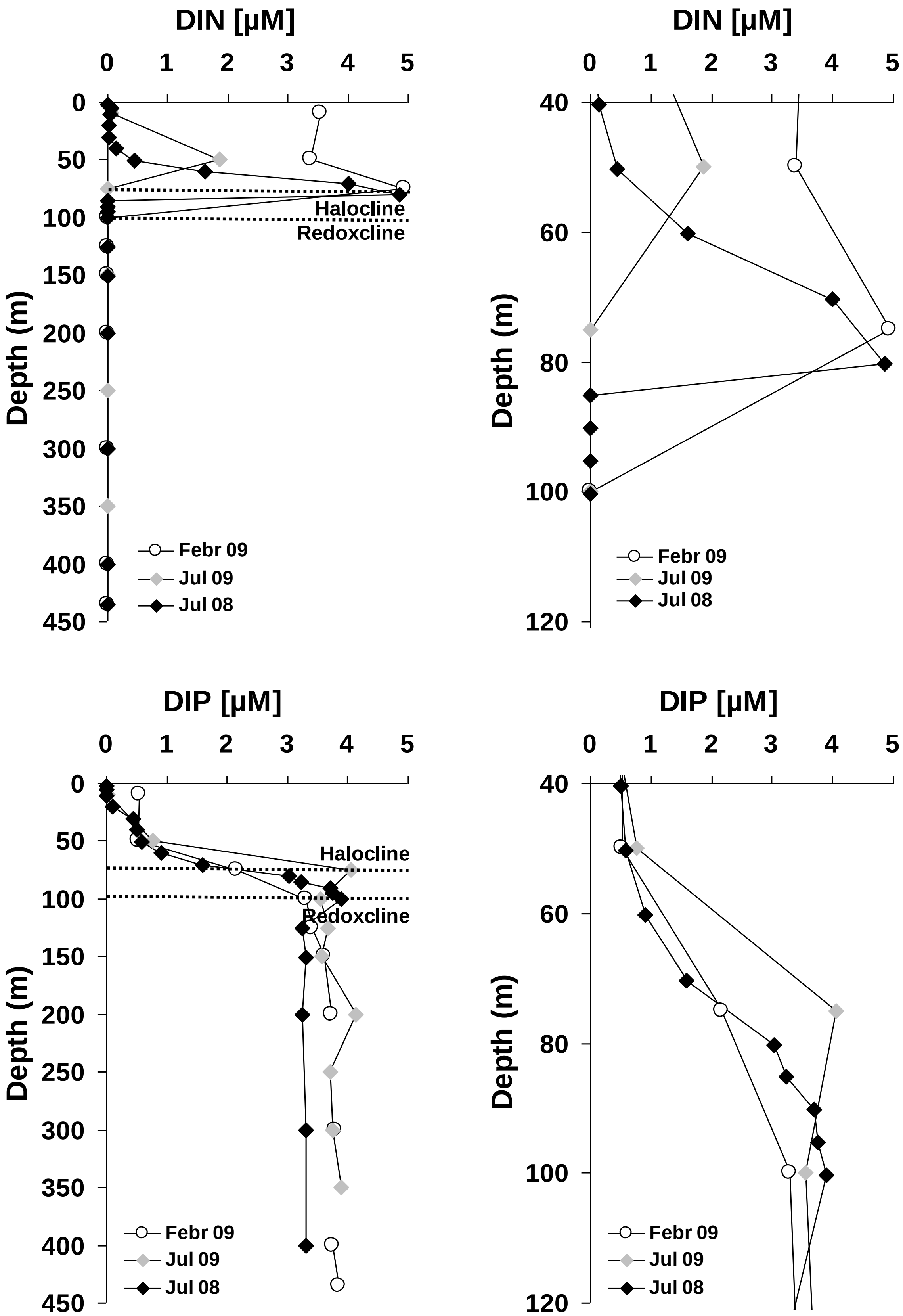

Figure 3.18. Dissolved inorganic nutrients profiles at the Landsort Deep in 2008 and 2009. Data provided by Dr. G. Nausch (IOW).

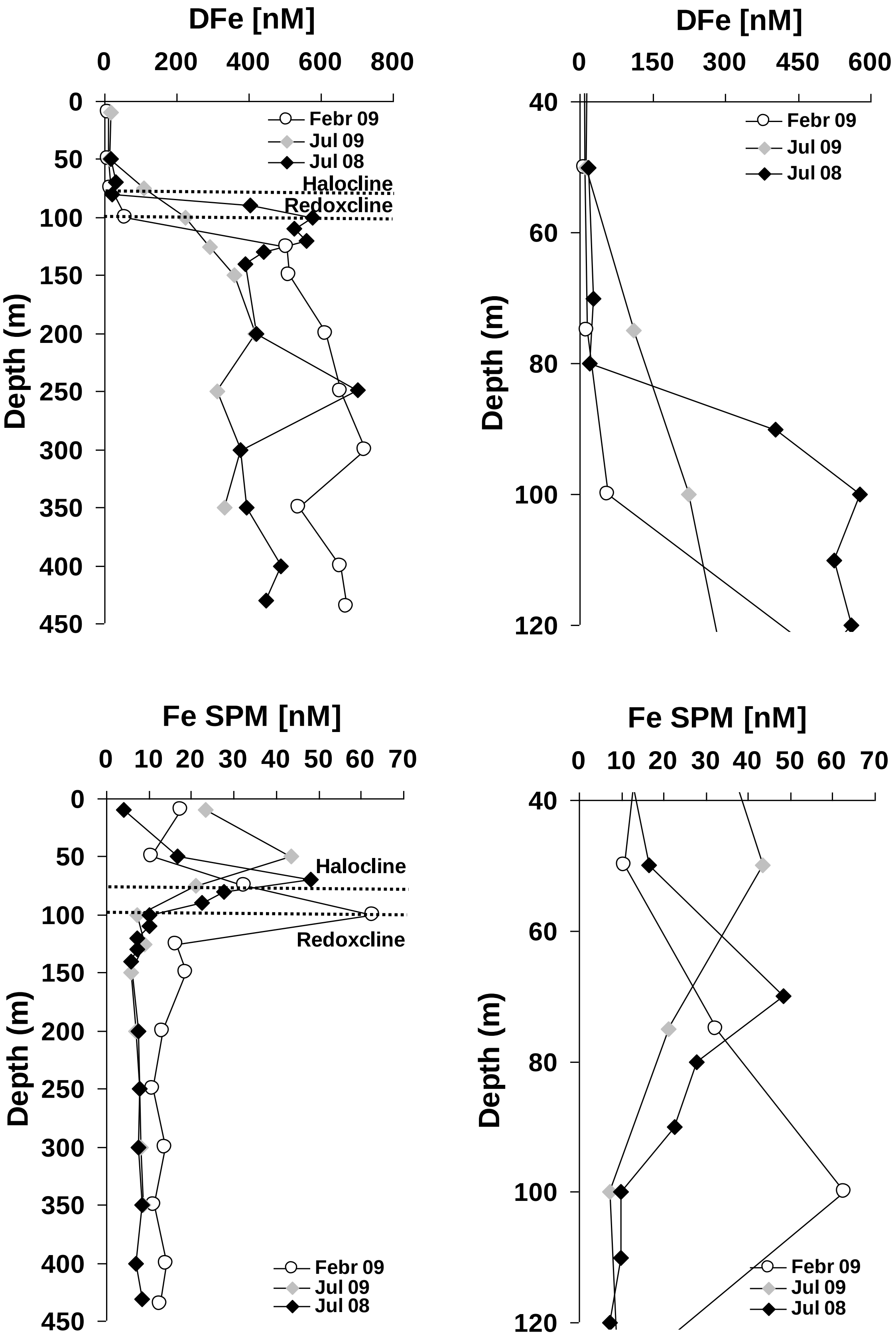

Figure 3.19. DFe and FeSPM profiles at the Landsort Deep in 2008 and 2009. Data provided by Dr. C. Pohl and U. Hennings.

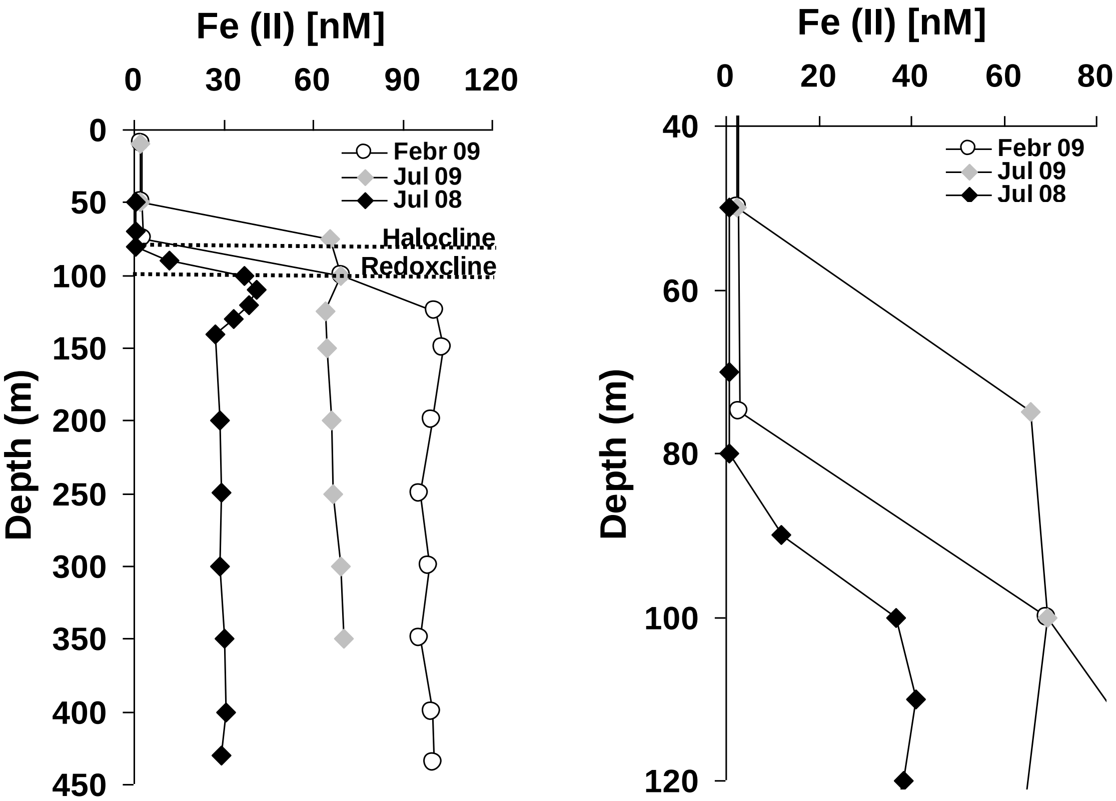

Figure 3.20. Fe (II) profiles at the Landsort Deep station in 2008 and 2009.

Bornholm Basin

Located in the western Baltic Proper at a longitude of 15° 58´ East and almost 85 m deep the Bornholm Basin has a halocline above 60 m and hypoxic conditions close to the bottom. During winter the water column remains well mixed from the surface down to the proximity of the halocline with salinity higher than 7.5 and oxygen content around 8 ml/L (Fig. 3.21). The deep-water masses located in the last 10 m of the water column reach salinity up to 15 and a deficit of oxygen with concentration below 1 ml/L.

In the Bornholm Basin the dissolved inorganic nutrients have the same pattern at the surface during winter as the Gotland Deep. Total depletion of nutrients in the surface layer is another common factor with the Gotland Deep. Below the halocline the DIP concentrations are lower in summer compared to winter. On the other hand, DIN increases by more than 3 µM its concentration between the thermocline and the halocline in summer (Fig. 3.21).

The content in dissolved iron in the whole water column is more than 3 times higher in summer than during winter. In July the concentration of DFe presents an increase below the halocline in contrast to the winter distribution. Particulate fraction shows similar trend, the exception is at the surface with higher values in winter related to the vertical mixing of the water column. The decrease of DIP and the increase of FeSPM at the deepest part of the profile could be related to the formation of Fe-Mn-hydroxides aggregates trapping inorganic phosphorus (Fig. 3.22). The higher penetration of oxygen during winter generates lower concentrations of Fe (II) in winter than summer. The profiles are characterised by an increase close to the bottom where the oxygen concentrations are below 1 ml/L (Fig. 3.22).

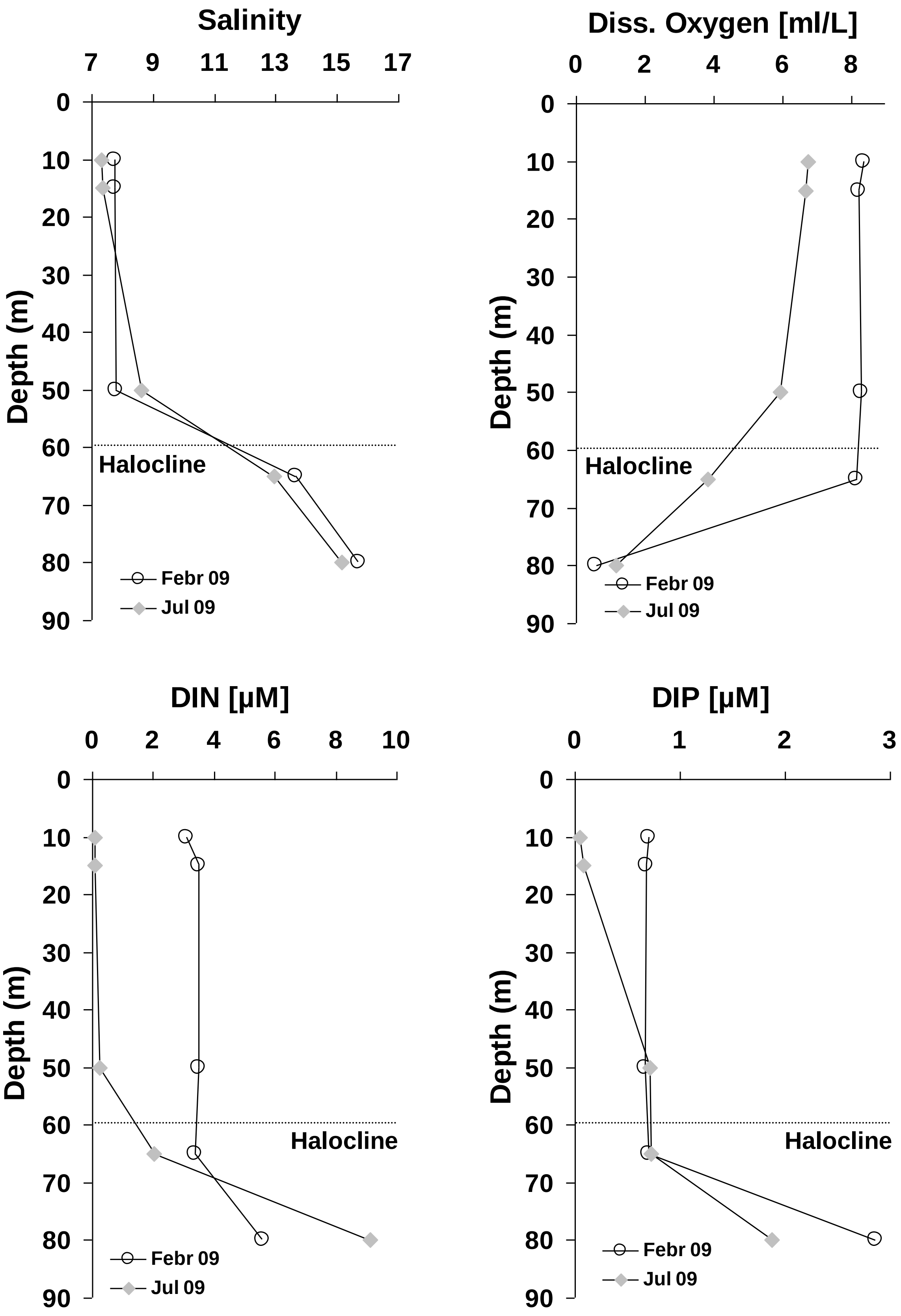

Figure 3.21. Salinity, dissolved oxygen and dissolved inorganic nutrients profiles at the Bornholm Basin in 2009. Nutrients data provided by Dr. G. Nausch (IOW).

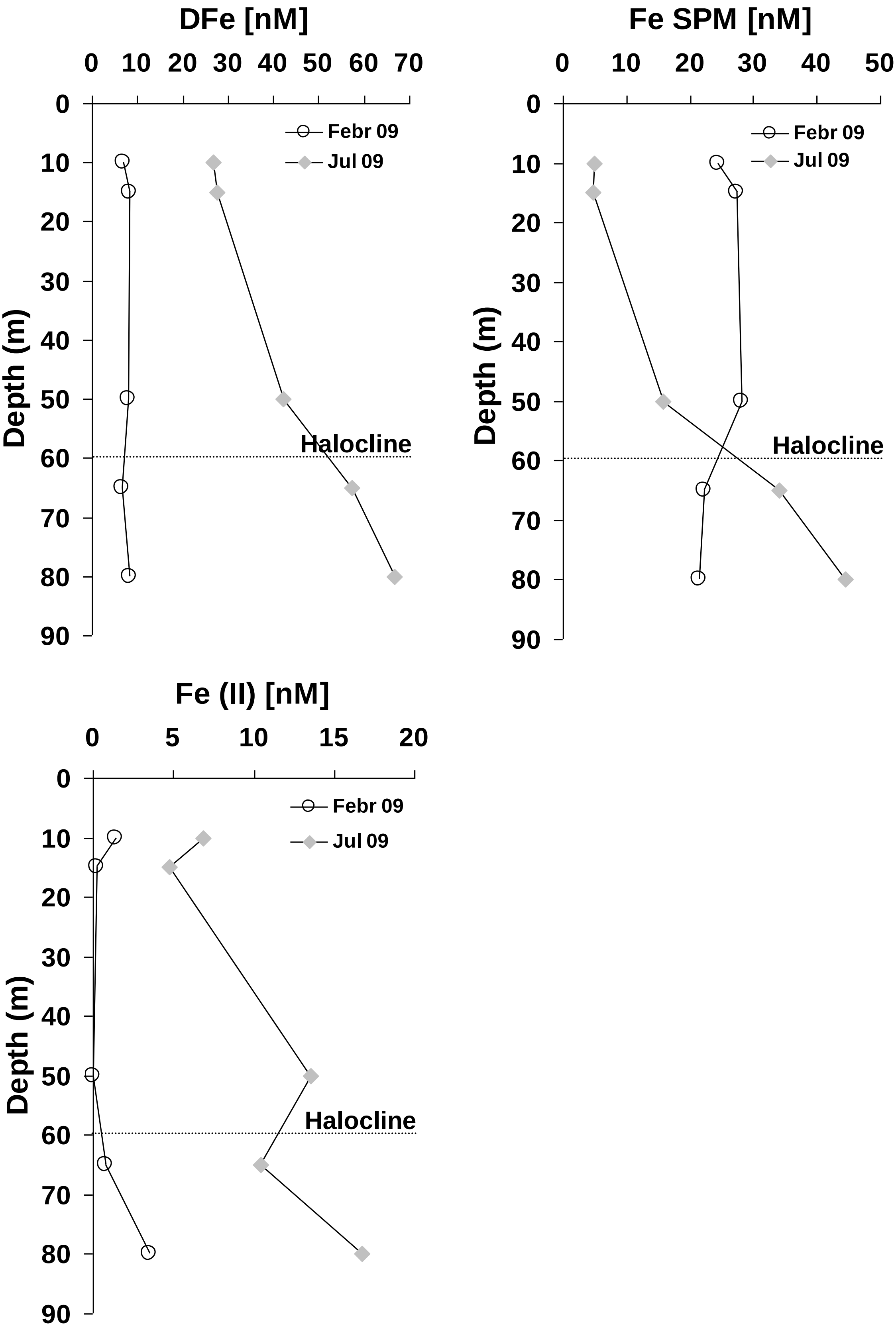

Figure 3.22. Fe speciation at the Bornholm Basin in 2008 and 2009. DFe and FeSPM data provided by Dr. C. Pohl and U. Hennings (IOW).

Cyanobacteria blooms during summer 2008 and 2009

After relating seasonal changes of different physical and chemical properties to changes in the iron speciation based on surface distributions and depth profiles, the next step is to consider the biological activity in the surface waters of the Baltic Sea during summer based on the picture obtained. A general view can be made based on satellite images extracted from HELCOM (Helsinki commission) website and provided by the Swedish Meteorological and Hydrological Institute (SMHI) (Appendix 5). July 2008 was warm and calm, sometimes presenting a cloudy Baltic Proper obscuring the accurate assesment of the bloom development. The favorable conditions during July allowed the accumulation of cyanobacteria almost along the whole Baltic Proper and Bothnian Sea by the end of the month. HELCOM provides a description of a bloom reaching the biggest extension in the last week of July with strongest accumulations found east of Gotland and southeast of Öland islands. Dense accumulations also reach areas as Bornholm, the Bothnian Sea and the western half of the Gulf of Finland. The bloom started its decay on the first week of August attributed to the decrease in sunlight and the dispertion of the bloom by wind and waves action. The normalization made by HELCOM shows that the different parameters of intensity, duration and extension that characterize the cyanobacteria blooms were slightly lower during the summer 2008 than the media reported for the period 1997-2007.

Summer 2009 presented more variable weather conditions that affected the evolution of the bloom in the Baltic Proper. Windy and cold conditions in the second part of July disaggregated the cyanobacteria accumulated in the surface waters during the last week of June and first days of July. The sampling period took place in the first two weeks of July, an unstable period with weather conditions from warm and calm to windy and cold and vice versa.

Short periods of calm and warm weather conditions in August this time favored the accumulation of cyanobacteria in the upper part of the Baltic Proper and the Bothnian Sea. The most intense period in the detection of the bloom is between the 12th and 20th of July covering a big area of the Baltic Proper south of Gotland island. The turn of the weather conditions allow the development of a bloom in 2009 quite similar in regional extension to the average blooms for the period 1997-2007, but well below in duration and intensity (Appendix V).

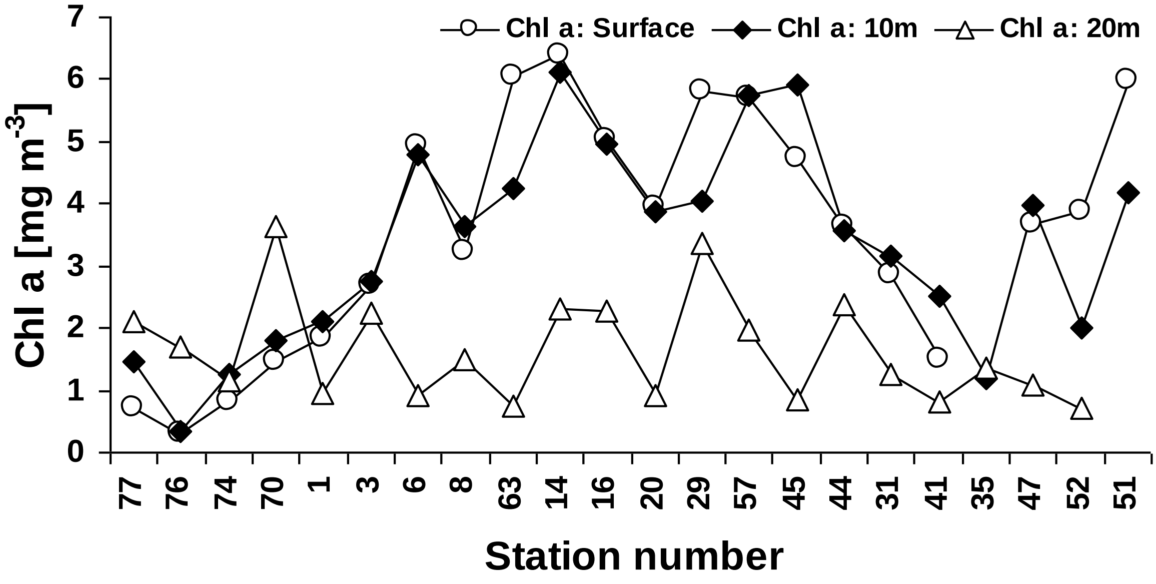

Figure 3.23. Chlorophyll a distribution along the Baltic Sea during summer 2008. Data provided by Dr. M. Nausch (IOW).

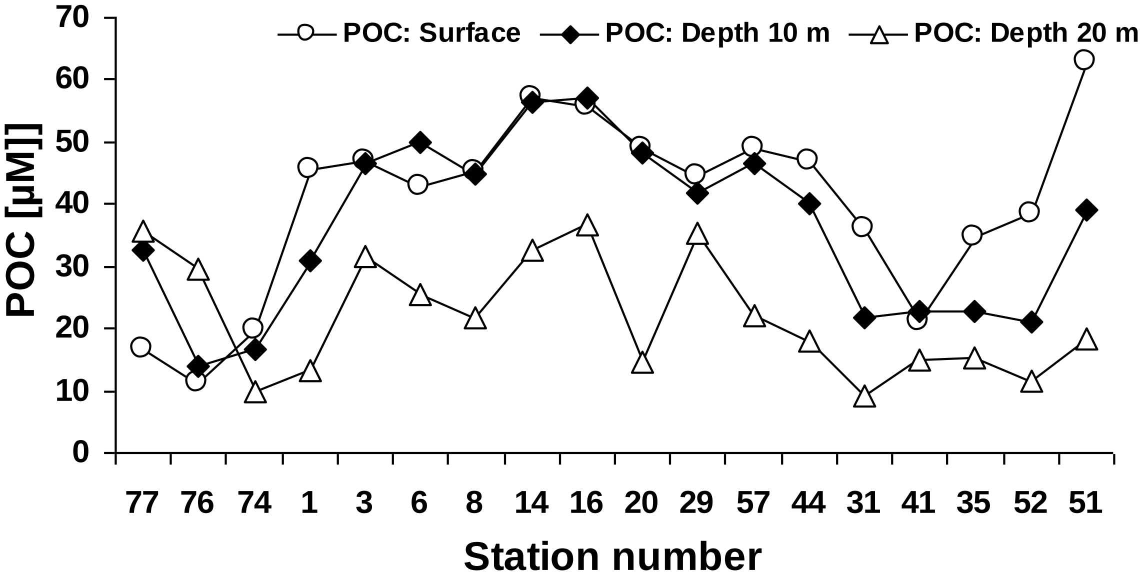

Figure 3.24. POC distribution along the Baltic Sea during summer 2008. Data provided by Dr. M. Nausch (IOW).

Chlorophyll a values measured by Dr. Monika Nausch (IOW) provided more details about the bloom development during the sampling period. Similar concentrations in both years were registered, but completely different estates of the blooms were sampled in both years. In 2008 the sampling in the open sea areas of the central Baltic Proper took place in the last two weeks of June. At that time the surface temperatures did not reach the highest values and the bloom was in the first stages of growth.

In summer 2008 lowest chlorophyll a values in the surface (< 1 mg m^{-3}) were found in the area of Skagerrak, followed by the areas of Kattegart and Belt Sea. Values between 2 - 4 mg m^{-3} were found (Fig. 3.24) at the stations of the Arkona Sea, Bornholm Basin, Northern Baltic Proper, Aaland Sea and Gulf of Finland. Highest concentrations up to 6 mg m^{-3} were found in the central Baltic Proper and in the west part of the Gulf of Finland, with the maximum at the stations close to the Gulf of Dansk (Fig. 3.23). Almost everywhere chlorophyll a concentrations were higher in the first 10 m of the water column with the exception of the Skagerrak. In the Skagerrak the values are higher at 20 m depth than in the upper part of the water column probably due to changes in phytoplankton community.

Particulate organic carbon (POC) shows the same trend maintaining the same coherence like Chlorophyll a concentrations both in horizontal and vertical distribution. Thus, the POC oscillate from the lowest values down to 10 µM in the transition area to the highest concentrations up to 60 µM close to the Gulf of Riga (Fig. 3.24).

In summer 2009 the sampling for Chlorophyll a was focused on the proximities of the Gotland Island mostly in the east part with transects from the Gotland coast to waters of Latvia. The exception was the stations 36 and 37, which belong to the Landsort Deep and the northern part of the Baltic Proper, respectively (Fig. 3.25). According to the area sampled, values were in the same range as during the year before. POC concentrations between the surface and 10 m depth shows a clear difference compared to the chlorophyll values (Fig. 3.26). High concentrations of chlorophyll and POC at 20 m close to the values registered at first 10 m depth suggests strong wind influence leading to the mixing of the uppest meters of the water column.

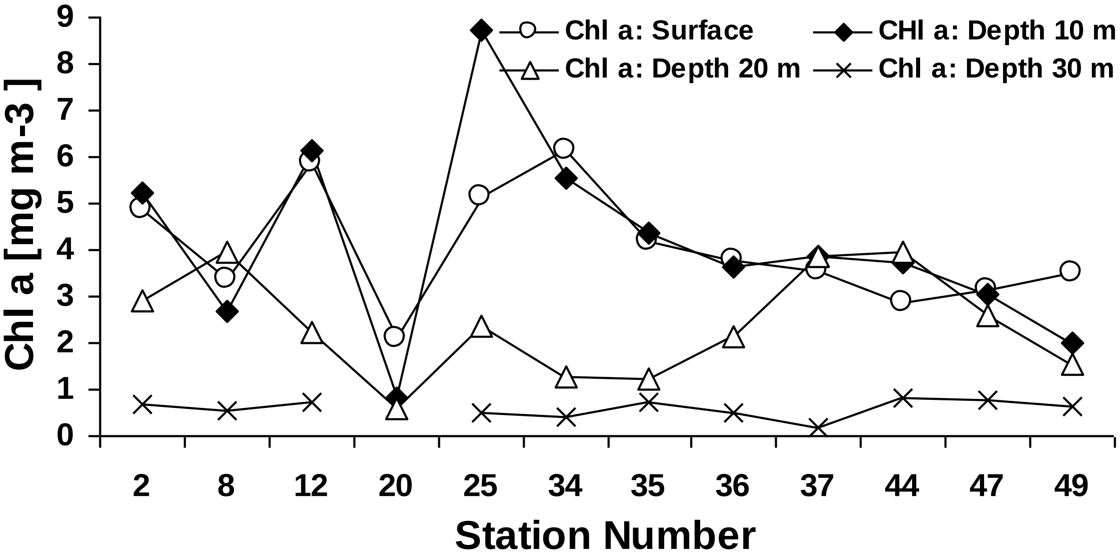

Figure 3.25. Chlorophyll a values measured in the surroundings of the Gotland island during summer 2009 on board of the R.V Alkor. Data provided by Dr. M. Nausch (IOW).

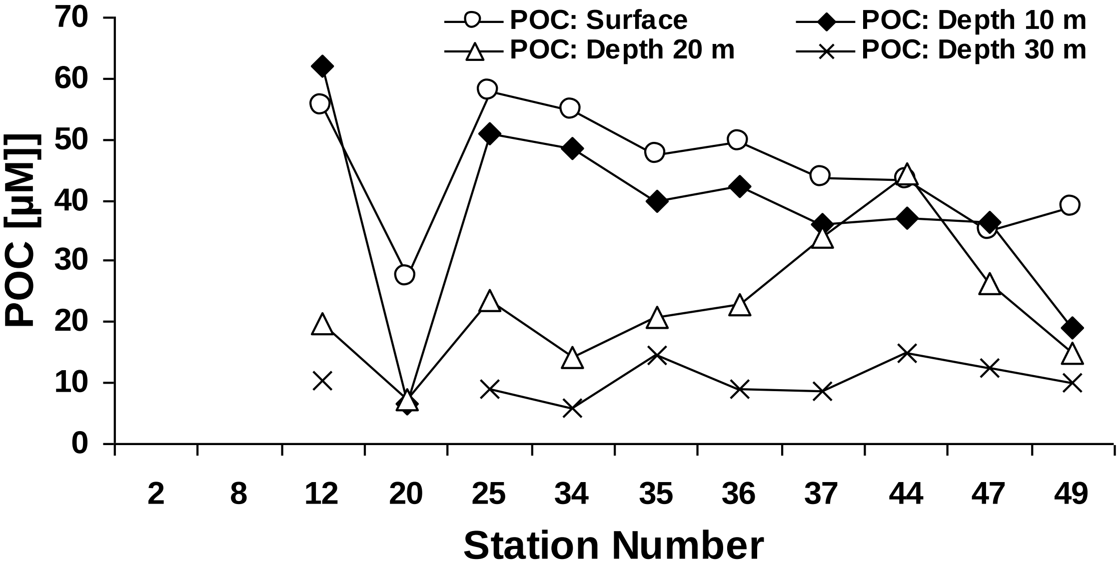

Figure 3.26. POC values measured in the surroundings of the Gotland island during summer 2009 on board of the R.V Alkor. Data provided by Dr. M. Nausch (IOW).

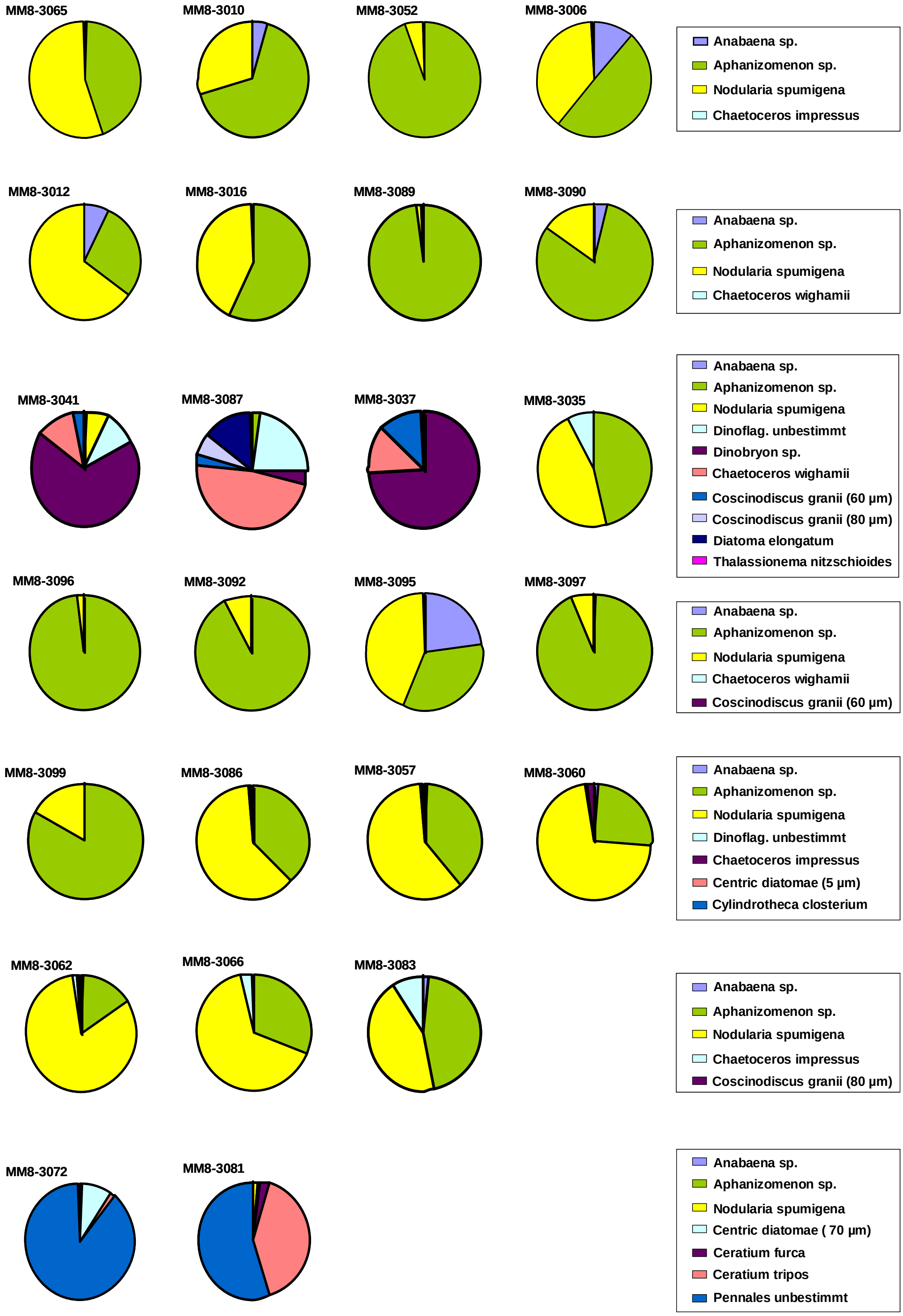

Figure 3.27. Characterization of phytoplankton based on net samples collected during the cruise MSM 08/03 in summer 2008. Data provided by Monika Nausch (IOW).

The phytoplankton population in summer 2008 reflects the predominance of Nitrogen-fixation cyanobacteria in the whole Baltic Proper as well as the Bothnian Sea and Gulf of Finland (Fig. 3.27 und Fig. 3.28). In the rest of the surface waters of the Baltic Sea, diatoms dominate the phytoplankton community in the transition area to the North Sea whereas the low salinity area of the Bothnian Bay is ruled by dinoflagellates (Fig. 3.28).

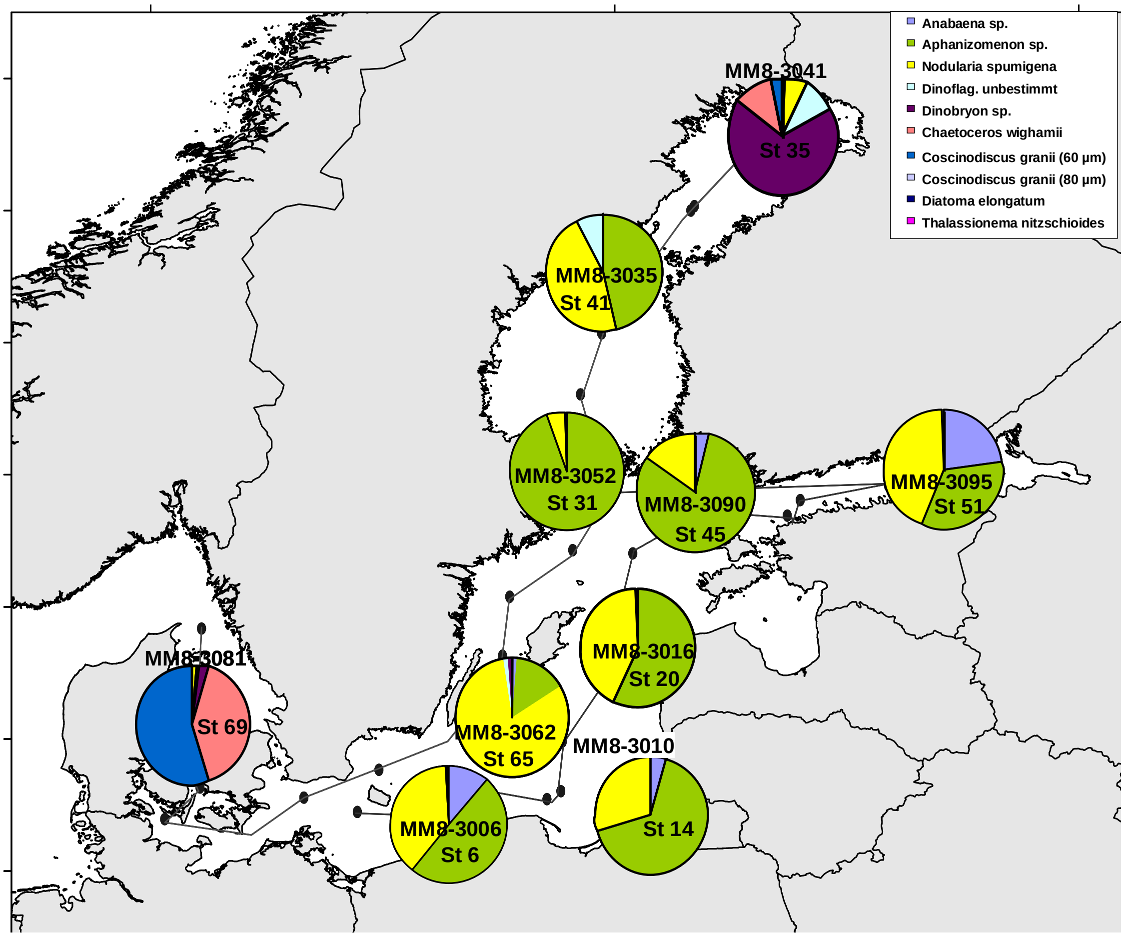

Figure 3.28. Phytoplankton distribution at the surface of the main basins of the Baltic Sea. Data provided by Monila Nausch (IOW).

Nodularia *spumigena* and Aphanizomenon *sp* are the predominant cyanobacteria species in the Baltic Proper. Anabaena *sp* is the third most abundant cyanobacteria specie in the Baltic Sea. The vertical profiles of dissolved and particulate iron show no specific trials of iron uptake. Despite the depletion of nutrients in summer, iron concentrations in the first 50 m of the vertical profiles remained stable. No gradient in concentrations between surface and the water masses immediately below thermocline was observed.

Variations between winter and summer, and the difference between the Baltic Proper and other areas as the Skagerrak or Kattegat are not enough to assert the impact of the iron content in the development of the seasonal cyanobacteria bloom. A wide discussion on the iron role in the cyanobacteria blooms in the Baltic Sea, with different calculations of biomass / iron ratio supported by data previously published will be presented in the following discussion chapter.

CHAPTER 4 – DISCUSSION

4.1. Iron speciation, sources and an analysis of physical and chemical processes in the Baltic Sea

Iron sources

The iron speciation is heterogeneously distributed in the Baltic Sea ruled by the characteristics fresh water supply, water circulation and oxygen content of each basin (Johnson et al. 1997). Samples located in coastal areas showed a different trend in iron speciation from the ones located in open sea areas (Fig. 3.6). A common fact in the three cruises is the highest content of Fe (Fe SPM + DFe) in surface waters up to ~ 85 nM in samples located in shallow areas of the central Batic Proper influenced by coastal proximity (Kattegat, Belt Sea, Swedish Coast, Gotland Island and the Gulfs). These areas present the highest percentage of Fe (II) in the dissolved fraction with values up to 40 % of the total dissolved fraction and the contribution of Fe fixed to the suspended material reach values larger than the 50 % of the total Fe fraction (Fig. 3.6 and appendix 2 - 4). Most of the Fe present in coastal environments is related to organic matter of terrigenic origin formed in rivers and groundwater; mostly humic substances (Laglera and van den Berg, 2009; Gelting et al. 2010). Lately, Breitbarth et al. (2009) and especially Gelting et al. (2010) reviewed the importance of river runoff related to the iron cycle in the Baltic Sea. Runoff can be considered one of the most important inputs of iron in the Baltic Sea in coastal waters together with huge amounts of other trace metals, nutrients and organic matter (Gelting et al. 2010). Furthermore, it influences the open sea surface waters and the deepwater conditions in the Baltic Proper due to horizontal advection and mixing of inflowing saline water in the transition area to the North Sea (Eilola and Stigebrandt, 1998; Matthäus and Schinke, 1999). Studies carried out along different rivers worldwide, show high concentrations of Fe, dissolved and particulate being dissolved Fe (II) a large fraction present (Saitoh et al. 1998; Hirata et al. 1999). The river runoff (481 km^3 year^{-1}) in the Gulfs constitutes 70 % of the total freshwater input of the Baltic Sea (Feistel et al. 2009). The annual average discharge in the Gulf of Finland is 110 km^3 (Vahtera et al. 2005). Thus, almost 50 % of the freshwater input takes place in the Gulf of Bothnia presenting an outflowing low saline water mass from the

Northern Baltic Sea mixed with the central Baltic surface water along the Baltic Proper (Baltic Proper presents a counterclockwise circulation of the surface waters). In estuaries, the iron discharged presented mainly as organic colloids and complexes in estuaries mixes with the different seawater cations forming aggregates that flocculate and sink along the salinity gradient. This provides a net export of dissolved and particulate iron from the surface waters along the coast explaining the iron surface distribution in the Baltic Sea (Duinker and Nolting, 1977, Boyle et al. 1977, Sholkovitz et al. 1978, Stolpe and Hassellöv, 2007 and Gelting et al. 2010). Along the salinity gradient in the mixing of river runoff and seawater, Sholkovitz et al. (1978) estimated that 60 - 80% of the total iron discharged from runoff was removed at salinities below 5. Stolpe and Hassellöv (2007) annotated that the majority of iron removal occurred at salinities below 2.5. As mentioned above, the main runoff in the Baltic Sea occurs in the Gulf of Bothnia presenting a salinity gradient of 2 units (≈ 3 - 5) from the northernmost point (coast of Sweden and Finland) to the proximities of the Aaland Sea. In 2008 the sampling carried out in this Gulf; between the stations more located to the north (Station 35 and 36, Fig. 2.4) a decrease of 60 % of total iron concentration was reported (Fig 4.1). That reflects an important removal of iron from the surface in an area estimated to be 50 km long with a gradient of salinity of 0.1.

Otherwise, open sea areas present the lowest Fe content with values lower than 10 nM in the Bornholm Basin. Planktonic cells, their particulate metabolites and degradation products constitute the majority of the particulate matter in such areas, linking particulate iron to biological activity. The different iron phases (particulate, soluble or dissolve fraction) in surface waters show pretty stable values amongst the sampling periods with few exceptions like the main station of the Bornholm Sea; with a progressive increase of the dissolved fraction (Fig 4.2). In contradiction, Gelting et al. (2010) shows an increase close to 85 % of the total iron between the months of March to August for the main stations of the Bothnian Sea, Landsort Deep and Gotland Deep, where the last one has the softest decrease in content of iron. The lack of a more frequent sampling in our study and the fact that Gelting's work does not cover the winter season hampers the possibility to explore this point further.

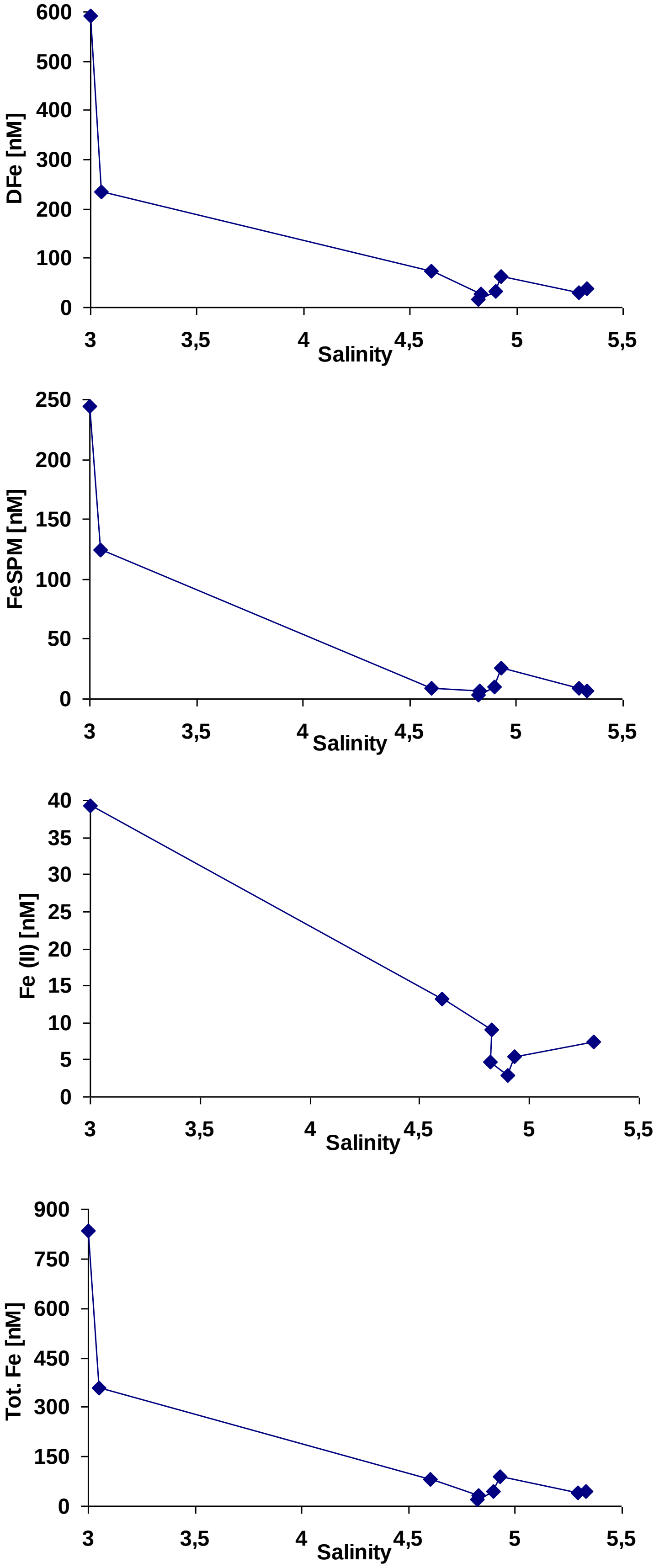

Figure 4.1. Fe speciation along the salinity gradient in the Gulf of Bothnia from the Finnish coast in the Bothnian Bay to the Aaland Sea; the entrance of the Gulf. DFe and FeSPM data provided by Dr. C. Pohl and U. Hennings.

It seems that the surface water stratification and the spring floods at the beginning of the season provides a high peak in the content of iron in the surface waters of the Baltic Sea that is consumed by the spring bloom and recycled sinking to layers below the euphotic zone (Gelting et al. 2010).

Dissolved iron and Fe (II) fraction in Baltic Seawaters and another world areas

Few previous studies have been carried out in the Baltic Sea on the determination of Fe (II) or on the iron speciation. A study by Breitbarth et al. (2009), focused at the stations of Gotland Deep and Landsort Deep during summer 2007 recorded values from the upper part of the water column of Fe (II) from 0 - 0.90 nmol L^{-1} and from 0-0.45 nmol L^{-1}, respectively. Those Fe (II) concentrations represented up to 20 % of the DFe fraction and are in the same range as the results obtained in this study. The difference in dissolved Fe (II) concentrations could be related to the sampling strategy carried out by Breitbarth employing 0.45 µm filtered samples. Meanwhile, the Fe (II) measurements in this study were based on unfiltered samples.

Related to total dissolved iron, in 2008 an analysis of 0.45 µm filtered samples taken at the Gotland Deep showed a concentration up to 5 times higher than the values recorded by Breitbarth et al. (2009) at the same station employing 0.22 µm filters. Organic complexed iron species are suggested to dominate the high-size fraction of dissolved iron. Gelting et al. (2010) carried out the fractionation of the soluble iron. DFe in the Gotland Basin in 0.22 µm filtered samples counted in an interval of the 23 - 54 % of the total iron content while in 2008 for 0.4 µm filtered samples were close to the 75 % of the total iron (Gelting et al. 2010). A possible hypothesis would be that beyond photochemical processes, high percentage of dissolved Fe (II) in the surface waters belongs to the colloidal fraction. Therefore the role of humic and fulvic acids in the iron speciation should be clarified in surface waters of the Baltic Sea (Berg 1995, Kawakubo et al. 1999). This hypothesis could be suported by the importance of photochemical processes releasing free Fe^{2+} ions (< 0.22 µm). In-situ and laboratory studies experiments covered the photoreduction effect on Fe (II) stability in oxic waters. However its exact contribution in the presence of bioavailable Fe (II) in oxic conditions has not been clearly evaluated yet (Kuma et al. 1996; Santana-Casiano et al. 2000; Croot et al. 2001; Kim et al. 2010). In 2008 our measurements at three deep stations (Gotland, Landsort and Aaland) showed Fe (II) concentrations decreasing from 1.86, 1.39 and 5.35 nmol kg^{-1} at the surface to 1.34, 0.52 and 1.75, respectively. For the stations of the Landsort and Gotland Deep, Breitbarth et al. (2009) noticed a decrease in Fe (II) concentrations below the euphotic zone compared to concentrations at surface below 1 nmol L^{-1} to values lower than the limit of detection. Those results together with desk incubation experiments support the role of photochemical reduction processes as an important source of Fe (II) in oxic surface waters.

In other areas of the world ocean large Fe (II) concentrations in oxic conditions were registered. A clear example resides in the work of Landing and Westerlund (1988) carried out in the Framvaren Fjord based on Fe (II) measurements and the role of H_2S interacting with Fe and the subsequent formation of Fe bisulphide complexes and particulate iron sulphides. Measurements from unacidified organic-rich surface samples of the fjord (Sweden-Norway border) reached values from 35 to 215 nM (Landing and Westerlund, 1988).

Besides photoreduction, rainwater and temperature influence the concentration and the stability of dissolved Fe (II) in surface waters. Rainwater is a potential source for both Fe (II) and Fe complexing ligands. Rain events wash out the atmosphere of aerosols particles. Part of those particles rich in iron is adsorbed and diluted on the water drops. Falkowska et al. (2008) registered high concentrations of dissolved Fe (II) (~ 1 - 100 nM) during rainwater events in the southern Baltic Sea (Gulf of Gdansk) depending on wind direction and rain events frequency. Furthermore, complexing ligands discharged with the rainwater can increase the Fe (II) half life ($t_{1/2}$) from tens of seconds to minutes (Willey et al. 2008, Breitbarth et al. 2009). Rain events took place just before the start of the research cruise in summer 2009 in the surroundings of the Gotland Island. Nevertheless, no increase of Fe (II) concentrations were measured in the area affected by precipitations except punctual locations in the coastal area of the island. Moreover, it is important to emphasize the absence of long rain periods when both summer cruises were carried out.

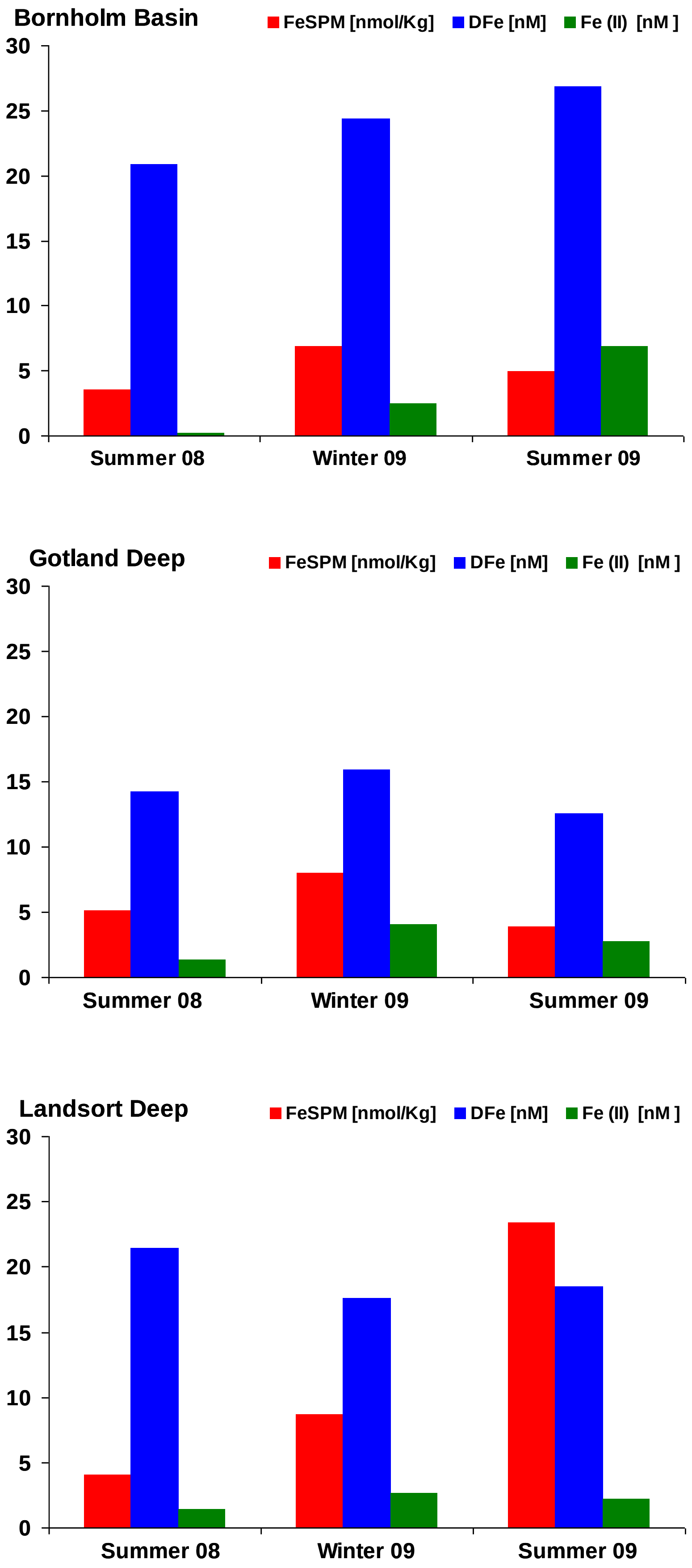

Figure 4.2. Seasonal changes in iron speciation at the three main deep stations in surface waters of the Baltic Sea. Dr. C. Pohl and Ursula Hennings (IOW) provided data of FeSPM and DFe.

The effect of the temperature on the Fe (II) stabilisation in seawater was theoretically and practically evaluated in the last decades, both in laboratory or “in-situ” experiments (Millero et al. 1987; Croot and Laan, 2002). Under oxygen saturation the halftime of Fe (II) varies from tens of minutes to ten of seconds for a temperature interval 5 - 25 ºC (Croot and Laan, 2002).

Halftime estimations for Fe (II) were made based on the measurements of different samples taken in February and July of 2009. The Fe (II) halftime values in summer were much higher than the values theoretically calculated based on the oxygen content, pH, salinity and temperature (Millero et al. 1987). An average halftime for Fe (II) of 35 min in summer surface waters of the Baltic Sea contrasts with the theoretically calculated value of 2 minutes (Table 4.1 and Table 4.2). This discrepancy could be explained by the lack of considering the influence of the organic species and the contribution of photochemical processes in theoretical calculations. The influence of the temperature is reflected in larger half time values for surfaces waters in winter reaching values up to 70 minutes than in summer (30min).

Table 1. Empirical halftime estimation for dissolved Fe (II) in surface waters of the Baltic Sea.

Station	t (1/2) min	Location	Season
Sample 38	40	West coast Gotland Island	Summer
Sample 22	38	North eastern Baltic Proper	Summer
Sample 101	25	Bornholm basin	Summer
Sample 111	37	German coast	Summer
Half Life Average	35		
Sample 122	55	German coast	Winter
Sample 130	72	German coast	Winter
Half Life Average	63		

Table 2. Theoretical dissolved Fe (II) halftime estimation compared to halftime values previously published for different aquatic environments.

Study	pH	Oxygen content	Halftime
This study (Baltic Sea)	8	saturation	2 min
Millero et al. 1987 (Biscayne Bay)	8	saturation	4.4 min
Roeckens and Grieken v. 1983 (North Sea)	8	saturation	2.7 min
This study (Baltic Sea)	7.25	OMZ*	162 h
Moffet et al. 2007 (Arabian Sea)		OMZ	200 h

* Oxygen Minimum Zone

4.2. Iron speciation related to the hydrography of the Baltic Sea: Water column stability, stagnation periods and water renewal

Iron speciation in suboxic and anoxic waters of the Baltic Sea

In general, a huge pool of bioavailable iron exists below the redoxcline of the deep anoxic basins in the Baltic Proper. As pointed out before vertical and horizontal diffusion and other vertical processes like local upwelling events could supply part of this iron reservoir into the euphotic zone, supporting diazotrophic nitrogen uptake during summer. Beyond thermodynamical calculations of the different species of iron along the water column and the fluxes of particulate and dissolved iron across the redoxcline; Brunt-Väisälä frequency (buoyancy frequency) profiles were calculated for different points of the Baltic Sea and for the three cruises (Fig 4.3). Buoyancy frequency profiles describe the water column stability evaluating the probability of real mixing processes between the different water masses (Waniek et al. 2005). This measurement of the water stratification was carried out using data collected from different CTD casts and the calculations were done following the equation: $N^2 = -(g/\rho)\ d\rho/dz$ [11], being N^2 the buoyancy frequency, g the gravity constants, ρ the density of the water mass and z the corresponding depth. Generally high levels of N^2 are related to stratified water columns, and this can be seen at the depth where the different clines are located. The profiles show that the development of a thermocline in early spring provides a high stability to the surface layer in the entire Baltic Sea leading to the nutrient limitation in the first 10 – 20 m of the water column during summertime. This thermocline seems weaker in coastal and shallower areas of the Belt Sea, Arkona and the Gulf of Finland, favouring the mixing with water masses below (Fig. 4.4).

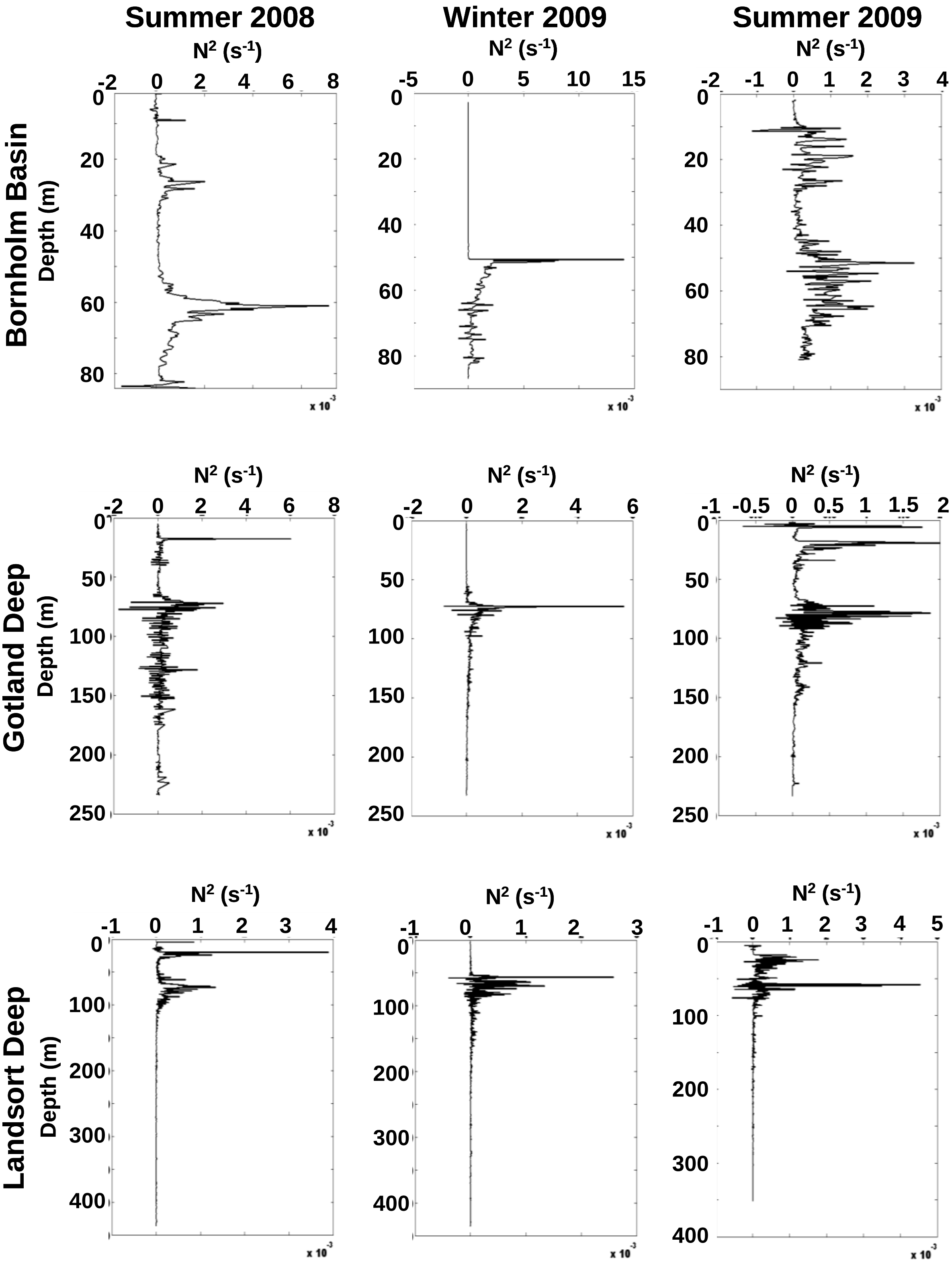

Figure 4.3. Buoyancy N^2 profiles of the water column at three main stations of the Baltic Proper between 2008 and 2009.

This fact could explain the presence of dissolved inorganic phosphate at the surface of these areas coming from layers immediately below as seen in the DIP profiles in the section 3.1. Stable water masses ($N^2 < 0$) can be identified in the different profiles. No movements of water masses and high stratification areas, mainly in the main stations of the Landsort Deep and Gotland Deep suggest that vertical transport from the deep anoxic reservoir is highly restricted.

Winter waters present a complete mixing in the first 75 – 80 m of the water column but the gradient between the water masses above and below the halocline is higher (Fig. 4.3). This is supported as we can see later by the larger upward flux of DFe in summer than winter through the clines at the main station of the Gotland Deep.

Fluxes of dissolved iron were calculated in order to clarify the effective vertical mixing across redoxcline. Considering the whole dissolved fraction of Fe below the redoxcline as different Fe (II) species; in the stagnation state of the deep waters there is a net upward flux of Fe (II) between 150 and 100 m depth of 10.1 µmol m^{-2} day^{-1} at the Gotland Deep in summer 2008.

At 100 m the oxygen concentration is around 0.02 ml L^{-1}, salinity 10.79, temperature 5.86 °C and other sources such as biological processes contribute to content of Fe (II) at this depth. Checking the values obtained from the depth profile, concentrations of DFe and Fe (II) dissolved are close to 31 nM and 4 nM, respectively. This reveals that almost 90 % of the Fe (II) crossing the redoxcline is reduced in the first 50 m.

Based on the work by Millero et al (1987) on Fe (II) oxidation kinetics in seawater, the pseudo-first order oxidation rate constant was predicted. Basic thermodynamical calculations assess the dimension of the iron cycle in the Baltic Sea.

From an interval of pH 5 - 9, temperature 5 - 45 ºC and salinity 0 - 35 the oxidation of ferrous iron is followed by

$$-d[Fe(II)]/dt = k_1 [Fe(II)], \qquad [12]$$

At 5 ºC with an interval of pH 7.5 - 8.5 and at a temperature of 25 ºC and pH 6.0 - 8.0 the oxidation is second order relative to pH;

$$-d[Fe(II)]/dt = k[Fe(II)][OH^-]^2[O_2] \qquad [4]$$

Where $\text{Log } k = \text{Log } k_0 - 3.29\, I^{1/2} + 1.52\, I$ and $\text{Log } K_0 = 21.56 - 1545/T$ ($T = 273.15 + t\,^{\circ}C$)

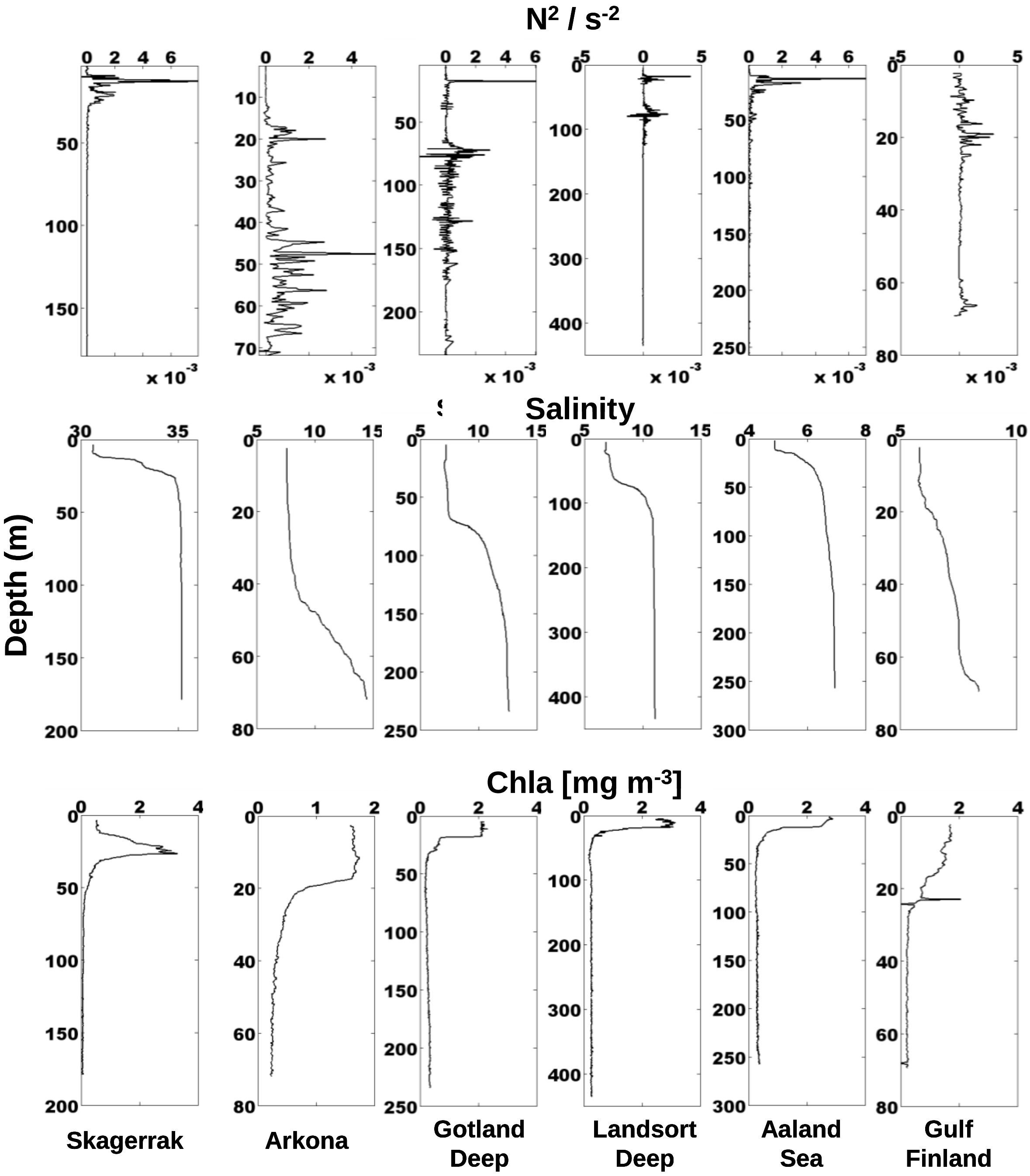

Figure 4.4. Buoyancy N^2, salinity and chlorophyll a profiles of the water column at different stations of the Baltic Proper in summer 2008. Chlorophyll a values provided by Dr. Monika Nausch (IOW).

Halftimes were calculated along the vertical profile of three stations (Gotland, Landsort and Bornholm). The ionic strength values were extracted from Millero et al. (1987). The Swedish Meteorological and Hydrological Institute provided the pH measurements. Taken as reference, the calculations for the Gotland Deep in 2008 were carried out using the average pH values registered on the 12th of June and 10th of July 2008. Fe (II) halftime in the redoxcline and immediately above assuming a pH value of 7.25 and a value calculated of log K ~ 14.8 provided a Fe (II) half time of 196 and 16 hours respectively (Table 4.2 and Table 4.3). This half life is higher than ones extracted from the literature and based on calculations for oxygen saturated open seawaters (e.g.: North Sea and Atlantic Ocean) with salinities close to 32 (Roekens and Grieken, 1984; Millero et al. 1987). Otherwise, similar physical conditions are found in the oxic-anoxic transition of the Arabian Sea where Moffett et al. (2007) calculated a half life of Fe (II) of 200 h, related to almost oxygen depletion. The half life of dissolved Fe (II) suffers two important increases with depth related to pH changes in the proximities of the clines due to the complete oxygen depletion, organic matter degradation and hydrogen sulphide formation (Fig. 4.5). The graph shows perfectly the influence of the pH in the stability of the Fe (II) dissolved ions. At pH higher than 8 and oxygen saturation the half time of ferrous iron result in order of seconds or of few minutes taking account the temperature (Croot and Laan, 2002). The half times are an estimation excluding the interaction of organic matter and any photochemical processes or external influence (rain events) in the oxidation of ferrous dissolved forms (Millero and Izaguirre; 1989; Liang et al. 1993). Due to this influence of the physicochemical conditions of the water mass, processes where deep-water masses (60 - 80 m) are dislocated upward (upwelling-downwelling) can be considered the most effective route for a punctual supply and uptake of biologically suitable dissolved Fe (II). Such movement of water masses can serve as a trigger increasing the biological activity in surface waters. In the Baltic Sea, specifically in the Gulf of Finland major nutrients as phosphate and nitrate were connected to upwelling processes and the development of different phytoplankton blooms (Laanemets et al. 2004; Vahtera et al. 2005; Laanemets et al. 2006).

Table 3. Theoretical calculations of Fe (II) halftimes along the water column of three different stations.

		July 2008	February 2009	July 2009
Bornholm	**Depth (m)**	**Halftime Fe (II)**		
	10		112 s	11 s
	15		2 min	39 s
	50		4 min and 19 s	7 min and 50 s
	65		44 min	101 min
	80		18 hours	11 hours
Gotland	**Depth (m)**	**Halftime Fe (II)**		
	10	9 s	97 s	10 s
	30	118 s	101 s	92 s
	50	2min and 6 s	101 s	4 min 58 s
	60	2 min and 51 s	1 min and 44 s	8 min and 29 s
	70	8 min and 50 s	43 min	26 min
	80	16 hours	11 hours	10 hours
Landsort	**Depth (m)**	**Halftime Fe (II)**		
	10	22 s	106 s	19 s
	20	82 s		
	30	2 min and 28 s		2 min and 6 s
	40	2 min and 54 s		3 min
	50	4 min	112 s	4 min and 38 s
	60	20 min		
	70	2 hours		
	80	14 hours	5 hours	154 hours (> 6 days)

The iron cycle in the Baltic Sea is associated with another trace metals and macronutrients as mentioned above. Gotland Deep is used as example to describe this interaction along the water column. Oxygen content determines the speciation of the three elements. Nitrogen and phosphorus in surface waters are strongly dependent on the biological activity and water mixing. The role of nitrogen and phosphorus in surface waters during summer will be discussed in the section 4.3. In the proximities of the halocline and the redoxcline different processes occur involving the equilibrium between different dissolved and particulate species.

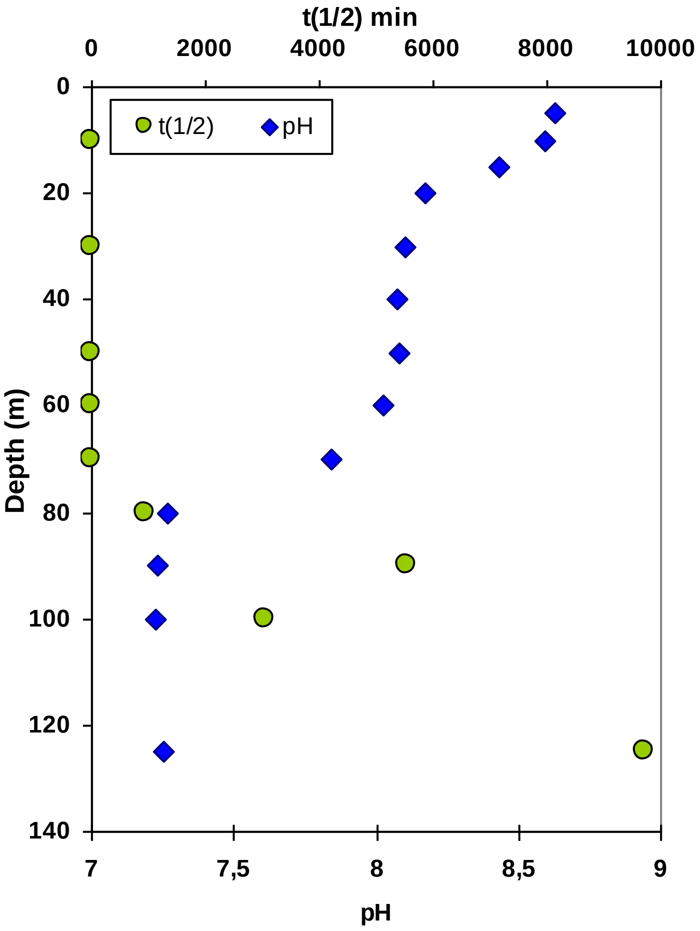

Figure 4.5. Theoretical half-life of dissolved Fe (II) in Gotland Deep compared to the pH profile for the summer 2008. Values of pH provided by the SMHI institute.

Bacteria carry out many processes involving nitrogen where iron can act as a possible acceptor or donor of electrons in suboxic environments. A general view how Fe and N cycles interact can be found in Clément et al. (2005). Between 60 and 120 m the occurrence of nitrification and denitrification processes is characteristic for the Gotland Deep. Anaerobic nitrification can carry out the reduction of ferric ions. At 80 m, nitrate reaches the highest peak as dissolved Fe (II) concentrations start to increase. It seems that ferric ions reduction is not connected directly to nitrate formation or is not its main source (Clément et al. 2005). Typical for the Gotland Deep immediately above the redoxcline is a narrow zone approximately 10 m thick where denitrification occurs (Rheinheimer et al. 1989). At 100 m coinciding with the maximum concentration of dissolved Fe (II) between the clines, 62 % of DIN belongs to nitrite ions (fig. 3.14). A possible reduction of iron associated to a nitrite maximum at the Gotland Deep follows the identical pattern that takes place in the Arabian Sea.

Under suboxic conditions, denitrificaton involves enzymatic iron requirements providing a high percentage of Fe (II) at the depth of the maximum nitrite concentration in the Arabian Sea (Moffett et al. 2007). Otherwise, Rheinheimer et al. (1989) suggests that nitrite predominance is due to the oxygen depletion at 100 m avoiding the last step of the nitirification process (Nitratation) locating the narrow denitrification area around 120 m depth.

In addition, the density gradient in the proximities of the halocline provides an environment rich in particulate matter. Mineralization processes with organic matter as electron donor are a potential source of dissolved Fe (II) due to reduction of ferric ions (Lovely and Phillips, 1986).

Dissolved inorganic phosphorus (DIP) is considered the limiting nutrient in the Baltic Sea during summer (Nausch et al. 2004). Hence, DIP has a key role in the dynamics of cyanobacteria blooms and therefore in the reduction of atmospheric CO_2 levels. At marine pH and redox potential inorganic phosphorus is present as HPO_4^{2-} and $H_2PO_4^-$. During long stagnation periods, a pool of apparently “available” DIP for uptake is located below the oxic/anoxic interface. Fe together with Mn inhibits the upward transport of DIP from the deep anoxic waters to the upper layers trapping part of this DIP in the proximities of the redoxcline (Dellwig et al. 2010; Turnewitsch and Pohl, 2010). Fe and Mn precipitates are considered small settling particles with diameters between 1 - 10 µm and settling velocities up to 10 m d^{-1}. The formation of these aggregates and the timescales of their transport downwards are in an order of days to weeks. These compounds below the redoxcline suffer dissolution rapidly with HS^- as reductant. Fe oxyhydroxides with higher degree of crystal (goethite) react with sulfide in an order of days up to hundred of days, and meantime the aggregates with lower degree of crystal (lepidocrocite) react in an interval of minutes to hours. Dellwig et al. (2010), focused on the characterisation of Fe SPM in oxic / anoxic interphase corroborated the formation of iron-oxyhydroxo-phosphates and the existence of a mixed phase of Mn-Fe-P particles in the lower part of the redoxcline. The fast oxidation of Fe (II) from the anoxic water leads to a formation of FeOOH in the redoxcline by using the sinking MnOx from the upper part of the cline as nuclei. Possible oscillations in the location of the redoxcline can carry out both dissolution of oxides and thus the release of DIP or precipitation of Fe and Mn in the sediments at the rimes of the basin (Fig. 4.6). This shuttle or cycling can increase the gradient between surface and deepwaters. Fe and Mn mediated downward transport of DIP is expected to limit the turbulent diffusive upward transport of DIP reaching almost the ceasing of upwards transport during long stagnation periods. Not only the transport across the redox interface is restricted, the strong density gradient between the 65 m and 80 m of the water column inhibits the turbulent diffusive upward transport of DIP and DFe (Turnewitsch and Pohl, 2010).

Turnewitsch and Pohl calculated trapping efficiencies as function of particles density in 2010 applying the equation:

$$\boldsymbol{E = S_{plot} / T_v} \qquad [13]$$

The efficiency (E) of the trap is expressed as the downward transport (S_{plot}) divided by the upward flux of DIP across the redoxcline. Upward transport (T_v) is the sum of vertical advective transport “A_v“ (downwelling and upwelling processes) and vertical turbulent diffusive transport D_v. During stagnation periods, advective transport is not significant in comparison to the turbulent diffusive transport (Meier et al. 2006) and therefore the equation can be simplified ($T_v \approx D_v$). Calculations of DIP diffusive flux from the anoxic deepwaters of the Gotland Deep to the upper part of the redoxcline with a gradient of 93.2 ± 25.5 µmol m^{-4} DIP turned out in an upward transport of 64.7 ± 18.5 µmol $m^{-2}d^{-1}$. Calculations of the sinking DIP flux, settling adsorbed on Mn and Fe oxides were carried out estimating the P proportion in Fe and Mn particles. The downward flux (S_{plot} / µmol $m^{-2}d^{-1}$) is expressed as the product of the FeSPM concentrations multiplied by the Fe/P ratio (Bernard et al. 1989; Neretin et al. 2003) and settling velocities (m d^{-1}). This requires the approximation that the whole content of particulate iron is present in the form of oxyhydroxides (Turnewitsch and Pohl, 2010). Settling velocities (ω) were calculated by the Stoke’s expression:

$$\boldsymbol{\omega = g\,(\rho_s - \rho_w)\, d^2 / 18\,\mu} \qquad [14]$$

Where g is the gravity constant (9.81 m s^{-2}), ρ_s and ρ_w are the densities of the Fe particles and seawater respectively, d is the diameter of the single particles and μ the dynamic viscosity (1.4992 10^{-2} g cm^{-1} s^{-1} at T = 6 ºC and S = 11).

The values of these constants and parameters were selected taking as reference the study made by Neretin et al. in 2003. This study includes calculations of the number of Mn particles and aggregates per volume of water. Individual Mn particles have a diameter of ~ 1 µm and the aggregates showed diameters ~ 10 µm (Neretin et al. 2003). Assuming that FeSPM shows similar numbers and diameters as Mn particles; 3 different diameters of particles and 2 mineral densities (ferrihydrate / 3.8 g cm^{-3} and hematite / 5.2 g cm^{-3}) provided a settling flux of scavenged inorganic P of 23.4 ± 14.5 µmol $m^{-2}d^{-1}$ and 39.7 ± 22.8 µmol $m^{-2}d^{-1}$ for low and high density scenario respectively. Coupling both fluxes results in a trapping efficiencies of 0.38 ± 0.29 (low density) and 0.63 ± 0.45 (high density) (average ± SD). This provides a scenario where a percentage of 40 % to 65 % of the DIP flowing upwards through the redoxcline is adsorbed and scavenged onto settling Mn and Fe oxyhydroxides (Turnewitsch and Pohl, 2010). Continuing the line of Neretin et al (2003) and Turnewitsch and Pohl (2010) the Fe cycle in the proximities of the redoxcline was calculated based on the results of this study. The results obtained for the upward and downward fluxes for the three cruises in the Gotland Basin are compiled in the Appendix VII. Neretin et al. (2003) pointed out that the 92 % of the Mn particles above the redoxcline in the Gotland Deep present a diameter ~ 3.8 µm. A settling velocity of 0.9 m d^{-1} was obtained selecting a particle diameter of 4 µm and a particle density of 3.8 g cm^{-3}. The average of 15.9 ± 2.7 µmol $m^{-2}d^{-1}$ for upward turbulent flux and 42.2 ± 13.9 µmol $m^{-2}d^{-1}$ for settling Fe particles point towards a big supply of particulate iron from the upper parts of the water column turning the anoxic deep waters in a deposit of the iron discharged along the different basins of the Baltic Sea.

Thermodynamically, the reduction to Fe (II) from the whole dissolved fraction below the redoxcline is favoured (Strady et al. 2008). It seems, that a limitation in the Luminol chemiluminescent flow injection analysis (CL-FIA) applied for the dissolved Fe (II) fraction measurements in anoxic conditions exist due to the difference between the Fe (II) concentrations and the total dissolved fraction (Rose and Waite, 2002; Croot and Laan, 2002).

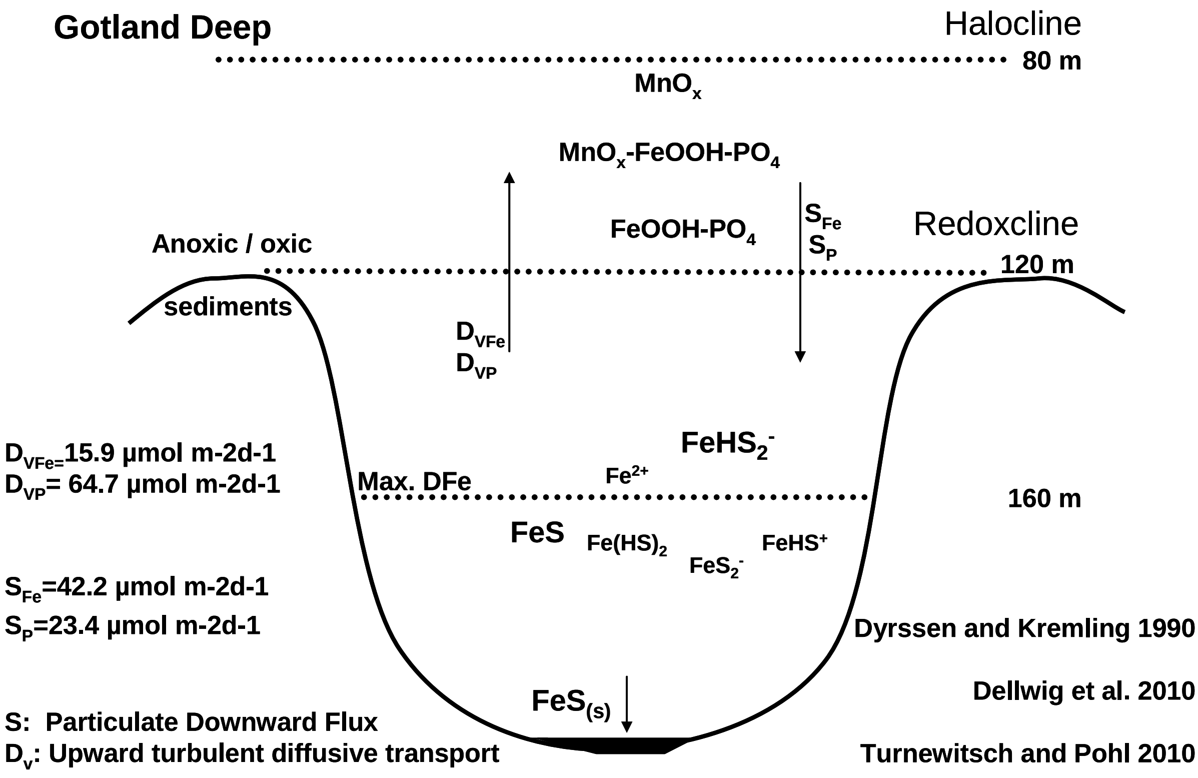

Figure 4.6. Fe cycle in deepwaters of the Baltic Sea coupled to N, P and S cycles based on the studies from Dyrssen and Kremling (1990), Dellwig et al (2010) and Turnewitsch and Pohl (2010).

Below the redoxcline the content of H_2S increases with depth interacting with Fe (II) forming dissolved Fe bisulphide complexes and particulate iron sulphides (Landing and Westerlund, 1988) (Fig. 4.6). Insensitivity to iron sulfides, could explain the discrepancy between the Fe (II) dissolved and the total dissolved iron fractions. Another explanation could be related to the anoxic state of the sample, affecting the reaction in the detection cell and thus the signal. However, Luminol CL-FIA provides a highly sensitive tool to measure Fe (II) ions in sub-oxic and oxygenated waters.

This study coincided with a stagnation period of the deepwater in the Baltic Sea. Apparently, the deepwater during the first part of the 80´s showed a similar state. Between 1981 and 1985 the deepwater of the Gotland Deep presented a rise in depth of the redoxcline by 20 m and an increase of the H_2S concentrations from 21 to 80 µmol L^{-1} (Dyrssen and Kremling, 1990). The concentration of dissolved iron in the bottom waters reported in this study agreed with an iron speciation in equilibrium with FeS and $FeHS^-$ as the main dissolved species.

It is suggested that the concentration of trace metals in the sulfidic bottom water appeared to be determined by scavenging with iron sulphide. The amount of iron scavenged seems to be related to the value of K_1K_{so} for the equilibrium

$$MS_{(s)} + H^+ \leftrightarrow M^{2+} + HS^- \quad \text{(Dyrssen and Kremling, 1990)} \qquad [15]$$

.

The current scavenging of iron below the redoxcline in the Gotland Deep was estimated using the data from the three water profiles collected between 2008 and 2009. It is possible to calculate log K_1K_{so} for FeS from the pH and the concentrations of sulphide and the dissolved iron together with a value of K_1 ~ 17 (protonization constant of S^{2-}) extracted from the paper published by Dyrssen and Kremling in 1990. The results are summarised in Table 4.4. Compared to the Dyrssen and Kremling study, the content of iron both in the dissolved and particulate phase is much lower from 200 m to the bottom in the actual period. The evolution from 1981 to 1985 with the rise in the hydrogen sulphide concentration provided lower DFe concentrations pointing out that the scavenging reaction of iron was more effective than the formation of soluble disulfide complexes. The actual content of Fe in the basin is much lower with a pH in the deepwater slightly higher 30 years ago (Table 4.4). The rise of the hydrogen sulphide concentrations between 2008 and 2009 shows the opposite tendency in respect to the log K_1K_{so} values than the study from 1981 - 1985. Dyrssen and Kremling (1990) following the results obtained, pointed out that the conditions in the Gotland basin were close to equilibrium. The concentrations from the different iron species and the values for the different equilibrium constants in the actual state of the Baltic Sea suggest a solubilisation from the sediments of FeS minerals possibly affected by mineralisation processes of sedimentary organic matter (Canfield et al. 1993; Jensen et al. 2003; Elrod et al. 2004).

Table 4. Average values of the iron content, hydrogen sulphide, pH and scavenging rate for the depth of 200, 220 and 237 m in 2008 and 2009 compared to published data of Dyrssen and Kremling (1990).

	$\log K_1 K_{so}$	DFe *	FeSPM *	% Total	H_2S (μM)	pH	[HS-] μM
Summer 2008	-3,01	890	8	0,9	43	7,25	60
Winter 2009	-2,69	1155	15	1,3	54	7,27	93
Summer 2009	-2,55	911	27	2,9	93	7,31	159
Dyrssen 1990 (1981)	-4,98	>2000			21	7,03	19
Dyrssen 1990 (1985)	-5,29	1900	57	2,9	80	7,11	49

- **Concentrations given in nmol kg^{-1}**

4.3. Biological role of iron in relation to cyanobacteria blooms. Study of the relationship between N:P ratio and the primary production as a function of the Fe distribution in the Baltic Sea.

Phytoplankton communities present a seasonal and geographical character marked by the salinity gradient and the nutrients concentrations at the surface and their sources in the Baltic Sea (Wasmund and Uhlig, 2003). Uptake requirements and their mechanisms vary for different phytoplankton species. In spring, diatom blooms occur in the western part of the Baltic Sea. Due to the formation of a stable thermocline in the first 20 m of the water column, the spring bloom carried out the consumption of dissolved inorganic nutrients as nitrogen, phosphorus and nitrogen. It is considered that nitrogen limits these blooms since the N/P ratio in winter surface waters (< 10) of the Baltic Sea is much lower than the N/P calculated by Redfield (16). This remains in a budget of DIP in the surface waters when the spring bloom ceases because of DIN depletion around the middle of April. Otherwise, it is suggested that diatom cells have a high efficiency in Fe (II) acquisition. Depletion of Fe (II) in the western part of the Baltic Proper may be related to biological uptake by diatoms (Sunda, 2001). Beyond interactions with organic matter, the larger halftime of Fe (II) during early spring related to the surface temperature compared to the summer time favours the uptake of this labile fraction of dissolved iron.

Schneider et al. (2009) noted a second biomass production period between the diatom spring bloom and the summer massive growth of atmospheric N_2-fixing cyanobacteria. This production period is defined by the author as a “cold fixation” period and contributed up to the 40 % of the total annual N_2 fixation (173 mmol m^{-2} y^{-1}) in year 2005. The cold fixation period takes place until the middle of May and is suggested that is carried out by common cyanobacteria species in the Baltic during summer (e.g.: *Aphanizomenon, Nodularia and Anabaena*). The hypothesis was based on the capacity of Aphanizomenon in the formation of heterocysts at the temperature of 5 ºC when DIN is depleted (Walve and Larsson, 2007; Schneider et al. 2009). Atmospheric nitrogen fixation processes requires 10 - 20 times more iron than DIN uptake. Not considering the possible cold fixation could mean underestimation of the iron requirements in the Baltic Sea. Since the main inflow of saline waters in summer 2003, the deep waters of the central Baltic Sea are in stagnation. Stagnation periods are characterised by accumulation of dissolved nutrients (e.g.: phosphorus and iron) in the anoxic deep waters. Major inflows of saline-oxygenated waters from the North Sea renew the deepwaters of the Baltic Sea carrying out the precipitation of huge amounts of particulate iron (oxyhydroxides) onto the sediments. During stagnation periods this particulate iron is reduced turning back to the water column. Appendix VIII shows the profiles of dissolved iron for the period 1996 - 2009 and the changes after the major inflows of 1993 and 2003. Iron profiles in the last decades and the state of the deepwaters in the central Baltic Sea do not correlate directly with satellite images of cyanobacteria blooms following the development of the diazotrophic blooms (Appendix VIII - IX). This verifies that beyond the stratification of the watrer column, more physical and chemical factors influences the development of the summer blooms. Figure 4.7 summarizes the conditions of the water column in the central Baltic Proper during the summers of 2008 and 2009, where coastal influences are neglected and lateral transport not affect the nitrogen fixation (Schneider et al. 2009). Positive values of DFe fluxes (red bars) point out the upward flux of dissolved iron. Upward fluxes of dissolved iron can be appreciated in the lower part of the redoxcline. It can be observed as the redox potential changes, the reduced dissolved fraction crossing upwards the cline decreases due to the formation of Mn-Fe oxyhidroxides aggregates.

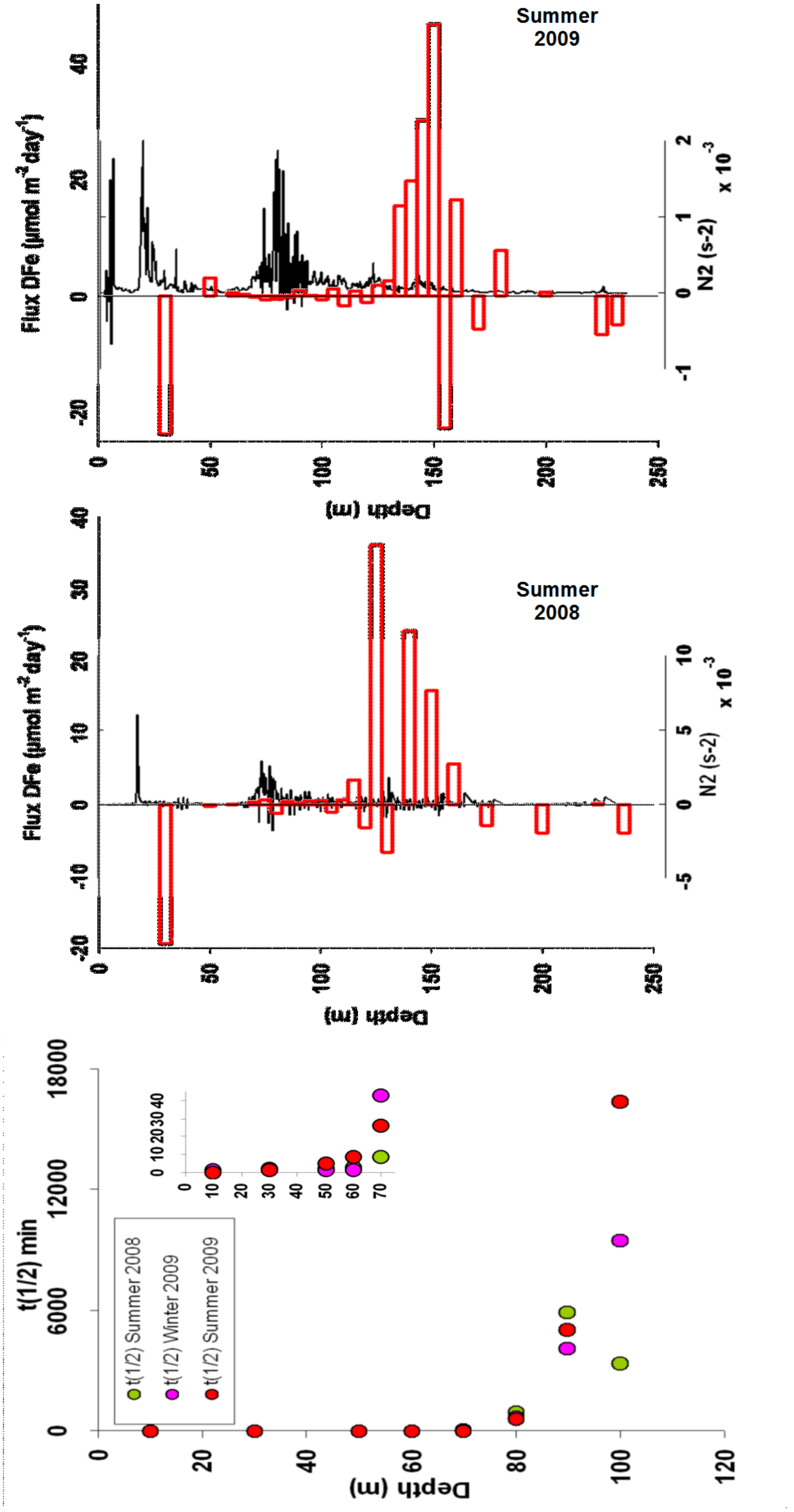

Figure 4.7. Seasonal theoretical halftime estimation for Fe (II), water column stability and advective flux in the Gotland Deep.

Downward transport of dissolved iron is expressed as “negative” flux. The sink of colloidal Fe (III) from the surface, reduction of particulate Fe aggregates in the lower part of the redoxcline and the sink in the bottom waters-sediments interface of free and complex reduced dissolved iron are the main downward transports in the Gotland Basin (Turnewitsch and Pohl, 2010). The stability of the clines and the low advective flux compared to the sedimentation of iron oxyhydroxides compromise the direct supply of Fe from the deep layers in the surface waters (Fig. 4.6 - 4.7). The division of the water column in different water bodies in summer can be perfectly visualised reinforced with the turbidity profiles in the Gotland Deep for summer and winter periods (Fig. 4.8). Therefore the most effective mixing processes in such areas and in areas close to the rims of the different basins are local upwelling events. The summer cyanobacterial blooms were related with such processes that bring available dissolved phosphorus from layers below supplying the diazotrophic growth (Nausch et al. 2008). Fluctuations in the temperature profile reflect colder waters along the Belt Sea, Swedish coast and Gulf of Riga serving as topographic references where vertical mixing is favoured. These wind induced upwelling events are generated predominately by westerly winds and are a common physical processes in regions like the Swedish coast and the Gulf of Finland bringing upwards water masses from the depth of 20 to 30 m (Myrberg and Andrejev, 2003). Differences in the amounts of the dissolved inorganic major nutrients (DIN and DIP) that reach the surface layer in these areas are most likely related to the position of the nutriclines below the thermocline. The differences in depth of the nutriclines were examined in several studies carried out in the Gulf of Finland (Kononen et al. 1996; Laanemets et al. 2004; Vahtera et al. 2005).

Data of nitrogen fixation provided by Dr. Bernd Schneider (IOW) in different regions of the Baltic Sea for the years 2008 and 2009 is used to support the comparison in the biomass production between both summers (Fig. 4.9). Nitrogen fixation calculations are based on high-resolution CO_2 partial pressure data measured on board of a cargo ship that crosses regularly in a 2 days interval the central Baltic Proper in a transect from Lübeck (Germany, southwester Baltic) to Helsinki (Gulf of Finland). CO_2 partial pressure data is used to calculate the organic carbon production applying two independent atmosphere-surface CO_2 mass balances (Schneider et al. 2009).

Typically, a minimum in the pCO_2 surface is reached in the middle of July, when the expansion and growth of cyanobacteria aggregates reach their maximum. Similar nitrogen fixation rates and chlorophyll a values were achieved for both summer seasons despite that the extent and the intensity of the diazotrophs growth in 2009 was much lower than in 2008 (Appendix V). Agglomeration of cyanobacteria blooms in the surface waters of the central Baltic Proper are strongly related to winds strength and direction (Robarts and Zohary, 1987; Wasmund, 1997).

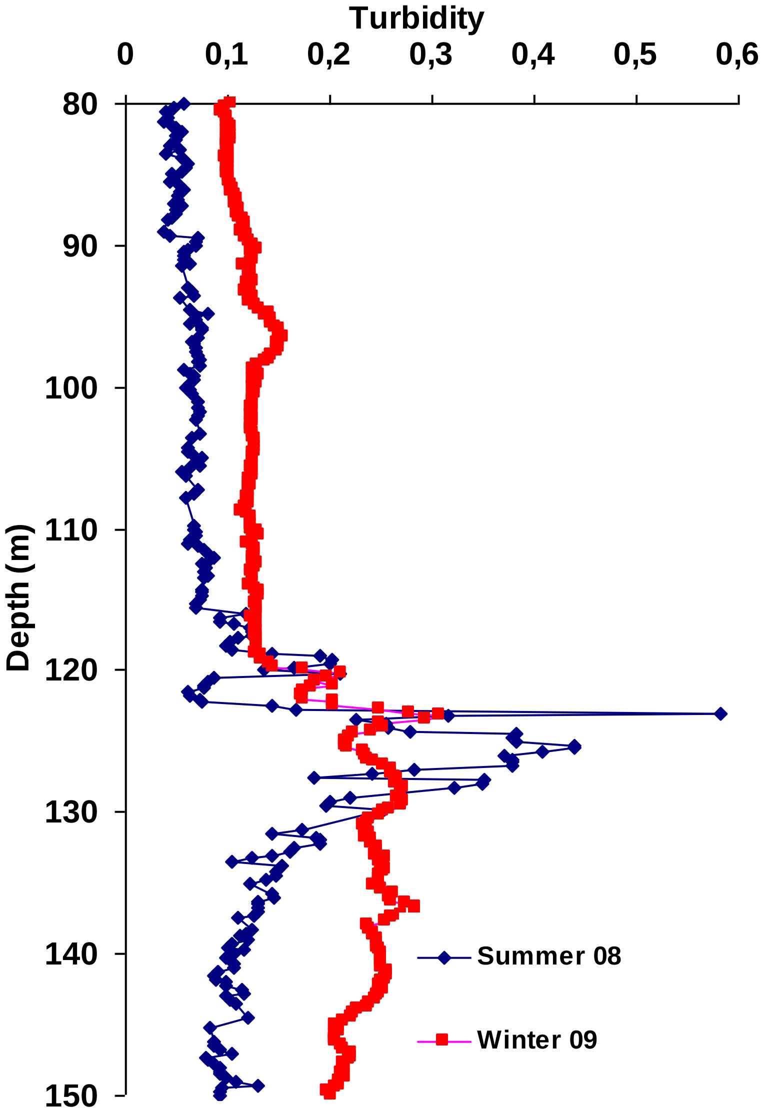

Figure 4.8. Turbidity measurements from a CTD profile at the Gotland Deep. Data provided by Dr. Joanna Wanieck (IOW).

This suggests that satellite images are a powerful tool for the monitoring of the development of the blooms but additional measurements are necessary to understand the different parameters ruling such summer blooms in surface waters (Janssen et al. 2004; Kahru et al. 2007). The sampling periods took place from the end of June until the middle of July in 2008 and during the second and the third week of July in 2009. Variations in the sampling time related to the nitrogen fixation rates and thus, to the development of the cyanobacteria blooms did not have an impact on the iron speciation (Fig. 4.2, 4.9 and Appendix X). The only exception could be the large concentration of particulate iron in the Landsort Deep in 2009 that could be related with a fast uptake of iron from the different diazotrophs present in the surface water in the early summer. The sampling in 2009 compared to 2008 was carried out in a moment at which the development of the cyanobacteria bloom was more advanced. The lowest values of chlorophyll a in the samples of 2009 showed that the intensity of the bloom was lower than the year before. In 2008, Nitrogen fixation values are in agreement with the GCI (Graphic computer image) generated using satellite images of the cyanobacteria blooms in the Baltic and provided by the SMHI (Swedish Meteorological and Hydrological Institute) showing the highest values for the North of the Baltic Proper and the eastern Gotland Basin (Appendix V). This agreement is in conflict with the situation in 2009, probably because of periods of dense clouds affecting the resolution of the satellite images. Despite the disagreement, it is possible to see the negative effect of the strong wind conditions and the decrease of temperatures that occurred in the central Baltic Proper on the nitrogen fixation values during the first week of July 2009 (Fig. 4.9). This biomass production limited by the phosphorus budget and based on atmospheric nitrogen uptake is dominated by three major nitrifying cyanobacteria. *Aphanizomenon* and *Nodularia* are the main cyanobacteria species in the Baltic Sea with *Anabaena* strains in a secondary place (Finni et al. 2001; Wasmund and Uhling, 2003). The growth of these species is restricted to characteristics salinity intervals, temperature and nutrients supply (Wasmund, 1997; Laamanen et al. 2002, Walve and Larsson, 2007). Related to iron, many researches weighed up the role of iron for the occurrence of these summer blooms. Laboratory, incubation experiments and in-situ measurements lead to the conclusion that iron is limiting factor in the growth of cyanobacteria (Paczuska and Kosakowska, 2003; Berman-Frank et al. 2007, Breitbarth et al. 2009). Further assessments of iron as possible limiting factor in the summer phytoplankton blooms in summer can be done carrying out a calculation of a potential new production based on the iron budget in the Baltic Sea.

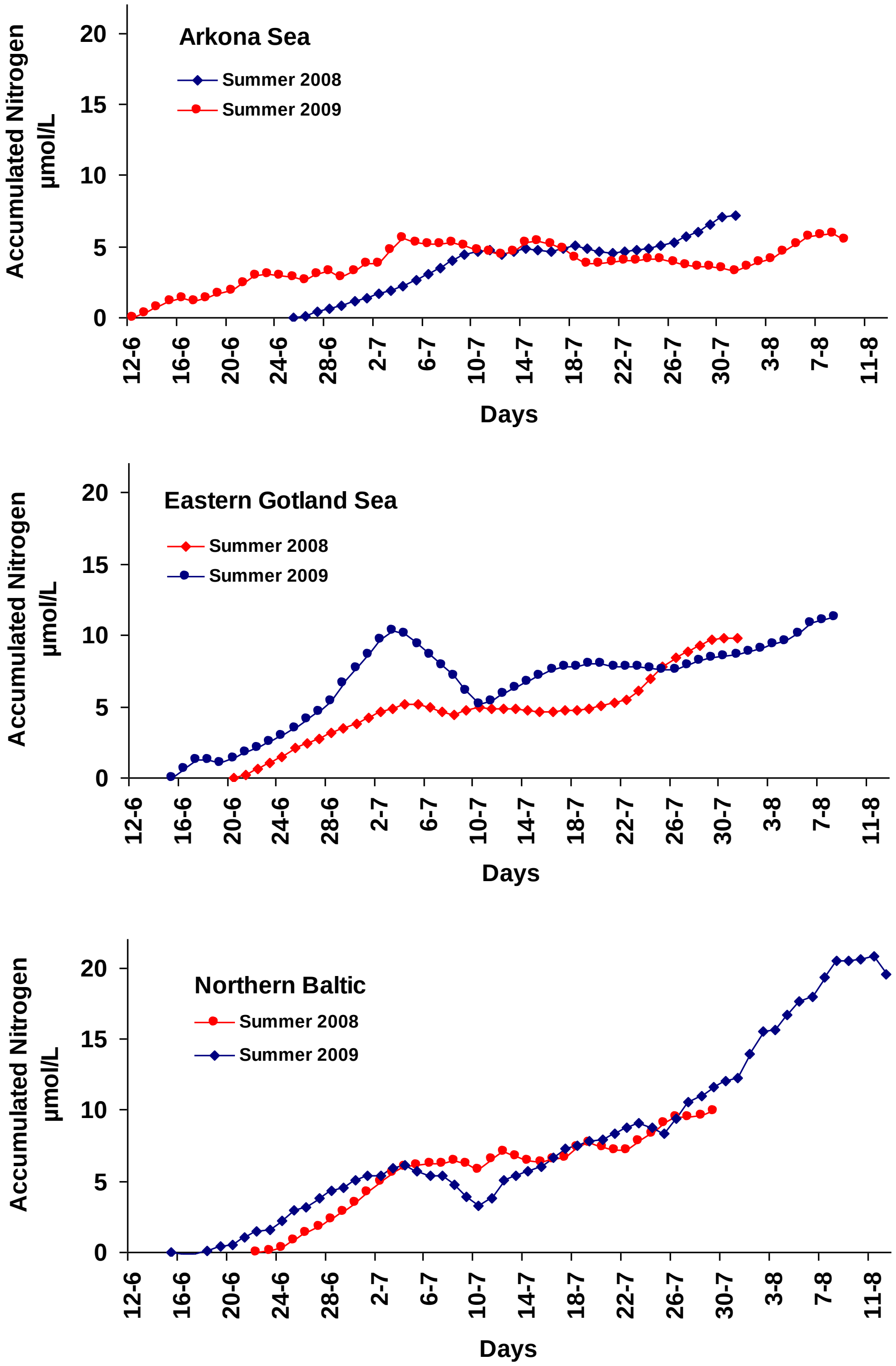

Figure 4.9. Nitrogen fixation in different locations of the Baltic Proper during the summers of 2008 and 2009. Data provided by Dr. B. Schneider (IOW).

For this subject, an appropriate C:Fe ratio has to be selected. C:Fe ratios vary widely along the literature. A compilation of different studies based on laboratory experiments or directly in-situ experiments supported in DFe and FeSPM profiles and biomass production show values from 10.000:1 up to 500.000:1 of C:Fe ratios (Anderson and Morel, 1982; Geider and La Roche, 1994; Gordon et al. 1997).

Based on the work elaborated by Gordon et al. (1997) and due to the variability in the C:Fe ratios, a range of values (100.000 - 500.000:1) will be used. The decision is supported on C:Fe ratios of ~ 100.000 - 500.000:1 found for some oceanic phytoplankton species (Sunda et al. 1991). Employing a mean value extracted from our measurements of 22 nM for dissolved iron in the surface of the central Baltic Proper during summer and assuming that the whole dissolved fraction would be consumed by phytoplankton; the C:Fe ratio provides a production of organic carbon of 2 - 11 mmol L^{-1}. Mean value of summer N_2 fixation of 5.5 µmol L^{-1} for 2008 and 2009 (Fig.4.9) leads to a new production of 36.3 µmol L^{-1} assuming that the biomass production follows the classical C:N ratio from Redfield (6.6:1). This value is in the order of the organic production (Pr^{OC}) calculated by Schneider et al. (2009) amounting 63 µmol L^{-1} of new production for a summer fixation of 6.8 µmol L^{-1} (summer 2005). Even hypothesizing that the dissolved Fe (II) fraction were the only source bioavailable for the cyanobacteria growth in the Baltic Sea; a mean Fe (II) concentration of 2.9 nM at the surface would provide a new production of the order 0.3 - 1.5 mmol L^{-1} for the Baltic Sea. This potential production using the whole budget of biovailable Fe (II) iron in the surface is much higher than the calculated from Schneider et al. (2009) suggesting that iron is a promoting factor of the cyanobacteria growth in the Baltic Sea but not a limiting one. Thus, other parameters as the phosphorus budget or different hydrographic conditions in winter and summer should be considered for regulating the biomass production in the surface of the Baltic Proper during summer. This study summarizes that the Baltic Sea beyond its restrictions in vertical mixing; the sources and the cycling of iron are enable to supply the different phytoplankton occurrence differing from other locations in the world such as the equatorial Pacific or the Southern Ocean.

CONCLUSIONS AND OUTLOOK

Different micronutrients (e.g.: copper, iron and molybdenum) are essential for phytoplankton growth. In some marine environments due to different reasons as low concentrations or the existence of chelating agents, these micronutrients could act as limiting or promoting factors for the biomass production. In this context this study was focused on the iron speciation in the Baltic Sea and its impact on the growth of diazotrophic cyanobacteria blooms in the Baltic Sea that take place during the summer season under differing conditions (low wind, high temperatures, efficient sunlight and low N:P ratio).

Macro and micronutrients concentrations in the Baltic surface waters in summer are strongly associated to the hydrographical conditions in winter. During winter, strong winds favoured the vertical mixing along the water column in the Baltic Proper and vertical turbulent diffusive transport of nutrients from deeper layers (40 - 60 m) to the surface is feasible. Highest values of Fe (dissolved, particulate and Fe (II)) occurred in the western Baltic Sea covering the Kattegatt, the Arkona Basin and the Bornholm Sea. Fe sources are basically the river runoff mostly discharged along the southwester Baltic Sea and the resuspension process carried out in the oxic water – anoxic sediments interphase in these shallow basins.

In the early spring, melting of the ice that covers the north of the Baltic Sea during winter and river floods spread a huge amount of nutrients including Fe and organic matter into the Baltic Proper. The surface warming of the surface gives rise to a thermal stratification in the first 10 – 20 m of the water column along the central Baltic Proper. Diatoms blooms during the spring season provoke the depletion of dissolved inorganic nitrogen and phosphorus mainly in the southern part of the Baltic Sea. The biomass produced after the exploitation of the available resources decays and sinks being remineralised in the limits of the halocline and redoxcline supporting the anoxia state of the deep waters in the central Baltic Sea.

After the set up of the thermocline, restriction of vertical turbulent diffusive transport leaves the river runoff and local upwelling events as the major sources of nutrients for surface waters in later spring and summer. River floods carry huge amounts of organic matter as humic acids; organic compounds able to complex the iron hydrolysed forming non-reactive oxyhydroxides found in river waters. Changes in the isotopic signature show this seasonality character in the speciation of the iron discharged with the runoff (Gelting et al. 2010). Photoreduction of these organic complexes in the euphotic layer releases free dissolved Fe (II) available for phytoplankton uptake.

Calculations of the water column stability and vertical profiles for the main central stations of the Baltic Proper (Gotland and Landsort Deep) present a water body highly stratified and anoxic deep waters. Those stagnant deep waters contain a reservoir of dissolved ferrous iron and phosphorus. The free Fe (II) transported upwards through the redoxcline is rapidly oxidised and precipitated forming amorphous Mn-Fe oxyhydroxides trapping the phosphorus crossing the cline. The availability of this Fe pool for the uptake of phytoplankton species in the surface waters seems unlikely. Results showed an increase of the upwards-diffusive flux and a decrease in the sinking particulate iron through the redoxcline along the three years of research. On the other hand, data from the last 15 years reflect no direct correlation between cyanobacteria blooms, iron concentrations and stagnation periods of the deep waters in the Baltic Sea. Sampling in summers 2008 and summer 2009 and calculations of hypothetical biomass production demonstrated that the iron content in the Baltic surface is large enough for supporting the blooms. FeSPM:Chl a ratio and DFe concentrations for both summers confirmed the role of iron as promoting factor.

Next steps in the research of the iron cycle and its role as micronutrient in the Baltic Sea should cover: A) the identification of the dissolved organic carbon fraction in the surface waters, B) the study of depth profiles of iron in areas characterized by local upwelling events and C) exhaustive sampling of the central Baltic Proper during a cyanobacteria bloom.

A) Identification and quantification of the organic carbon fraction able to complex iron is necessary to understand the impact of the organic fraction in the iron cycle. Knowing the origin of these compounds (biotic or terrigenic) and their content in the central Baltic Proper would increase the knowledge about the speciation and the real bioavailability of iron in the Baltic waters.

B) Local upwelling in coastal areas (e.g.: the western part of the Gulf of Finland and the Swedish coast) have been studied and suggested as trigger of cyanobacteria blooms in the Baltic Sea. Deep layers rich in dissolved inorganic phosphorus that replace the depleted-nutrients surface waters support the growth of the different diazotrophs. Calculations of the upwards transported iron by such physical phenomenon would complete the view of the bioavailable iron pool role below the thermocline and provide a better understanding of the metal influence in the development of the bloom.

C) Lack of continuous analysis of dissolved and particulate iron and calculations of C:Fe ratio in the Baltic inabilities calculating the real uptake of iron during diazotrophic growth. An exhaustive analysis of the different iron fractions (dissolved, particulate, colloidal and Fe (II)) in the different stages of a cyanobacteria bloom is necessary to relate the iron speciation and its uptake by cyanobacteria.

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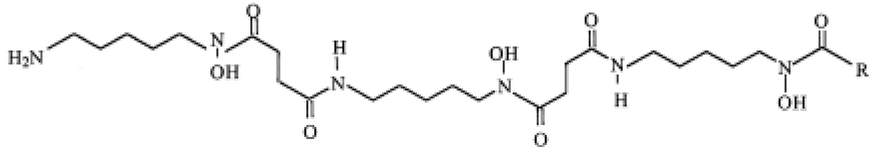
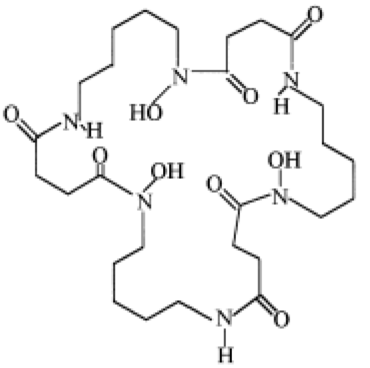
APPENDIX

APPENDIX I: Studying subsurface samples from the Gulf of Gdansk in the Baltic Sea region siderophores of unknown origin-ferrioxamine E and G, and rhodotorulic acid have been discovered and isolated by Mucha et al. (1999) using capillary electrophoresis.



Desferrioxamine B R = CH_3
Desferrioxamine G R = $(CH_2)_2CO_2H$



Desferrioxamine E, Nocardamine

APPENDIX II: Table with locations obtained during the cruise MSM 08/03 in June/July of 2008.

St	Latt (dec)	Long (dec)	Sal	T (°C)	PO4 (µM)	NO3 (µM)	DFe [nM]	FeSPM	DFe:SPM Ratio	Fe(II) nM
76	58.2	10.3	30.7	16.4	0.00	0.10	7.0	1.6	4.4	4.4
75	57.7	11.1	26.9	15.8	0.04	0.13	14.9	6.4	2.3	3.6
74	57.2	11.6	23.8	14.5	0.00	0.12	9.3	18.8	0.5	3.4
73	56.9	11.9	19.2	18.2	0.00	0.01	13.2	2.9	4.5	0.6
72	56.7	11.1	20.3	14.57	0.00	0.01	8.7	7.5	1.2	2.3
70	56.2	11.1	18.0	16.8	0.00	0.03	22.3	18.5	1.2	1.6
69	55.8	10.8	14.2	18.2	0.00	0.01	20.7	27.5	0.8	0.9
68	55.3	11.1	13.1	17.7	0.08	0.05	35.0	47.9	0.7	2.6
67	54.8	10.3	13.1	17.7	0.11	0.05	31.3	27.0	1.2	2.2
3	54.9	13.0	7.7	14.9	0.15	0.10	23.8	44.5	0.5	0.1
4	54.9	14.5	7.8	15.6	0.15	0.04	28.5	19.6	1.5	0.1
5	54.9	15.4			0.32	0.09	7.7	3.9	2.0	
6	55.3	16.0			0.31	0.08	8.1	3.5	2.3	
8	55.2	14.5	7.7	15.1	0.17	0.04	17.1	32.5	0.5	0.3
9	55.5	14.9	7.6	15.0	0.22	0.01	9.1	10.2	0.9	0.1
10	55.5	15.5	7.5	15.3	0.27	0.03	20.8	3.5	5.9	0.2
11	55.3	16.9	7.4	15.2	0.29	0.05	13.8	1.7	7.9	
12	55.3	17.8	7.4	15.1	0.25	0.02	7.4	2.9	2.5	
13	55.1	18.5	7.3	15.1	0.15	0.03	10.0	3.2	3.1	
14	54.9	19.2	7.2	15.1	0.11	0.03	8.4	2.7	3.1	
15	55.2	18.8	7.2	15.4			17.1	5.7	3.1	
16	55.6	18.4	7.4	14.7	0.30	0.01	7.0	1.7	4.2	
17	56.0	18.9	7.4	14.6	0.19	0.04	9.4	2.7	3.5	
18	56.4	19.4	7.3	14.8	0.12	0.02	9.0	1.8	5.2	
19	56.8	19.7	7.3	14.9	0.10	0.02	10.4	3.2	3.3	1.9
20 (GD)	57.3	20.0	7.2	14.7	0.06	0.01	14.2	5.1	2.8	1.3
27	57.8	20.1	6.3	14.0	0.06	0.02	12.7	4.8	2.7	
28	58.3	20.3	6.3	14.5	0.06	0.05	14.5	3.5	4.1	
66	55.1	13.3	8.1	18.0	0.05	0.02	30.3	10.1	3.0	1.2
65	55.9	16.5	7.6	16.7	0.13	0.02	19.7	8.5	2.3	
63	56.3	17.0	7.4	14.9	0.05	0.06	23.3	19.8	1.2	1.7
62	56.8	17.4	7.3	14.2	0.11	0.02	20.3	2.5	8.0	1.6
61	57.3	17.6	7.2	16.8	0.01	0.02	65.3	5.2	12.5	
60	57.7	17.4	6.8	16.3	0.01	0.03	28.8	4.4	6.6	1.8
59	58.2	17.7	6.9	14.9	0.05	0.01	26.5	6.4	4.2	0.6
57 (LD)	58.6	18.2	6.9	15.4	0.01	0.01	21.5	4.1	5.3	1.4
56	58.9	19.1	6.3	15.3	0.00	0.05	17.5	4.4	4.0	0.5
55	59.3	19.5	5.7	14.6	0.00	0.04	20.5	38.5	0.5	1.5
31 (AS)	60.2	19.1	4.9	13.1	0.00	0.02	62.1	26.2	2.4	5.4
43	60.7	19.2	5.3	12.4	0.02	0.01	30.7	8.6	3.6	7.5
42	61.2	19.3	4.8	13.6	0.01	0.02	15.3	3.1	4.9	4.6
32	61.7	19.5			0.01	0.02	45.2	13.6	3.3	
33	62.1	19.7	5.3	11.3	0.01	0.03	36.9	7.2	5.1	
41	62.6	20.0	4.8	12.1	0.00	0.03	26.3	6.3	4.2	9.0
40	62.7	20.1	4.9	12.3	0.01	0.01	33.00	10.1	3.3	2.9
34	63.0	20.5	4.6	11.3	0.01	0.02	74.2	8.9	8.4	13.2
341	63.6	21.0					128	51.0	2.5	20.8

St	Latt (dec)	Long (dec)	Sal	T (Cº)	PO4 (µM)	NO3 (µM)	DFe [nM]	FeSPM	DFe:SPM Ratio	Fe(II) nM
342	64.1	21.7					128	174	0.7	24.2
343	64.7	22.7					201	67.9	3.0	33.0
36	64.9	22.9	3.1	8.1	0.01	2.93	235	125	1.9	
35	65.4	23.5	3.0	7.8	0.00	1.94	592.1	244	2.4	39.3
45	59.5	21.0	5.9	15.3	0.01	0.04	15.6	4.0	3.9	5.6
54	59.2	21.3	6.4	16.5	0.00	0.01	23.5	54.3	0.4	3.1
46	59.5	22.0	5.9	13.7	0.06	0.02	19.8	8.6	2.3	2.2
53	59.3	22.4	5.8	16.4	0.00	0.00	17.4	24.1	0.7	3.2
47	59.4	23.0	6.0	13.9	0.05	0.04	26.0	12.1	2.2	1.0
52	59.4	23.7	5.7	14.1	0.00	0.03	36.5	96.3	0.4	7.6
48	59.6	24.0	5.6	14.1	0.00	0.02	37.9	8.6	4.4	2.2
49	59.8	24.8	5.5	14.9	0.02	0.02	43.0	43.6	1.0	2.9
50	59.8	25.9	5.2	14.2	0.03	0.02	27.6	151	0.2	2.6
51	59.8	26.6	4.5	13.7	0.00	0.01	25.9	62.1	0.4	1.4

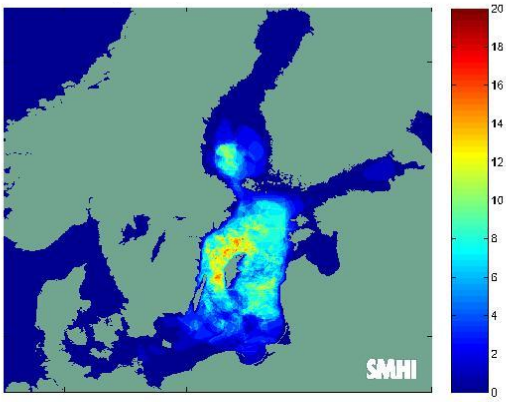
APPENDIX III: Table with sample locations obtained during the cruise in February of 2009 on board of the R.V. Alkor.

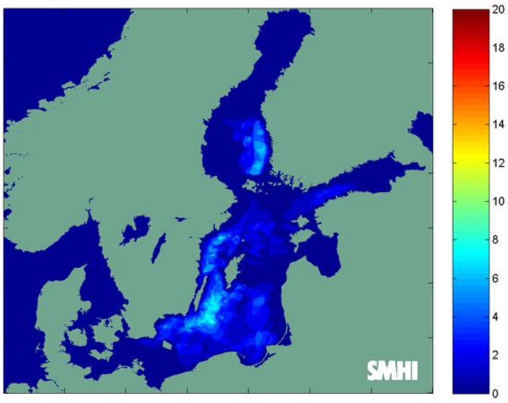
Stn	Latt (dec)	Long (dec)	Sal	T (°C)	PO4 (µM)	NO3 (µM)	DFe [nM]	FeSPM (nmol/L)	DFe:SPM Ratio	Fe(II) nM
TF0010	54.6	11.3	10.7	2.5	0.6	3.3	109	26.2	4.1	
TF0012	54.3	11.6	12.1	2.5	0.7	3.9	145	8.2	17.5	1.6
TF0046	54.5	12.2	9.1	3.9	0.6	3.3	52.9	12.1	4.3	
TF0030	54.7	12.8	8.2	2.3	0.6	2.7	31.1	12.3	2.5	7.6
TF0069	55.0	13.3	8.1	2.7	0.5	2.7	44.9	14.6	3.1	0.1
TF0113	54.9	13.5	8.3	2.7	0.6	2.8	37.5	14.3	2.6	0.9
TF0109	55.	14.1	8.3	2.7	0.5	3.0	31.6	11.8	2.7	0.1
Ob boje	54.1	14.2	8.0	0.8	0.6	6.4	256	255	1.0	3.3
TF0152	54.6	14.3	8.1	2.1	0.6	3.6	22.9	14.2	1.6	1.8
TF0213	55.3	16.0	7.8	4.0	0.7	3.1	24.4	6.8	3.5	2.5
TF0222	55.2	17.1	7.6	3.9	0.7	3.1	12.2	9.2	1.5	2.1
TF0256	55.3	18.2	7.6	4.1	0.7	3.4	12.6	8.5	1.5	2.5
TF0259	55.5	18.4	7.6	4.3	0.7	3.5	13.1	7.7	1.7	2.3
TF0253	55.8	18.9	7.5	3.9			16.6	6.5	2.5	1.6
TF0250	56.1	19.2	7.5	4.1	0.6	3.3	16.2	8.0	2.0	1.9
TF0263	56.3	19.4	7.4	3.9			14.4	8.0	1.8	1.9
TF0260	56.6	19.6	7.4	3.8	0.6	3.2	13.7	8.0	1.7	1.9
TF0272	57.1	19.8	7.4	3.9	0.6	3.2	13.0	5.3	2.4	
TF0271	57.3	20.0	7.4	4.0	0.6	3.6	15.9	7.9	2.0	4.0
TF0284	58.6	18.2	7.0	3.0	0.5	3.6	17.6	8.6	2.1	2.6

APPENDIX IV: Table with sample locations obtained during the cruise in July of 2009 on board of the R.V. Alkor.

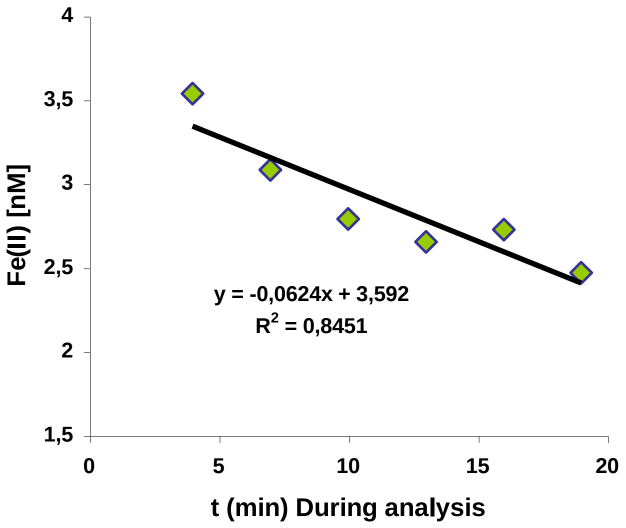
Stn	Latt (dec)	Long (dec)	Sal	T (°C)	PO4 (µM)	NO3 (µM)	Dfe [nM]	FeSPM	DFe:FeSPM Ratio	Fe(II) nM
Sn 71	54.4	12.3	8.4	19.2			37.2	19.5	1.9	3.9
Sn 69	54.6	12.7	8.0	18.2			51.3	14.5	3.5	4.4
Sn 66	54.8	13.3	7.6	18.1			31.0	12.1	2.6	3.6
Sn 62	54.9	14.3	7.5	18.3			36.8	9.3	4.0	4.0
Sn 60	55.0	14.8	7.6	18.4			35.6	9.4	3.8	3.7
Sn 57	55.1	15.5	7.4	18.0			32.2	8.8	3.7	2.9
BB	55.3	16.0	7.3	17.9	0.05	0.07	26.8	4.9	5.4	6.9
Sn 56	55.3	16.1	7.3	18.3			19.2	3.6	5.3	4.9
Sn 53	55.4	16.9	7.3	18.3			14.2	4.1	3.5	5.4
Sn 50	55.4	17.6	7.1	18.7			18.8	3.1	6.0	6.0
Sn 47	55.6	18.4	7.2	17.9			13.8	1.7	8.3	5.0
Sn 40	56.5	19.2	7.2	17.9			20.0	1.9	10.4	3.5
Sn 35	57.1	19.8	6.9	17.9			18.4	3.1	6.0	8.3
GD	57.3	20.1	7.0	14.6	0.03	0.01	12.6	3.9	3.3	2.7
Sn 26	58.0	19.9	6.6	14.1			17.3	1.9	9.1	1.2
Sn 21	58.3	20.1	6.2	13.7			14.2	2.4	5.9	1.1
Sn 17	58.6	20.2	6.3	14.4			8.1	2.6	3.1	0.7
Sn 13	58.8	20.3	6.3	14.4			8.1	1.9	4.3	1.2
Sn 9	58.8	19.8	6.1	14.6			9.4	2.2	4.3	1.5
Sn 5	58.8	19.1	6.1	14.3			10.9	2.9	3.7	3.2
LD	58.6	18.2	5.7	14.3	0.02	0.06	18.4	23.3	0.8	2.2
Sn 1	58.3	18.1	6.4	14.4			8.2	3.4	2.4	0.9

APPENDIX V: Satellite images of the cyanobacteria blooms extension and intensity during the summers of 2008 and 2009. Images were extracted from the Helsinki commission website and provided by the Swedish Meteorological and Hydrological Institute (SMHI). Intensity of the blooms is related to days of cyanobacteria accumulation in surface waters of the Baltic Proper.





APPENDIX VI: Evolution of the Fe (II) content in a sample from the Northeastern part of the Baltic Proper in July 2009.

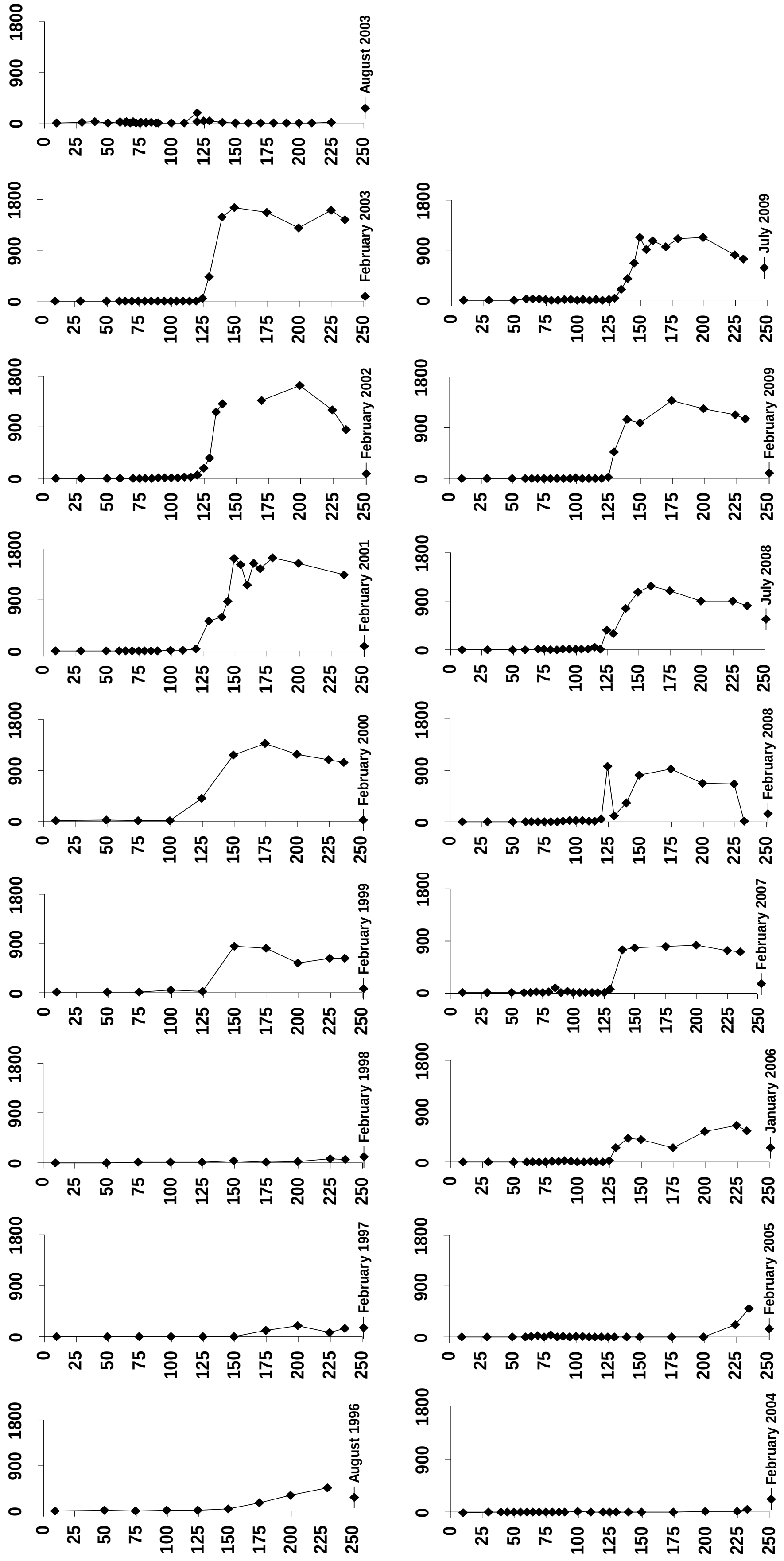


APPENDIX VII: Mean values of sinking and advective upward transport of iron calculated for the mean station of the Gotland Deep.

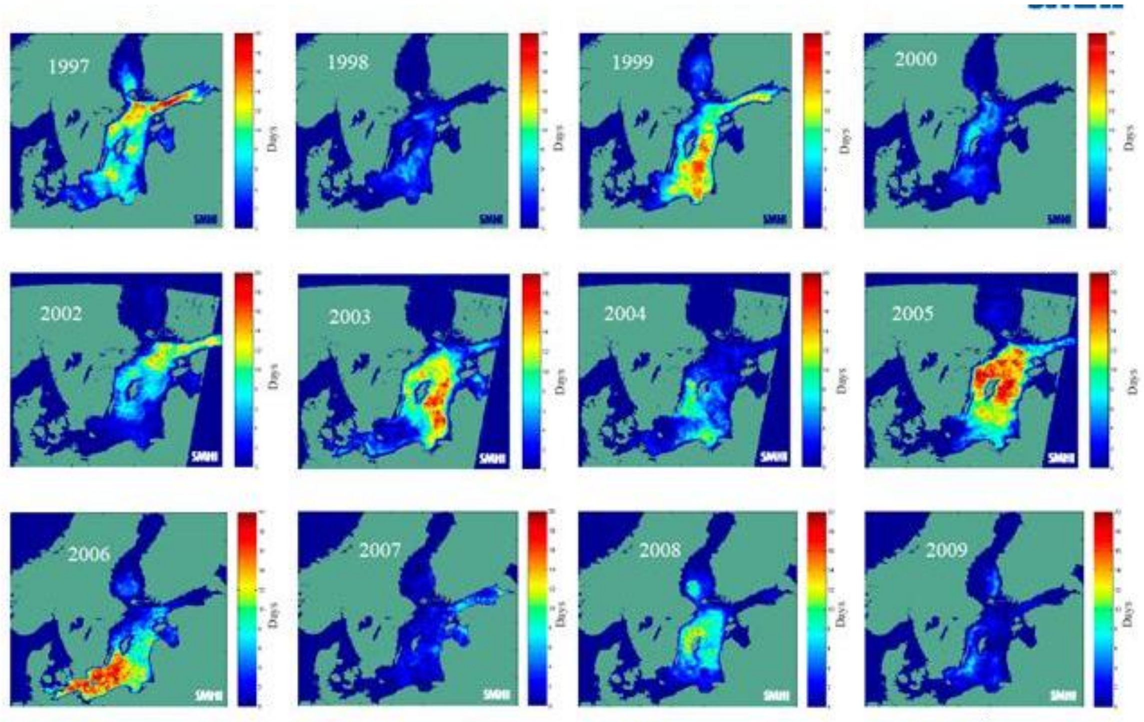
Season	Downward Flux *	Advective Upward Transport*
July 2008	57.1	15.3
February 2009	39.7	12.9
July 2009	29.7	19.5
Average	42.2 ± 13.9	15.9 ± 2.7

* in units of µmol $^{-2}$ day $^{-1}$

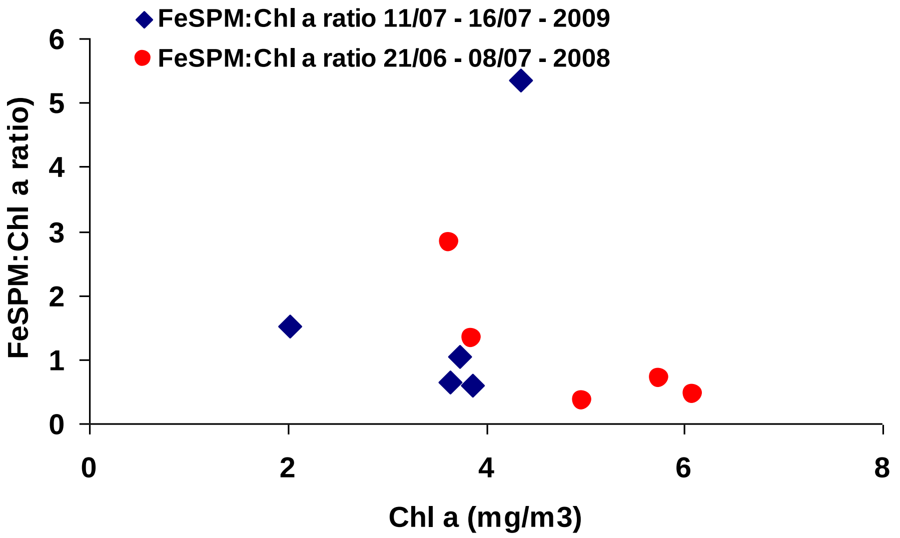
APPENDIX VIII: Evolution of the DFe concentrations [nM] along the water column of the Gotland Deep 1996 - 2009. Data provided by Dr. C. Pohl (IOW).

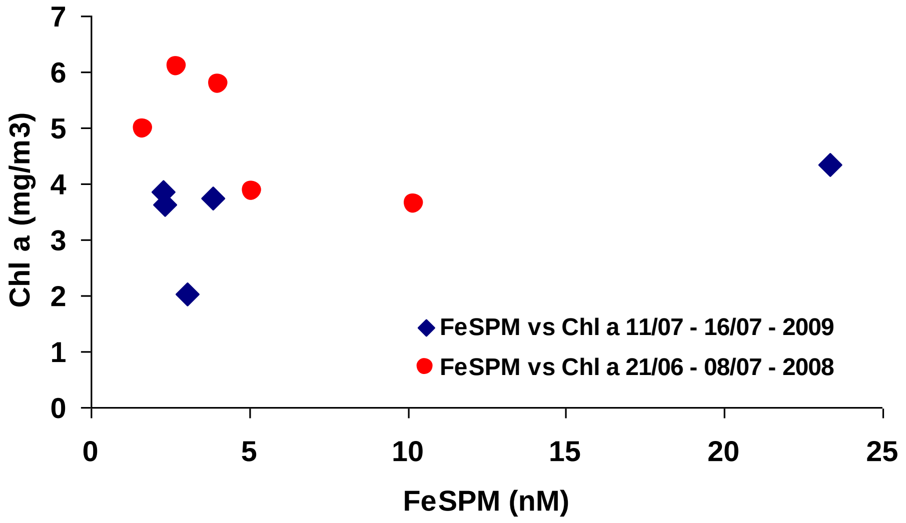


APPENDIX IX: Evolution of the cyanobacteria blooms between 1997 and 2009. The coloured scale shows the number of days with cyanobacteria observations along the different summers. Data extracted from HELCOM website.



APPENDIX X: FeSPM, Chl a concentrations and FeSPM:Chl a ratio in summer 2008 and 2009.





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PUBLICATIONS AND CONFERENCE

Paper: **Iron distribution and speciation in oxic and anoxic waters of the Baltic Sea. Marine Chemistry**. Pohl C and **Fernández-Otero E**. In press.

Poster: **Iron (II) determination in the Baltic Sea. Studies on the distribution and speciation in the context of cyanobacteria growth. Fernández-Otero E**, Schulz-Bull D, Nausch G, Nausch M and Pohl C. **7th Baltic Sea Science Congress (BSSC)**, Tallinn (Estonia) in 2009.

REFERENCES

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Ich versichere hiermit an Eides statt, dass ich die vorliegende Arbeit selbstständig angefertigt und ohne fremde Hilfe verfasst habe, keine außer den von mir angegebenen Hilfsmittel und Quellen dazu verwendet habe und die den benutzten Werken inhaltlich und wörtlich entnommenen Stellen als solche kenntlich gemacht habe.

Rostock, 30th of August, 2011