Spatio-temporal variability of carbon and silica fluxes through the inner Elbe estuary, Germany

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Thorben Amann
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Prof. Dr. Jürgen Oßenbrügge
(Leiter des Fachbereichs Geowissenschaften)

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Thorben Amann

Content

Abstract

In global biogeochemical cycles, estuaries play an important role as agents between the terrestrial and marine cycles. The role of silica (Si) and carbon (C) cycle and their interconnection in the transition from land to ocean was examined, regarding the Elbe estuary as an exemplary system. This system, as an important pathway for matter fluxes towards the North Sea, is strongly affected by anthropogenic activities. The Elbe River and its estuary were characterised by high pollution far into the 1980s, but a recovery has been observed after 1989. Despite the improvements the ongoing intense perturbations of the ecosystem qualify the Elbe estuary as a suitable site for studies of anthropogenic impacts on estuarine systems.

In the first part of this thesis, the effects of water quality restoration on the carbon cycling in the inner Elbe estuary were examined, using an extensive historical monitoring database. While in the period of high pollution dissolved organic carbon (DOC) was utilised by bacteria, particulate organic carbon (POC) passed the estuary virtually unaltered. The mineralisation of DOC led to near anoxic conditions in the water column of large estuarine parts. Improved water quality allowed for better oxygenated waters, but a subsequent switch to POC mineralisation and subsequent CO_2 production resulted in a reappearance of oxygen minima. This thesis focusses especially on the freshwater part of the estuary, which has not been examined to date. The conversion of about 50% of the riverine POC to CO_2 renders the freshwater area a strong filter for POC and a source for CO_2, a fact which has not been considered in previous studies of other estuarine systems. Generally, the maximum turbidity zone (MTZ) occurring in many estuarine zones has been described to be the strongest source of CO_2 to the atmosphere. In contrast, it is hypothesised in this thesis that the region before the MTZ is a hotspot for CO_2 fluxes in the Elbe estuary.

With a focus on the inorganic carbon system, 18 surveys were conducted between 2009 and 2011 with the aim to cover temporal and spatial variations of carbon fluxes through the Elbe estuarine system. To explore fluxes of dissolved inorganic carbon, a tentative budget was constructed. Results corroborate the hypothesis that the freshwater area in the vicinity of the city of Hamburg features the highest per area CO_2 effluxes. This area covers about 10 % of the total estuarine surface and contributes 10 % of the CO_2 fluxes to the atmosphere and 82 % of dissolved CO_2, which is transported seawards. Yet, the MTZ is the largest contributor to CO_2 fluxes due to the larger surface area. Overall the estuary is, as many estuaries in a similar geographical setting, net heterotrophic and releases 13.2 x 10^9 mol CO_2 a^{-1} to the atmosphere.

Additionally, it was elaborated that the Elbe estuary is a source for DIC other than CO_2. The total excess DIC production and addition amounts to 23 x 10^9 mol C a^{-1}, which is 40 % of the overall input from the area upstream of Hamburg. The largest part of excess DIC, 60 %, is attributed to CO_2 production and subsequent evasion. Furthermore, DIC is exported from marshes and sediments in the form of alkalinity. With the Elbe as one of the larger contributors of TA to the North Sea, additions along the estuary can have an important effect on North Sea budgets, which to date rely on river flux data from upstream sampling stations. However, while a net addition was observed, individual transects were also characterised by TA consumption processes. This relatively unsteady behaviour points towards yet another change in the ecosystem, which are presumed to be traced back to ongoing intervention by human activities.

A further part of this thesis comprises observations on Si cycling in the inner Elbe estuary, which are of particular interest as data on Si fluxes through estuaries are generally scarce, especially regarding the particulate form biogenic silica (BSi). It was possible to reconstruct historical BSi data with POC monitoring data from a positive correlation of POC and BSi, derived from data of the recent cruises. The combination of historical data on dissolved silica (DSi), measurements of DSi and BSi from recent cruises, and reconstructed BSi data, enabled the construction of a tentative Si budget. This revealed that the Elbe estuary is a source for DSi and a strong sink for BSi, contradicting the general assumption of estuaries being a filter for DSi and a source for BSi. The Elbe River delivers 2.8 x 10^9 mol DSi a^{-1} and 0.9 x 10^9 mol BSi a^{-1}. On an annual average, 18 % of DSi are added along the inner estuary and 88 % of BSi are lost. Tributaries are assumed to contribute most of the excess DSi to the estuarine waters, while sedimentation is the single largest sink for BSi, leading to a sharp decline of the relative BSi fraction of the total Si delivered to the coastal zone. With 3 % BSi fraction of total Si, this fraction by far lower than the global average of 16 %. It was hypothesised that large amounts of BSi are removed permanently from the estuarine cycle by sediment dredging.

In summary it could be demonstrated that a system, having recovered from heavy pollution, does not regain its natural ecosystem function. Fluxes of CO_2 remain high and the expected retention of silica was not observed due to an environment, which is still strongly altered. Sediment dredging is assumed to play a significant role in estuarine matter fluxes, not only based on the removal of BSi from the system, but in addition due to the disturbance of sediment porewater processes and alteration of estuarine hydrodynamics.

Zusammenfassung

In globalen biogeochemischen Stoffkreisläufen spielen Flussmündungen in Form von Ästuaren eine wichtige Rolle als Vermittler zwischen dem terrestrischen und marinen Kreislauf. In dieser Arbeit wurden die Rollen des Silizium- und Kohlenstoffkreislaufs und deren Verbindung im Übergang vom Land zum Meer an Hand des Ästuars der Elbe als beispielhaftes System untersucht. Die Elbe stellt einen wichtigen Weg für die Stoffflüsse in Richtung Nordsee dar und ist stark durch anthropogene Aktivitäten beeinflusst. Waren die Elbe und ihr Mündungsbereich durch hohe Wasserverschmutzung bis in die späten 1980er Jahren gekennzeichnet, so wurde eine Erholung nach 1989 deutlich. Die weiterhin anhaltenden intensiven Eingriffe in das Ökosystems machen dieses System gerade deswegen zu einem geeigneten Standort für die Untersuchung anthropogener Einflüsse auf Ästuare.

Im ersten Teil dieser Arbeit wurden die Auswirkungen der Wasserqualitätsverbesserungen auf dem Kohlenstoffkreislauf in der inneren Elbmündung untersucht. Dabei konnte auf eine umfangreiche historische Monitoring-Datenbank örtlicher Behörden zurückgegriffen werden. Daraus lässt sich erkennen, dass in Zeiten starker Verschmutzung gelöster organischer Kohlenstoff (DOC) von Bakterien als Energiequelle genutzt wurde und partikulärer organischer Kohlenstoff (POC) das Ästuar nahezu unverändert passierte. Der mikrobielle Abbau des DOC führte in weiten Teilen des Elbeästuars zu nahezu anoxischen Bedingungen in der Wassersäule. Mit steigender Wasserqualität verbesserte sich auch die Sauerstoffdurchlüftung des Gewässers. Der Rückgang der Verschmutzung bewirkte jedoch eine Veränderung in der Qualität des DOC, so dass eine Umstellung auf von DOC auf POC Mineralisierung erfolgte. Durch einen erhöhten Flusseintrag von POC stieg auch die CO_2-Produktion. Dies führte zu einem Wiederauftreten der Sauerstoffminima.

In dieser Arbeit wurde ein besonderer Fokus auf den Süßwasserteil des Ästuars gelegt, der in Ästuarstudien bisher generell vernachlässigt wurde. Die Umwandlung von etwa 50 % des vom Fluss eingetragen POC zu CO_2 bewirkt eine starke Filterwirkung für POC im Süßwasserbereich. Die damit verbundene Quelle für CO_2 wurde bisher in Studien anderer Ästuar-Systeme nicht berücksichtigt. Generell wird die Zone maximaler Trübung (MTZ), die in vielen Ästuaren beschrieben worden ist, als stärkste Quelle von CO_2 für die Atmosphäre angesehen. Im Gegensatz dazu wurde in diesem Teil der Arbeit die Hypothese aufgestellt, dass die Region vor der MTZ ein Hotspot für CO_2 Ausgasung im Elbeästuar ist.

Zusammenfassung

Mit einem Schwerpunkt auf dem anorganischen Kohlenstoffkreislauf wurden zwischen 2009 und 2011 18 Ausfahrten durchgeführt, um zeitliche und räumliche Variationen der Kohlenstoffflüsse durch das Elbeästuar zu untersuchen. Mit den Ergebnissen konnte ein vorläufiges Budget für gelösten anorganischen Kohlenstoff (DIC) erstellt werden.

Die Untersuchungsergebnisse bestätigen die Hypothese, dass der Süßwasserbereich in der Nähe der Stadt Hamburg die höchsten CO_2-Ausgasungsraten pro Fläche aufweist. Dieser Bereich deckt etwa 10 % der gesamten Ästuaroberfläche ab und trägt 10 % der CO_2-Flüsse in die Atmosphäre bei sowie 82 % des gelösten CO_2, das seewärts transportiert wird. Dennoch leistet die MTZ aufgrund der weit größeren Fläche den größten Beitrag zur CO_2-Ausgasung. Insgesamt ist das Elbeästuar, wie viele Ästuare in einer ähnlichen geografischen Lage, netto heterotroph mit einer jährlichen CO_2-Ausgasung von 13.2×10^9 mol CO_2 a-^{1}.

Darüber hinaus konnte gezeigt werden, dass das Elbeästuar neben einer Quelle für CO_2 ebenso eine Quelle für DIC in Form von Alkalinität (TA) ist. Der gesamte Überschuss an produziertem DIC beträgt 23×10^9 mol C a^{-1}. Das sind etwa 40% des gesamten DIC Eintrags aus dem Ästuärbereich oberhalb Hamburgs. Der größte Teil des zusätzlichen DIC, etwa 60%, ist auf bakterielle CO_2-Produktion und anschließende Ausgasung zurückzuführen. Der verbleibende Teil wird von Marschen und Sedimenten im Wesentlichen als TA exportiert. Da die Elbe ein wichtiger Lieferweg von TA in Richtung Nordsee ist, können zusätzliche Quellen entlang des Ästuars einen wichtigen Einfluss auf Nordsee Budgets haben, die zurzeit auf Daten aus Messstationen im Süßwasserbereich beruhen.

Während im Mittel aller Fahrten eine Zugabe von DIC beobachtet werden konnte, waren einzelne Längsprofile auch durch einen Rückgang an TA gekennzeichnet. Dieses relativ wechselhafte Verhalten kann möglicherweise auf eine weitere Veränderung des Ökosystems hindeuten, bedingt durch anhaltende Eingriffe durch die Menschheit.

Ein weiterer Teil dieser Arbeit besteht aus Beobachtungen zum Siliziumkreislauf im inneren Elbeästuar. Die Ergebnisse dieser Beobachtungen sind von besonderem Interesse, da Daten zu Si-Flüssen durch Ästuare selten erhoben wurden, speziell in Hinblick auf die partikuläre Form biogenes Silizium (BSi). Da eine positive Korrelation von POC und BSi Konzentrationsdaten der aktuellen Fahrten abgeleitet werden konnte, ergibt sich die Möglichkeit, historische BSi Daten mit Hilfe von POC Monitoring-Daten zu rekonstruieren. Die Kombination aus historischen Daten zu gelöstem Silizium (DSi), Messungen von DSi und BSi während der jüngsten Ausfahrten, und rekonstruierten historischen BSi Daten, ermöglichte die Erstellung eines vorläufigen Si-Budgets.

Dabei zeigte sich, dass die Elbmündung eine Quelle für DSi und eine starke Senke für BSi ist. Dies steht im Widerspruch zur allgemeinen Annahme, dass Ästuare ein Filter für DSi und

eine Quelle für BSi sind. Der Fluss Elbe liefert 2.8 x 10^9 mol DSi a^{-1} und 0.9 x 10^9 mol BSi a^{-1}. Im Jahresdurchschnitt werden 18 % DSi entlang des inneren Ästuars hinzugefügt und es gehen 88 % des BSi verloren. Es wird davon ausgegangen, dass Nebenflüsse, die sich entlang des Ästuars befinden, die größten Teile des zusätzlichen DSi beitragen, während Sedimentation die größte Senke für BSi ist. Das führt zu einem starken Rückgang des relativen Anteils von BSi an der gesamten Si Menge im Bereich der Mündung, d.h. im Übergang zum äußeren Ästuar. Mit 3 % ist dieser Anteil weitaus geringer als der globale Durchschnitt von 16 %. Es besteht die Vermutung, dass große Mengen an BSi durch Instandhaltungsbaggerungen des Fahrwassers und der Hafenbecken dauerhaft dem ästuarinen Siliziumkreislauf entzogen wird.

Insgesamt war es möglich zu zeigen, dass ein System, dass sich von starker Verschmutzung erholt hat, nicht wieder seine natürliche Ökosystemfunktion erreicht. Ausgasungen von CO_2 bleiben hoch und die erwartete Retention von Si kann nicht beobachtet werden. Dies ist darauf zurückzuführen, dass in das System Elbeästuar weiterhin stark eingegriffen wird. Es ist anzunehmen, dass die Ausbaggerung von Sediment wichtige Auswirkungen auf ästuarine Stoffflüsse hat, nicht nur aufgrund der Entfernung von BSi aus dem System, sondern auch aufgrund der Störung von sedimentären Porenwasserprozessen und der Veränderung der ästuarinen Hydrodynamik.

Abbreviations

a	year
atm	atmospheres (unit of pressure)
BSi	biogenic silica
c	concentration
Chl-a	chlorophyll-a
CO_2	carbon dioxide
d	days
DIC	dissolved inorganic carbon
DO	dissolved oxygen
DOC	dissolved organic carbon
DSi	dissolved silica
F	flux
L	liter
MTZ	maximum turbidity zone
NH_4	ammonia
NO_2	nitrite
NO_3	nitrate
OMZ	oxygen minimum zone
PC	particulate carbon
pCO_2	partial pressure of CO_2
PIC	Particulate inorganic carbon
POC	particulate organic carbon
post-MTZ	post maximum turbidity zone
pre-OMZ	pre oxygen minimum zone
Q	discharge
Sal	salinity
SPM	suspended matter
TA	total alkalinity
TOC	total organic carbon

List of publications

Parts of this thesis were published in an international peer-review journal, while others were prepared to be submitted. A list of publications is given below, including work, the author of this thesis contributed parts to. A description of contributed parts is given in Appendix A.

Published

Amann, T., Weiss, A., Hartmann, J., 2012. Carbon dynamics in the freshwater part of the Elbe estuary, Germany: Implications of improving water quality. Estuarine, Coastal and Shelf Science 107, 112-121, DOI: 10.1016/j.ecss.2012.05.012.

This publication is part of the thesis (chapter 3)

Weiss, A., Amann, T., Hartmann, J., 2012. Silica dynamics in tidal marshes along a salinity gradient in the Elbe estuary, Germany. Silicon, DOI: 10.1007/s12633-012-9131-1.

In preparation

Amann, T., Weiss, A., Hartmann, J., in prep.. Inorganic carbon cycling and CO_2 fluxes in the inner Elbe estuary, Germany.

This publication is part of the thesis (chapter 4)

Amann, T., Weiss, A., Hartmann, J., in prep.. A silica budget of the inner Elbe estuary, Germany.

This publication is part of the thesis (chapter 5)

Schwichtenberg, F., Pätsch, J., Amann, T., Schartau, M., Thomas, H., Winde, V., Dellwig, O., van Beusekom, J., Böttcher, M., Grashorn, S., Salt, L., in prep.. Impact of internal and external Alkalinity fluxes on the carbonate system in the German Bight / SE North Sea - A model study for the years 2001-2009.

Weiss, A., Amann, T., Hartmann, J., in prep.. Sources and export of DIC and TA from tidal creeks along a salinity gradient in the Elbe estuary, Germany.

1 Introduction

Matter fluxes around the globe determine the shape of our earth. A major pathway for matter in this global cycle is the mobilisation from rocks and their transport via rivers to the ocean. On its way, this matter is undergoing intense biogeochemical transformation, which has to be studied in order to determine the direction and magnitude of fluxes through the compartments.

As one of the most essential elements for life on earth, carbon is mobilised by chemical weathering of rocks. This weathering type leads to mobilisation of dissolved inorganic carbon (DIC), regarded as carbonate alkalinity (=summed charges of bicarbonate, HCO_3^- and carbonate, CO_3^{2-}). Specifically, the weathering of silicates leads to a release of silica (Si), in the dissolved form (DSi) an essential nutrient for aquatic organisms such as radiolaria, sponges, and diatoms, and in consequence important for the biological Si cycle.

Mobilised silica and carbon are transported via rivers to the coastal zone of the ocean (e.g. Kempe, 1979; Tréguer and De La Rocha, 2013). On the way downstream, they undergo turnover processes. The important role of carbon cycling in inland waters was highlighted by Cole et al. (2007), who introduced terrestrial aquatic environments as places of carbon transformation loss. These ecosystems are also characterised by Si turnover processes and retention (Conley, 2002). Reaching the ocean, DSi fuels coastal diatom blooms (Ragueneau et al., 2006), which at the same time consume river derived CO_2. In addition, riverine alkalinity, among other sources, has the ability to increase the buffer capacity of the shelf sea (Thomas et al., 2009).

Estuaries as transit pathways from land to ocean

On its way between river and ocean, mobilised matter has to pass estuaries, the transition from land to ocean. Estuaries are highly diverse ecosystems, which differ in biogeochemical turnover processes from rivers and the adjacent coastal ocean. The difference originates mainly from the mixing with seawater. Additionally, estuarine hydrodynamics can be strongly governed by tidal action. The interplay of tidal influence and river runoff can lead to residence times from days to months (Wolanski, 2007). Long residence times and strong tides can lead to the formation of a spatially confined area called maximum turbidity zone (MTZ), characterised by strongly increased suspended matter concentrations. They are particularly relevant for biogeochemical turnover processes in the water column (Herman and Heip, 1999). Furthermore, estuaries suffer from intense anthropogenic perturbation, because mankind has settled near estuaries around the globe centuries ago. They provide a well sheltered area for a harbour and at the same time give access to waterways in inland direction as well as towards the ocean. Because of the convenient natural infrastructure, population continues to grow and subsequent anthropogenic pressure increases, leading to loss of biodiversity (Lotze et al., 2006 and references therein) and ecosystem service functions (Barbier et al., 2011).

A unified concept of estuaries enables the description and comparison of estuaries around the globe. One of the first definitions based on the influence of salinity, defining an estuary as “semi-enclosed coastal body of water which has a free connection with the open sea and within which sea water is measurably diluted with fresh water derived from land drainage” (Pritchard, 1967). Many studies on estuaries follow this definition, which omits freshwater areas with tidal influence. Since this thesis includes the study of processes in the tidal but freshwater part, it refers to the inner estuary as defined by Fairbridge (1980; in Elliot and McLusky, 2002) as consisting of two parts: “a middle estuary subject to strong salt and freshwater mixing; and an upper or fluvial estuary, characterized by freshwater but subject to strong tidal action. The limits between these sectors are variable and subject to constant changes in the river discharges.”

Carbon cycle in estuaries

Various processes, dependant on their geographical and anthropogenical settings, exert a strong influence on carbon fluxes through estuaries. Riverine carbon can undergo a complete turnover. Bacterial respiration turns organic carbon into CO_2, leading to net heterotrophy of inner estuaries (Borges, 2005). This process is an efficient filter for organic carbon, removing up to 80 % of POC before it enters the coastal ocean (Abril et al., 2002). Furthermore, heterotrophy is supported by subaquatic groundwater discharge (Kempe et al., 1991) and adjacent marshes (e.g. Cai and Wang, 1998). The produced and received CO_2 is, due to extended residence times of the water, to large parts evaded to the atmosphere. This leads to an estimated carbon flux to the atmosphere of about 0.26 x 10^{15} g C a^{-1} (Laruelle et al., 2010; Cai, 2011; Chen et al., 2012). In contrast, continental shelves are sinks for CO_2 in the same order of magnitude. In a comparison of the surface areas, the significance of estuarine systems is emphasised: They occupy only 4 % of the shelf area, yet they are able to balance the CO_2 budget (Cai, 2011).

While heterotrophy dominates, where turbid waters inhibit photosynthesis, primary production is likely to occur in estuarine areas with less suspended matter and sufficing nutrient availability (Heip et al., 1995 and references therein). This can lead to a decline of dissolved CO_2 in the water column.

Besides processes, that directly influence the pCO_2, non-conservative mixing of DIC was described in some estuaries: Carbonate formation and dissolution (i.e. Abril et al., 2003), nitrification and denitrification (Berounsky and Nixon, 1993; Frankignoulle et al., 1996), and sulphate oxidation and reduction (Krumins et al., 2012) lead to consumption (former process of each couple) or release of alkalinity (latter process of each couple). In consequence, the DIC flux from rivers is likely to be changed during the estuarine passage.

Silica cycle in estuaries

The cycle of silica is closely coupled to the carbon cycle via diatoms, which are responsible for up to 75 % of the primary production in coastal zones (Nelson et al., 1995). The fixation of CO_2 and subsequent export of POC to deeper layers of the ocean is regarded as the biological carbon pump (Broecker and Peng, 1982; Volk and Hoffert, 1985), which regulates the long term atmospheric pCO_2. Furthermore, diatoms are an important part in the marine food web, leading to a transfer of carbon from lower to higher trophic levels (Cushing, 1989).

These interconnections show that the coastal ecosystem functioning strongly depends on Si supply from rivers. They deliver about 62 % of the global ocean Si input (Tréguer and De La Rocha, 2013), which underlines the relevance of this source. Due to the strong eutrophication of many coastal ecosystems, it is of key importance to evaluate the fluxes of DSi and BSi to the coastal zone in order to identify a threatening shift towards Si limitation, which could lead to the formation of harmful algal blooms (Smayda, 1990). As estuaries are filters for carbon, they are also able to retain silica. Globally, about $6.2 \pm 1.8 \times 10^{12}$ mol are delivered as DSi from rivers, and $1.1 \pm 0.2 \times 10^{12}$ mol are in the form of BSi (Tréguer and De La Rocha, 2013). It is estimated, that 21 % of the total Si river input are retained in estuaries, which is important considering that river input is by far the largest source of Si to the ocean (Tréguer and De La Rocha, 2013).

The manifold sources and sinks of the different forms of Si are contradicted by the scarcity of data from estuaries, and result in uncertainties of flux calculations (Conley, 1997; Chou and Wollast, 2006; Ragueneau et al., 2006; Tréguer and De La Rocha, 2013).

Biological DSi transformation to BSi is majorly influencing the form, in which Si is delivered to the ocean (Conley, 1997). As particulate material, BSi settles, but it can be recycled by benthic processes and resupply the water column by benthic-pelagic coupling (D'Elia et al., 1983). Marshes are known to be another major source of both BSi and DSi (Struyf et al., 2005; Struyf et al., 2006). As a further resupply process, BSi dissolves in the water column more readily than silicate minerals, a process, which is enhanced by the presence of seawater ions (Barker et al., 1994; Loucaides et al., 2008) and bacteria (Roubeix et al., 2008). Subsurface groundwater discharge can be a direct source of DSi, since it was estimated that up to 10 % of the global runoff are discharged below the surface (Taniguchi et al., 2002). Furthermore, estuaries can receive Si from coastal upwelling and atmospheric input (Bianchi, 2007 and references therein).

Anthropogenic effects on estuaries

Anthropogenic activities have shaped the form of estuaries especially in the last century, marked by intense industrialisation. The increasing nutrient input to rivers stimulated primary production in estuaries and coastal zones (Kempe, 1988). Furthermore, the input of organic matter from industry, agriculture, and municipal waste induced an increased biological and chemical oxygen demand (Kempe, 1988). This led to hypoxia in the estuarine waters, a phenomenon that occurs naturally in deep basins, upwelling areas, and fjords (Helly and Levin, 2004), but was observed to form in shallow coastal areas as well, during the last 50 years of intensified anthropogenic perturbation (Rabalais et al., 2010). Hypoxia is considered to be a major threat to aquatic organisms (Vaquer-Sunyer and Duarte, 2008). While processes leading to hypoxia are well understood (Conley et al., 2009), the recovery effects towards a less polluted system are insufficiently described (Steckbauer et al., 2011).

On a more physical perspective, estuaries are often important waterways, connecting inland and ocean, that need to be managed by dredging because of tidal pumping of sediment from the sea in upstream direction (Perillo, 1995). The removal of sediment most likely disturbs benthic exchange processes, but the impact is insufficiently investigated. It was hypothesised that dredging of Elbe waterways led to a decline of sedimentary denitrification processes, diminishing the valuable ecosystem service of removing a surplus of nitrogen on the way to the coastal zone (Dähnke et al., 2008). A similar effect can be expected for the benthic supply of carbon or silica.

1.1 Research gaps

DIC fluxes through estuaries to the coastal zone are poorly constrained (Hossler and Bauer, 2013). As rivers are an important source of DIC to the coastal ocean, it is essential to identify key areas and processes that act on DIC fluxes in estuaries, which lead to subsequent alteration of carbon fluxes towards the sea. Estimates on DIC supply from the Elbe to the North Sea are, until now, based on singular measurements in the freshwater part of the estuary and had to be considered as unchanged through the estuary due to scarcity of data from the inner estuary (Pätsch and Lenhart, 2011).

While the various assessments of estuarine CO_2 fluxes seem to deliver similar values lately, in part due to the same data base, their calculations are still subject to large uncertainties. These range from large scale geographical classification issues (Laruelle et al., 2010), over local scale surface area calculation (Borges et al., 2005), to process based variability like the determination of gas exchange across the air-water boundary (Raymond and Cole, 2001) and the derivation of partial pressures of CO_2 (pCO_2) from measured quantities like pH and DIC (Millero, 2010). In addition, daily, seasonal, and tidal variability of pCO_2 are not sufficiently represented in upscaling of fluxes (Cai, 2011; Chen et al., 2012)

The question of the impact scale of anthropogenic interferences on estuaries was tackled early (Kempe, 1988), and is still subject to discussion (Canuel et al., 2012). Systems located in the mid-latitudes in the northern hemisphere suffered from the worst water pollution in the 1970s and 1980s and are now subject to restoration efforts (Elliott et al., 2007; Borja et al., 2010), while large estuarine systems in Asia are still afflicted with increasing pollution (e.g. Li and Daler, 2004). The impact of globalisation on coastal zones in general remains to be discussed, with estuaries having a special place as agents between coastal and watershed management (Swaney et al., 2012). The impact of water quality restoration on the carbon cycle is not adequately studied.

The global riverine delivery of Si to the coastal ocean is of key importance for the marine Si cycle. Therefore, it is relevant to evaluate a potential retention of Si estuaries. So far, studies have focussed on DSi cycling in estuaries, mostly omitting the second quantity, BSi, in their estimates (Chou and Wollast, 2006). This leads to rather high uncertainties in global upscaling of Si fluxes through estuaries (Tréguer and De La Rocha, 2013). As BSi is fairly soluble in estuarine conditions, it is a potential source for DSi, that needs to be discussed.

This was first addressed by Conley (1997), but since then, the only extensive estuarine study was conducted in the Scheldt (Carbonnel et al., 2009; Carbonnel et al., 2012). Because this system is highly eutrophic and residence times are prolonged (Soetaert et al., 2006), a general global applicability of findings from the Scheldt seems questionable. More data on BSi transformation in estuaries are required to constrain fluxes to the ocean globally.

1.2 Contributions of this thesis

This thesis examines the carbon and silica cycling in the inner Elbe estuary. It is an estuary of particular interest, because it is situated in a densely populated area, struggling with conflicting interests of stakeholders, who value economic, environmental, or recreational advantages. Furthermore, the Elbe is one of the largest rivers of Europe and a major pathway for nutrients and carbon towards the German Bight, North Sea.

1. The first aim of this thesis is to answer the question how the carbon cycle in the Elbe estuarine system has changed during the last three decades, on its path from a highly polluted to a partly restored system. This study is focussing on the tidal freshwater part, which was omitted in previous studies and is hypothesised to contribute above average to POC consumption and concomitant CO_2 fluxes. Historical monitoring data are used to analyse the effect of water quality changes during summer season.

2. The second part of the thesis analyses the modern day inorganic carbon system in the inner Elbe estuary. The results of 18 transects between Geesthacht and Cuxhaven reveal the hypothesised hotspot for CO_2 fluxes in the freshwater part of the estuary. Sinks and sources of DIC and TA are discussed. In addition, geographic information system (GIS) software is used, in conjunction with bathymetric data, to determine the permanently flooded areas in order to derive a more precise surface area, which is further used to calculate CO_2 fluxes.
Due to technical constraints, the CO_2 transfer between water and air could not be determined directly, so this study has to rely on published methods to calculate fluxes. To bracket the estimates, two different approaches were chosen. However, the author of this thesis was able to significantly refine the calculation of $p\mathrm{CO}_2$ from DIC and pH by factoring in the individual ionic strength of riverine waters, which was never done before.
Four transects provided data on $\delta^{13}C_{DIC}$ isotopic data, which were included in the discussion, to further differentiate processes.

3. The close coupling of Si and C cycle was found in the data gained during recent cruises. Observations revealed a dependency between BSi and POC data. This relationship is used to reconstruct BSi concentrations from POC monitoring data. Since long-term BSi data are scarce, this is an opportunity to study seasonal fluxes of this species in conjunction with DSi, to answer how much and in which form Si is delivered from the river to the inner estuary, and from inner part towards the North Sea.

2 The study site

The Elbe estuary has been studied and monitored since more than 60 years. Some of the earliest reliable water chemistry data date back to the 1950s (Kempe, 1982a). These early-collected data already showed the very large anthropogenic impact on the system (Kempe, 1988). Within the SCOPE/UNEP project “Transport of carbon and minerals in major world rivers”, efforts have been taken to examine a comprehensive set of rivers and estuaries (Degens, 1982b). For the Elbe estuary, a survey with R/V Valdivia was conducted in October 1981, undertaking the first study of carbonate equilibria and mixing processes (Kempe, 1982b). An additional study by Brasse et al. (2002) investigated the $p\mathrm{CO}_2$ in the water column of the Elbe estuary during a cruise in 1997.

The river Elbe forms - with a length of 1,094 km and a catchment area of 148,268 km^2 - the fourth largest river basin in central Europe. The catchment area is inhabited by more than 24.5 million people (as of the year 2003) with densities varying from 40 to more than 3,000 inhabitants per km^2 (IKSE, 2005). No major changes in population density occurred in the Elbe catchment during the study period (MPIDIR, 2012).

The Elbe can be divided into the non-tidal middle and upper Elbe and the tidal stretch (the latter one is 142 km in length), which is located in Northern Germany and feeds into the German Bight, North Sea (Fig. 2.1). Any given Elbe-km count in this study refers to the distance from the point where the Elbe passes the border from the Czech Republic to Germany.

The Elbe runoff features high discharges in winter and spring with a long-term maximum occurring in April (Kempe, 1992). The mean annual long-term discharge of the Elbe river at the last non-tidal gauge of Neu Darchau (Elbe-km 536) is 704 m^3 s^{-1} (standard deviation: 442 m^3 s^{-1}; years 1900-2011). This gauge has a catchment area of 131,950 km^2 which represents 89 % of the total catchment (IKSE, 2005). Data for the summer mean discharge are shown in Fig. 3.7A.

The study area comprises the entire tidal part of the Elbe, which is separated from the non-tidal part by a weir at Elbe-km 585.5 (Geesthacht, Fig. 2.1C). The tidal Elbe is a turbid, well-mixed, macrotidal estuary (Middelburg and Herman, 2007) with a pronounced maximum turbidity zone (MTZ), on average located around Elbe-km 695 (Brunsbüttel). The range of the semi diurnal tide at the Hamburg harbour is 3.6 m. High tidal current velocities (up to 1.8 m s^{-1}) (Bergemann and Gaumert, 2010) cause a steep horizontal salinity gradient. The freshwater section reaches from the weir downstream to about Elbe-km 670 (Glückstadt). The water residence time in the tidal stretch ranges from 2 to 12 weeks depending on discharge (Tab. 2.1).

For a better characterisation and differentiation, we divided the Elbe estuary into four distinct zones (Fig. 2.1; Tab. 2.1) with different dominating biogeochemical processes:

I. The pre-oxygen minimum zone (**pre-OMZ**), zone characterised by high values of dissolved oxygen (DO) due to upstream primary production (salinity <1);
II. The oxygen minimum zone (**OMZ**), including the harbour of the city of Hamburg, shows the abrupt decrease of oxygen. Its formation occurs mainly during the summer months (salinity <1);
III. The maximum turbidity zone (**MTZ**) with high concentrations of suspended matter (SPM) due to a long residence time (salinity range between <1 and 5);
IV. The transition to the full marine system (**post-MTZ**) of the German Bight shows increasing salinity and stabilised DO and SPM values (salinity range between 1 and 20).

Tab. 2.1 shows the surface area distribution of the identified zones. The area was determined by intersecting of bathymetric data with mean low tide gauge data from authorities (both: Waterways and Shipping Administration of the Federal Government, WSV) to derive the area of permanently flooded regions. This was done with the software program ArcMap 10 (ESRI). Because of the funnel shape of the estuary, the innermost pre-OMZ is the smallest zone, while the seaward post-MTZ features the largest area. The residence time given in Tab. 2.1 is strongly dependant on the discharge and lies on average at around one month for the full inner estuary.

Between 2009 and 2011, 18 cruises were carried out within project ESTUCARB with the aim of best possible spatial and seasonal data coverage. Most of the cruises cover transects from km 609 in the pre-OMZ to the estuarine mouth, km 724 in the post-MTZ (Tab. 2.2). The majority of surveys were conducted on the research vessel Prandtl, operated by the Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, but also with a sailboat and working boats from local authorities, when the Prandtl was not available. Dates and station count of the cruises are listed in Tab. 2.2.

On station, surface water samples (~0.5 m depth) were taken with a NISKIN type vertical water sampler. Subsamples for the different measured parameters were drawn in order of their sensitivity to gas exchange with the atmosphere. A detailed description is given in the method sections of the individual chapters. A comprehensive table with the analysis results of all samples including derivative calculations is given in Appendix B.

Tab. 2.1: Length, area, and typical residence time in the four zones of the Elbe estuary as a function of low, mean and high discharge (Q) (Bergemann et al., 1996). Typical summer discharge ranges between 300 and 550 m^3 s^{-1}. Areas are derived by GIS software and take only permanently flooded areas into account.

zone	river-km	length [km]	area [km^2]	relative part [%]	residence time [days]		
					Q=250 m^3 s^{-1}	Q=700 m^3 s^{-1}	Q=1200 m^3 s^{-1}
pre-OMZ	585-620	35	11.8	4.3	3	1	<1
OMZ	620-650	30	27.5	9.9	11	4	2
MTZ	650-705	55	113.0	40.9	35	14	10
post-MTZ	705-730	25	124.3	45.0	30	11	6
total	585-730	145	276.6	100.0	79	30	<19

Tab. 2.2: List of conducted surveys within project ESTUCARB. Mean discharge of the respective day and month were added to allow analysis of the representative state of taken samples. (WSA= water and shipping authority Hamburg).

cruise	month	year	# of stations	covered river-km	daily mean discharge [m^{3}s^{-1}]	monthly mean discharge [m^{3}s^{-1}]	ship
EC-01	7	2009	12	589-644	609.0	749.7	WSA vessel
EC-02	8	2009	7	619-644	344.0	391.7	WSA vessel
EC-03	9	2009	16	609-729	274.9	258.3	R/V Prandtl
EC-04	10	2009	16	609-724	335.0	360.4	R/V Prandtl
EC-05	3	2010	18	570-724	1134.3	1382.5	R/V Prandtl
EC-06	4	2010	14	609-729	1669.0	1189.3	R/V Prandtl
EC-07	5	2010	19	570-724	606.2	750.6	R/V Prandtl
EC-08	7	2010	9	644-719	339.0	393.5	private sailing boat
EC-09	8	2010	16	609-724	562.0	1032.2	R/V Prandtl
EC-10	9	2010	16	609-724	864.0	922.1	R/V Prandtl
EC-11	10	2010	14	609-724	1881.0	1306.4	R/V Prandtl
EC-12	11	2010	14	609-724	1491.0	1025.9	R/V Prandtl
EC-13	2	2011	14	609-724	1592.6	1441.6	R/V Prandtl
EC-14	4	2011	16	609-724	665.0	776.6	R/V Prandtl
EC-15	7	2011	14	609-709	495.0	515.9	R/V Prandtl
EC-16	9	2011	14	609-724	592.0	617.7	R/V Prandtl
EC-17	10	2011	14	609-724	606.0	543.1	R/V Prandtl
EC-18	12	2011	14	609-724	640.0	573.0	R/V Prandtl

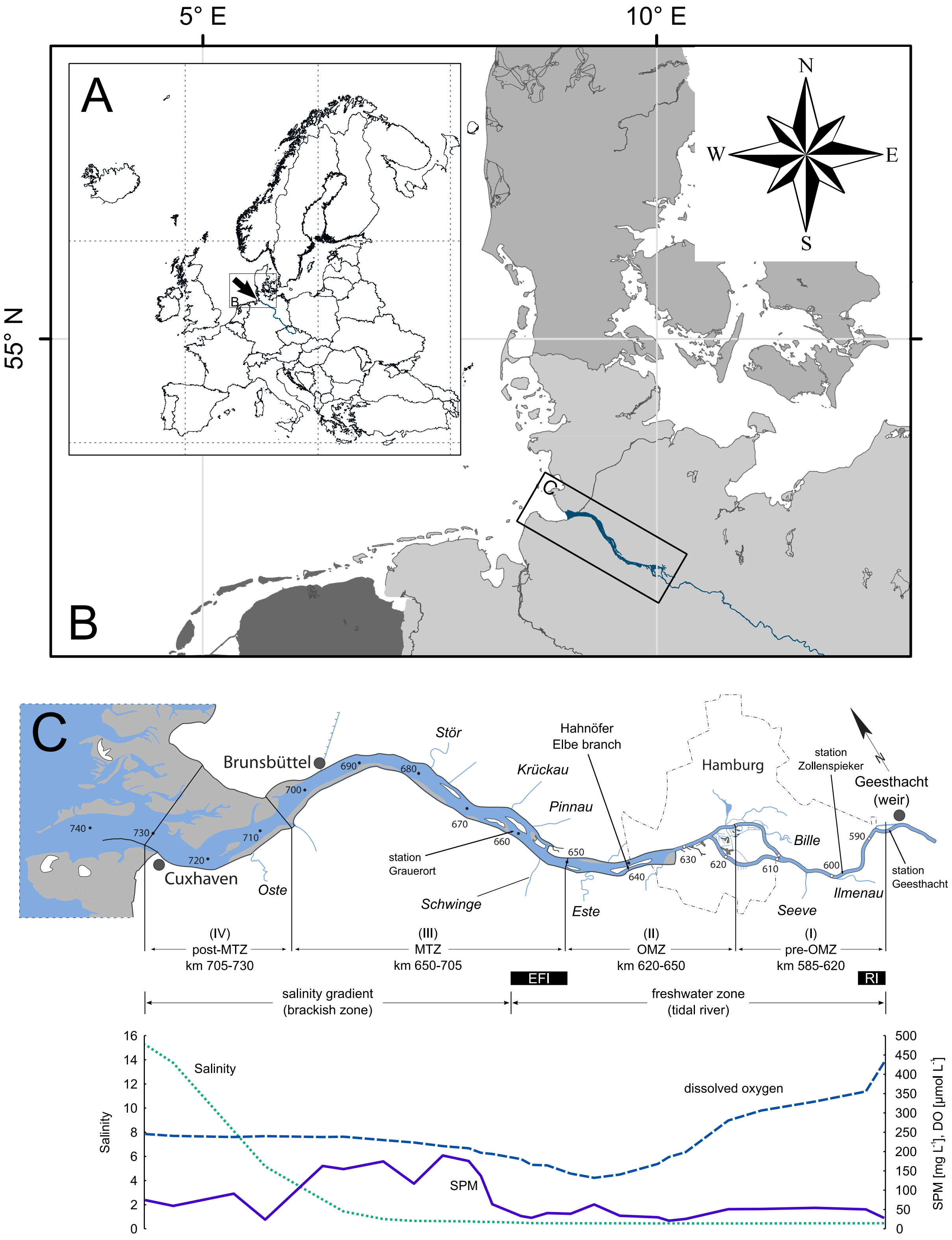

Fig. 2.1: (A) Overview of Europe, (B) Elbe estuary (marked with rectangle) located in Northern Germany, (C) detailed view on the estuary, numbers are river kilometers (count starts at the border Germany-Czech Republic), depicted zonation refers to the list given in Tab. 2.1. Bottom graph shows an exemplary distribution (2007 summer means) of the zone characteristic parameters suspended matter (SPM), dissolved oxygen (DO) and salinity. The marked salinity gradient delimits the studied zone but extends further towards the German Bight, North Sea. The black bars mark the area that was used to integrate Si concentration data for fluxes from the river (RI) and from the estuarine freshwater part (EFI). Graphic: courtesy of ARGE Elbe, modified.

3 Carbon dynamics in the freshwater part of the Elbe estuary: Implications of improving water quality

3.1 Introduction

Estuaries are major pathways for the transport of nutrients and organic matter towards the coastal zone. Considering particulate organic carbon (POC), large amounts are received by inner estuaries from the adjacent rivers. A comprehensive compilation of data, emphasising the importance of carbon cycling on the way to the coastal zone was published by Degens et al. (1991).

During transit through the estuary, riverine POC is mineralised (e.g. Cadée and Laane, 1983; Eisma et al., 1985; Abril et al., 2002; Middelburg and Herman, 2007). Globally 0.17 (Ludwig et al., 1996) - 0.50 Pg (1 Pg = 10^{15} g) (Richey, 2004) POC is transported to coastal zones per year of which 40 % (Abril et al., 2002) - 70 % (Keil et al., 1997) is transformed into CO_2 (Frankignoulle et al., 1998; Borges, 2005; Chen and Borges, 2009). It is estimated that inner estuaries release 0.27±0.23 Pg C a^{-1} to the atmosphere, which is close to the amount that is absorbed on the continental shelf (Laruelle et al., 2010), emphasising the relevance of estuaries for the carbon cycle in the land-ocean transition zone.

In the inner parts of estuaries, POC remineralisation seems to be spatially confined to two different zones. The maximum turbidity zone (MTZ), where particle concentrations are high and long residence times promote remineralisation (e.g. Morris and Bale, 1982; Herman and Heip, 1999), and an oxygen minimum zone (OMZ) in the tidal freshwater part, where the residence time is shorter but high rates of aerobic respiration can be observed (e.g. Kerner, 2000; Vanderborght et al., 2007).

As Abril et al. (2002) showed for several European estuaries, two major factors control the POC remineralisation in the MTZ: the compositional character of POC and the residence time of particles. In estuaries with low residence times such as the delta-type Rhine estuary, POC is flushed out to the coastal zone before it can be modified microbially and, thus, virtually no POC is lost during the estuarine transit (Abril et al., 2002). In estuaries with longer residence times and a comparable water quality, such as the Elbe estuary (a drowned river valley), the slower transition of POC through the system allows for an enhanced remineralisation. The compositional character of POC determines the remineralisation efficiency because the input of sewage and/or autochthonous algal production in eutrophic catchments increases the percentage of labile POC (Etcheber et al., 2007). However, in pristine systems POC consists mostly of refractory terrestrial material (Abril et al., 2002; Etcheber et al., 2007). This leads to differences in the POC loss rates in eutrophic versus pristine systems. While in highly polluted systems such as the Scheldt estuary, 82 % of the POC is lost, less than 10 % is lost in pristine systems or in systems with short residence times (Abril et al., 2002).

While the MTZ has received some scientific attention, less is known about the role of the OMZ in the removal of POC and its behaviour considering changing river water quality. In the Elbe estuary, a well-mixed macro-tidal estuary located in northern Germany, the processes responsible for the formation of the OMZ are well known. The city of Hamburg, situated in the tidal freshwater part, features the second largest harbour in Europe. Due to this, river-borne phytoplankton entering the estuary dies while passing the harbour area, because of deeper and more turbid waters (Wolfstein and Kies, 1995). This labile POC is then readily remineralised by heterotrophic bacteria (Klages, 1995; Kerner, 1997, 2000), which leads to an oxygen minimum. This knowledge enables us to analyse the influence of water quality on the removal of POC, i.e. the POC filtering capacity of the OMZ.

Despite intensive process-based studies in this important biogeochemical zone, it has not been analysed in relation to its POC filtering capacity. The Elbe estuary is a suitable model system for this study because the Elbe river system underwent a high pollution period until the late 1980s, showing a recovery from high nutrient loads since the 1990s due to enhanced waste water treatment and decline in industrial organic pollutant and heavy metal inputs since the reunification of Germany in 1990 (Adams et al., 1996). It shows an exemplary change from a highly polluted to a partly restored system. During this change, a consistent monitoring program by the “Arbeitsgemeinschaft zur Reinhaltung der Elbe” (Working group for pollution control of the Elbe, ARGE Elbe, now: Flussgebietsgemeinschaft Elbe, FGG) provides 23 years of hydrochemical data. This makes it possible to track changes in the carbon dynamics. We analysed the temporal development of carbon concentrations in the tidal freshwater part of the Elbe estuary and hypothesise that changes in water quality affect the filtering capacity of organic carbon in the OMZ of the Elbe estuary. Findings show that POC mineralisation rates in summer increased with the recovery of the river water quality after a period of high pollution, indicating that processing rates of POC are closely connected to changes in the upper catchment area. This enhanced mineralisation led in turn to increased partial pressures of CO_2 (pCO_2) in the OMZ compared to the upstream pre-OMZ.

3.2 Methods

Since the 1950s, the Elbe river and estuary have been subject to intense monitoring programmes by the local authorities (Kempe, 1982a). In this study, we used a water chemistry dataset obtained by the ARGE Elbe, covering almost monthly transects from 1985 to 1993. From 1994 to 2007 data were acquired in February, May-August and November. Samples in the estuary were gained every 5-10 km by helicopter. The survey started at the most downstream location at full ebb stream and was carried onward in upstream direction, ensuring that the measurements represent approximately the mean concentrations of both tidal phases (ARGE Elbe, 2000). The advantage in authority-based regular data collection lies in good comparability of the data over the years. In addition, for Chlorophyll-a (Chl-a) data, a database from the fixed monitoring station “Zollenspieker” (Elbe-km 598.7, Fig. 2.1C) was used. These data were acquired on average once a month from 1993 to 2008. Data are provided in Appendix C-3.

In general, samples were analysed in accordance with standard methods of the German Institute for Standardisation (detailed listings can be found at the reports website of the International Commission for the Protection of the Elbe River (IKSE, 2011). For filtered samples, 0.45 µm cellulose nitrate filters were used if not stated otherwise. Values for dissolved inorganic carbon (DIC) were derived during analysis of dissolved organic carbon (DOC) and values unfortunately seem imprecise as they are given in mg L^{-1} and rounded to whole numbers (Bergemann, pers. comm.). Nevertheless, we included these data to assess trends in DIC concentrations, which are still visible in the data despite its uncertainty. A list of the conducted analysis is provided in Tab. 3.1. Note that detailed reports on methods are only available for the years 1997-2007. There is no official documentation available for the time before, but we assume that significant changes have not been made. Regarding the pH measurements, official specifications do not state the pH scale which was used. Since the NBS scale is the most commonly used scale in freshwater analyses, we can only assume that it was used here as well. DIC, nutrients, pH and salinity data were used to calculate $p\mathrm{CO_2}$ with the program *CO2SYS* (Lewis and Wallace, 1998) using the constants of Millero et al. (2006). For the description of water quality development with time, annual means were calculated for the pre-OMZ, which is considered as the input zone of the estuary. The total number of measurements per year ranged between 24 and 96.

Tab. 3.1: Overview of the methods and their respective significance and indication of results. Analyses were conducted according to German industry standards (DIN). Specifications are trusted for the years 1997-2007. For the time before, we expect, that analysis did not differ, but there is no official documentation available. Reports (from 2004 onwards) in German and Czech are available on the website of the International Commission for the Protection of the Elbe River (IKSE, www.ikse-mkol.org).

parameter	description	unit	DIN #	significant digits / indication of results
pH	potentiometrically with glass electrode	-	DIN 38404-C5	2 / 0.1
temperature	electrometrically with resistance thermometer	°C	DIN 38404-C4-2	2 / 0.1
conductivity	electrometrically with platinum probe	mS m^{-1}	DIN EN 27888-C8	3 / 0.1
SPM	vacuumfiltration on GF/C glassfibre filter (Whatman)	mg L^{-1}	DIN 38409-H2-3	2 / 1
DO	electrometrically with membrane oxygen probe	mg L^{-1}	DIN EN 25814-G22	2 / 0.1
TOC, DOC, (DIC)	catalytic high-temperature oxidation, CO_2 detection via IR detector	mg L^{-1}	DIN 38409-H3-1/ DIN EN 1484-H3	2 / 0.1 (1 / 1)
Chl-a	photometrically	µg L^{-1}	DIN 38 412-L16	2 / 1
NO_3	photometrically reduction to NO_2, azo dye	mg L^{-1}	DIN EN ISO 13395-D28	2 / 0.1
NO_2	photometrically, azo dye	mg L^{-1}	DIN EN ISO 13395-D28	2 / 0.001
NH_4	photometrically	mg L^{-1}	DIN EN ISO 11732-E23	2 / 0.01
PO_4	photometrically, ammonium molybdate	mg L^{-1}	DIN EN 1189-D11	2 / 0.01

To analyse changes in the pre-OMZ and the OMZ we analysed measurements from May to August. During these months, temperatures allow a high microbial activity, which can affect POC concentrations. April was omitted, as data for this month are only available from 1985 to 1993. Mean summer values were calculated by summing all measurements available between May and August in the respective zone and divided by the sum by the total number of measurements. The total number of the measurements in summer varied between 9 and 24 for the pre-OMZ and between 14 and 36 for the OMZ. Three years did not cover the full four summer month: 1989 and 1997 lack the August measurement, 1994 the June and July values. In 1991, no data are available for DOC/POC/DIC because of partial suspension of the monitoring programme. A detailed list of available data is provided in the electronic supplementary file. Atmospheric *p*CO_2 data used in Fig. 3.7B were derived from the GLOBALVIEW-CO_2 (2011) database, which provides modelled CO_2 concentrations for latitudinal bands. The band 52.17° was chosen as it represents the study area well. A comparison with actual data from the nearest monitoring station of the federal environmental agency (UBA) in Westerland, Northern Germany (data from 1972 to 2003) agree well.

3.3 Results and discussion

3.3.1 Temporal development of the water quality

Human impacts on rivers and estuaries and the effects of subsequent partial restoration have been generally described for river systems by Meybeck (2002). As the Elbe river basin is heavily influenced by anthropogenic activities (e.g. Kempe, 1988), water quality of the river and its estuary has changed strongly over the past from a highly polluted system to a regenerated system with improved water quality (e.g. Adams et al., 1996; Adams et al., 2001). The transition was reflected in decreasing phosphorous and nitrogen concentrations (Fig. 3.1) as well as in changes in the organic carbon (Fig. 3.2) and oxygen concentrations (Fig. 3.3). Comparison of pollutant loads from 1987 and 2007 also mirrored the improvement in water quality (Tab. 3.2).

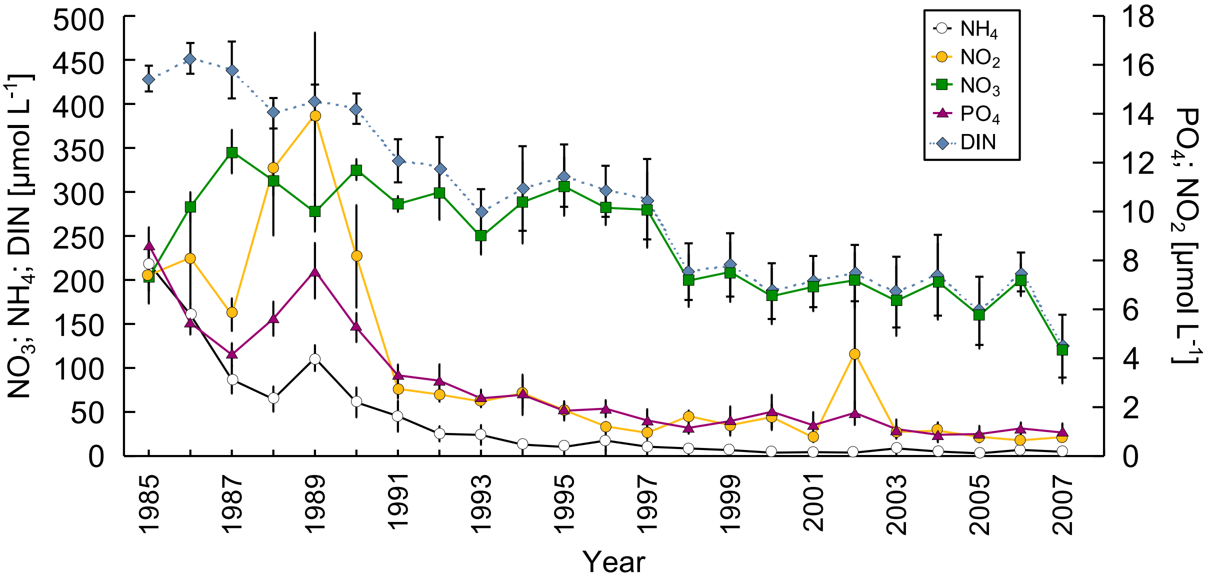

Fig. 3.1: Temporal development of mean annual nutrient concentrations in pre-OMZ (NO_3: green square; NO_2: yellow circle; NH_4: open circle; PO_4: lilac triangle; DIN: blue diamonds). The NO_2 peak in 2002 is due to an extremely strong flood event in August, which flooded sewage treatment plants along the river. Whiskers indicate 95 % confidence intervals of the mean.

The earliest available data for inorganic nutrients covered a period from 1958 to 1982 (Kempe, 1992) and even then shows very high concentrations of phosphorus (PO_4, around 5-15 µmol L^{-1}) and an increase of nitrate (NO_3) from about 160 to 400 µmol L^{-1} in the 1970s and 1980s. That confirms that the earliest data used in this study still represents the high pollution situation.

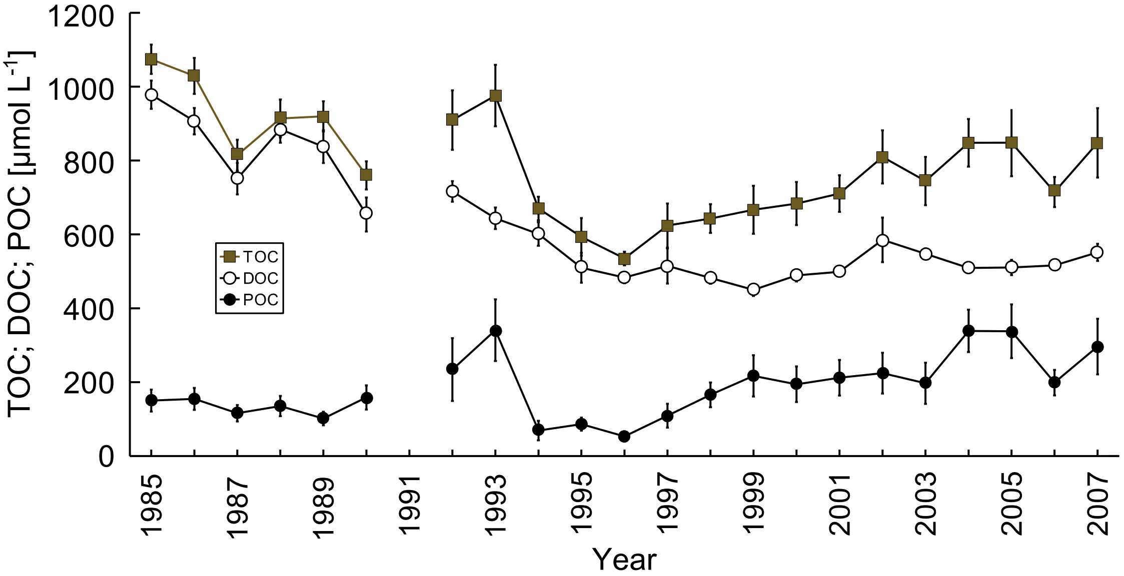

Fig. 3.2: Time series of mean annual organic carbon concentrations in pre-OMZ (DOC: open circles; POC: filled circles; TOC: brown rectangles). Values of 1991 are missing because no sampling conducted in this year. Whiskers indicate 95 % confidence intervals of the mean.

The largest concentration changes towards lower concentrations were observed in the 1980s and 1990s with an overall decrease by approximately one order of magnitude. Between 2000 and 2007 the concentrations of ammonia (NH_4), nitrite (NO_2) and PO_4 decreased only slightly while NO_3 concentrations decreased by 66 % (Fig. 3.1). The reduction of nutrient concentration was accompanied by an increase of the dissolved oxygen (DO) concentration in the pre-OMZ (Fig. 3.3). The observation of nutrient reduction together with increasing oxygen concentrations is well documented in other estuarine systems that recovered from eutrophication such as the Scheldt (Soetaert et al., 2006; Cox et al., 2009), the Delaware (Sharp et al., 2009) and the Thames systems (Tinsley, 1998). The decrease of the nutrient concentration as well as the reduction of organic pollutant and metal loads in the estuary after 1989 can be attributed to structural changes in the industry, agriculture and the urban centres of Eastern Germany and the former Czechoslovakia that followed the fall of the Iron Curtain in 1989. Installation of sewage treatment plants, closure of chemical industries and the collapse of the former communist agricultural complexes are examples for structural changes which led to a reduced input of pollutants and nutrients in the Elbe estuary (Adams et al., 1996; Guhr et al., 1999; Adams et al., 2001). While changes in the form of dissolved inorganic nitrogen (DIN) occur, the sum of DIN components entering the estuary shows an overall decrease in the analysed period (Fig. 3.1).

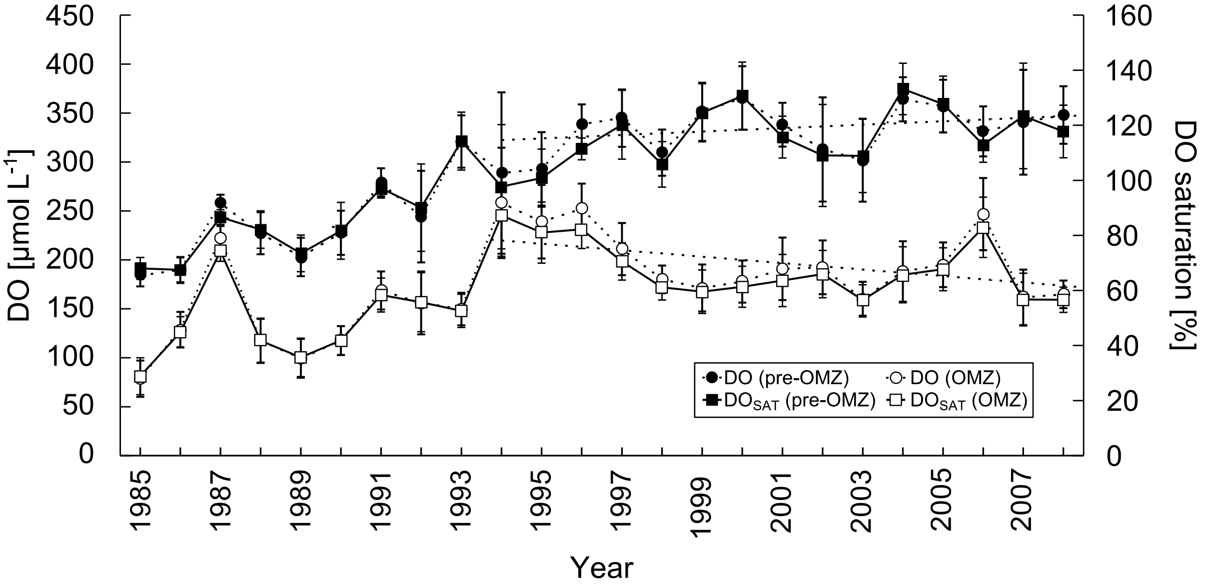

Fig. 3.3: Temporal development of dissolved oxygen (DO) summer mean concentrations (squares) and saturations (circles) in the pre-OMZ (filled symbols) and OMZ (open symbols). Trend lines incorporate data from 1994 onwards. Whiskers indicate 95 % confidence intervals of the mean.

Tab. 3.2: Extract of annual pollutant loads (in t a^{-1}) in the Elbe at station Schnackenburg (middle part of the Elbe river, km 474) (ARGE Elbe, 2007).

pollutant	1986	2007	change (%)
inorganic			
Mercury (Hg)	22	1.2	-95
Cadmium (Cd)	13	2.6	-80
Lead (Pb)	120	56	-53
Zinc (Zn)	2,400	790	-67
Copper (Cu)	370	100	-73
Chromium (Cr)	260	27	-90
Nickel (Ni)	270	64	-76
Iron (Fe)	30,000	9,300	-69
Arsenic (As)	110	65	-41
organic			
Trichlorobenzene	1.620	0.030	> -99
Trichloroethene	31	0.058	> -99
Tetrachloroethylene	22	0.120	> -99
Hexachlorocyclohexane	0.921	0.003	-96

3.3.2 Organic carbon

Concentrations of DOC and POC in river water entering the estuary were also affected by these structural changes. Between 1985 and 1996, DOC dominated the organic carbon fraction, on an average accounting for 86.9 % of the total organic carbon (TOC) concentration (Fig. 3.2). Absolute values of 800-1000 mmol L^{-1} are within the range of the German estuaries Ems and Weser (Ittekot et al., 1982) and other estuaries investigated in (Degens, 1982a). POC only contributed 16.9 % to the organic carbon pool as an input to the Elbe estuary. In the early years of the study, the absolute TOC values compare to data published by Kempe (1982a) for the years 1975-77, which reflects a long history of elevated organic loads. However, in the late 1980s, while there was little change in the relative amount of DOC, the absolute concentrations decreased from around 1000 µmol L^{-1} to around 500 µmol L^{-1}. After 1996, a shift in the relative contributions of POC and DOC to the total organic carbon pool occurred. DOC concentrations remained at a constant level while POC concentrations started to increase. After the year 2000, the TOC pool was comprised of ca. 30 % POC and 70 % DOC. This ratio lies in the same range as in other estuaries in Europe (Abril et al., 2002).

The fluctuating values and the change in the partitioning of the organic carbon species in the 1990s resemble similarly variable patterns observed in the Scheldt, Belgium. These are explained by Cox et al. (2009) by the concept of a heavily eutrophic estuary moving from hypereutrophication to classical eutrophication via a transitional phase characterised by two co-existing steady states with large swings in values of hydrochemical parameters. The authors argued that high ammonia concentrations, persistent hypoxia and the production of harmful substances such as hydrogen sulphide inhibited algal growth and photosynthesis during hypereutrophication. For the Elbe estuary, a similar scenario could be assumed, but with different factors limiting phytoplankton growth in the Elbe river and estuary. Inputs of industrial pollutants such as heavy metals and halogenated organic compounds are known for their toxic effect on aquatic biota including phytoplankton (Crompton, 2007). A comparison of datasets from 1986 and 2007 at the monitoring station Schnackenburg (ARGE Elbe, 2007) located in the middle Elbe showed a significant reduction of the pollutant loads in this time period (Tab. 3.2). All measured heavy metal and organic pollutant loads decreased more than 40 % and over more than 95 %, respectively. Furthermore, phytoplankton growth could be reduced due to CDOM (coloured dissolved organic matter) induced light limitation. CDOM absorbs photosynthetically active radiation, reducing its penetration into the water column with negative effects on phytoplankton growth (Ferrari et al., 1996; Kostoglidis et al., 2005). CDOM does not only originate from natural sources but is also found in sewage effluents

(Hudson et al., 2007; Guo et al., 2010). The existence of CDOM in the Elbe is reported e.g. in Lübben et al. (2009). Gienapp (1982) investigated CDOM as "Gelbstoff" and found concentrations of 0.5-6 mg L^{-1} in the outer estuary during a cruise in August of 1978. Decreasing DOC concentrations and the construction of sewage treatment plants after the fall of the Iron Curtain suggest that the concentrations of CDOM were also reduced leading to an improved light climate for phytoplankton growth.

For the inner estuary of the Elbe, POC concentrations are considered a proxy for phytoplankton biomass as δ^{13}C-POC values of -28‰ (Kerner and Krogmann, 1994) indicate abundance of freshwater phytoplankton (Fry and Sherr, 1984). Furthermore, Brockmann (1994) showed that 20 % of the particulate fraction of organic carbon in the freshwater area was made up by phytoplankton biomass, supporting the hypothesis that the POC increase is partly due to increased phytoplankton growth. The analysis of annual mean summer Chl-a concentrations (Fig. 3.4) from the weekly sampling station Zollenspieker (Elbe-km 598.7) in the pre-OMZ confirmed the pattern visible in the POC concentrations. Between 1993-1998 and 2005-2008, mean Chl-a concentration increased from 91±51 µg L^{-1} to 141±44 µg L^{-1}. The mean POC:Chl-a ratio of the Elbe estuary of the latter time period was 25.4. Converting the Chl-a increase of 50 µg L^{-1} into POC concentrations using this ratio results in a mean POC increase of 107 µmol L^{-1}. This is well within the range of the observed mean POC increase (~144 µmol L^{-1} difference between the mentioned time intervals). During the years 1999-2004 very large fluctuations of Chl-a concentrations with a maximum of 190 µg L^{-1} occurred. The fluctuations of POC and Chl-a concentrations support the idea that the Elbe estuary was in transition from its heavily polluted state to a cleaner state.

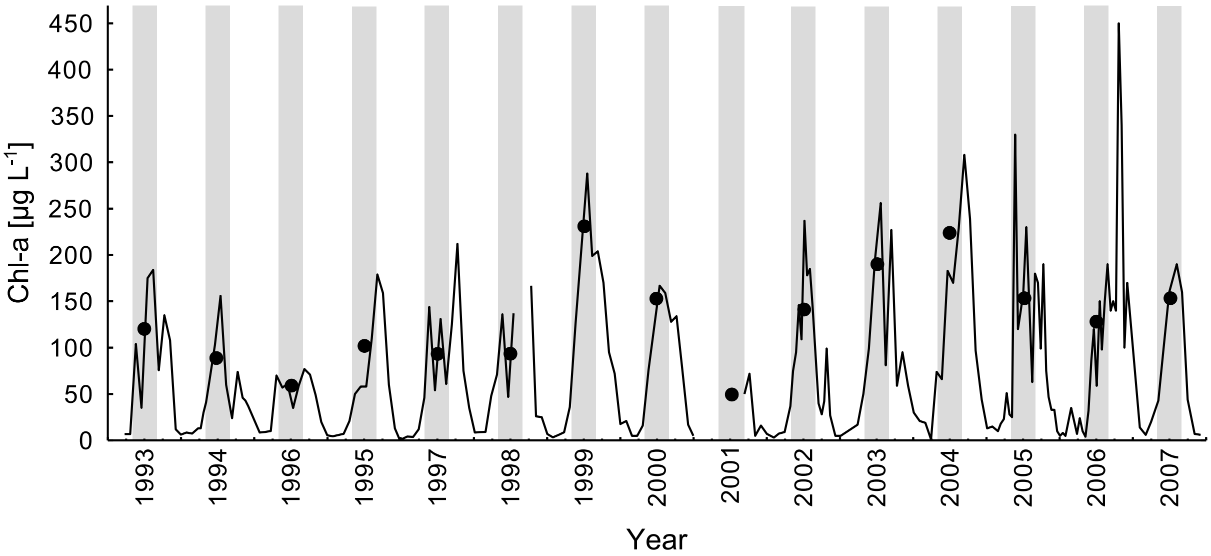

Fig. 3.4: Temporal development of Chl-a concentrations at monitoring station "Zollenspieker" (in the pre-OMZ, see Fig. 2.1). Circles indicate the summer mean values for each year; the summer season is indicated by the shaded areas.

3.3.3 Changes of summer POC dynamics in the OMZ with improving water quality

The comparison of POC concentrations in the pre-OMZ and the OMZ (Fig. 3.5A) revealed a change in the OMZ filtering capacity for POC with time. We define the term “filtering capacity” as the magnitude of POC removal in the OMZ given by the difference between the POC concentrations in the pre-OMZ and the OMZ. Quantifying the filtering capacity of carbon in the OMZ is important for the understanding of the organic carbon dynamics in the estuarine system. The earlier study of Abril et al. (2002) calculated for the Elbe estuary in 1997 a mineralisation efficiency of 38 %, meaning more than one third of the POC is removed from the system on its way to the coastal zone. The authors followed the definition of “estuary” by Pritchard (1967), not taking the freshwater part of the system into consideration. We analysed the POC filtering capacity in the two freshwater parts of the Elbe estuary, the pre-OMZ and the OMZ, to determine if the OMZ plays a significant role in POC filtering.

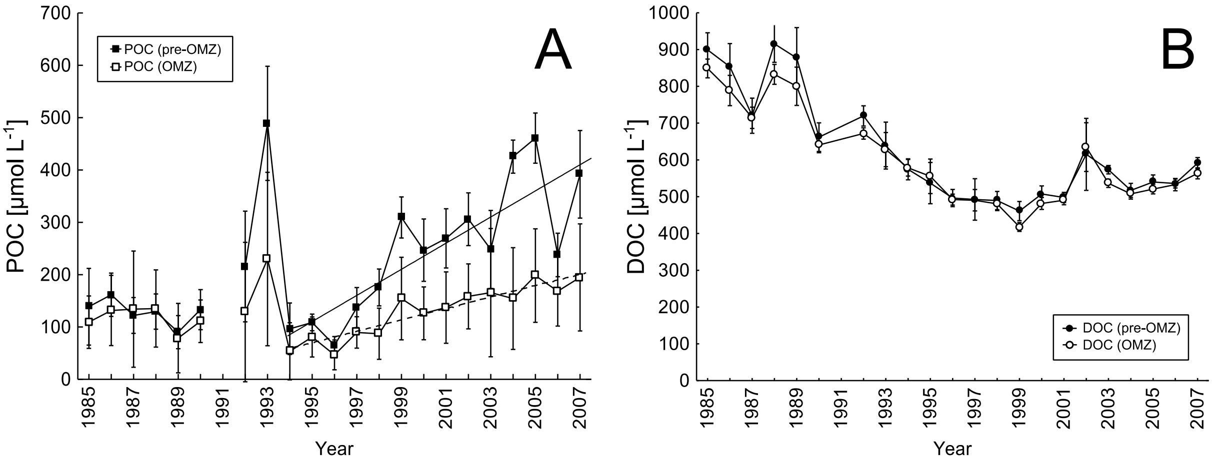

Fig. 3.5: (A) Temporal development of particulate organic carbon (POC) concentrations (summer means) in the pre-OMZ (filled squares) and OMZ (open squares). Whiskers indicate 95 % confidence intervals of the mean. Trend lines incorporate data from 1994 onwards (slope ± stdev pre-OMZ: 24.7 ± 4.7 µmol C L^{-1} a^{-1}, $r^2 = 0.70$; slope ± stdev OMZ: 11.5 ± 1.4 µmol C L^{-1} a^{-1}, $r^2 = 0.84$). (B) Temporal development of dissolved organic carbon (DOC) concentrations (summer means) in the pre-OMZ (filled circles) and OMZ (open circles). Whiskers indicate 95 % confidence intervals of the mean.

Between 1985 and 1990, average POC concentrations in both zones were nearly identical with 129 and 117 µmol L^{-1} in pre-OMZ and the OMZ, respectively (Fig. 3.5A). This indicates a transport of POC through these zones (see below). The following two years showed a sudden increase from 216 µmol L^{-1} in 1992 to 489 µmol L^{-1} in 1993. After the high fluctuation POC concentrations decreased to levels comparable to those between 1985 and 1990 (mean concentration 1994-1998: 102 µmol L^{-1}). This variable development could be attributed to the aforementioned ecosystem state of unstable equilibrium and on-going major changes in the upstream catchment in the aftermath of the reunification of Germany which are described in e.g. Guhr et al. (1999). From thereon concentrations in both zones increased steadily, but differentially. In pre-OMZ the mean annual increase from 1994 to 2007, indicated by the linear regression line, was 25.6±4.7 µmol L^{-1} a^{-1} and in the OMZ the increase averaged 11.5±1.4 µmol L^{-1} a^{-1} (Fig. 3.5A).

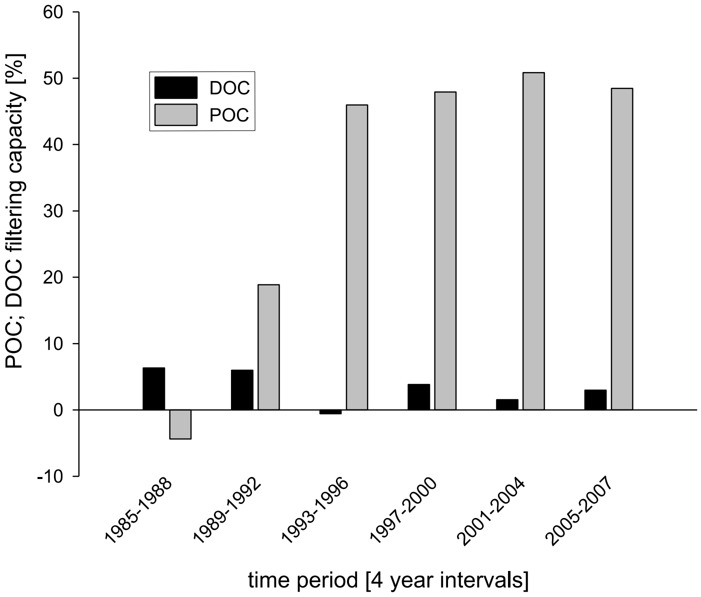

Fig. 3.6: Temporal development of the OMZ filtering capacity (organic carbon removal in the OMZ) for POC (grey bars) and DOC (black bars) plotted in 4-year means. Expressed in percent: $(C_{pre\text{-}OMZ} - C_{OMZ}) / C_{preOMZ} * 100$, where C is the POC or DOC concentration of the respective zone.

To assess the change of the DOC and POC filtering capacity we divided the study period into six four-year intervals. The first interval represents the high pollution period, the next two the transitional phase and the last three the periods of a recovered system. For each interval, the four-year mean of the filtering capacity was calculated. The results show that the POC filtering capacity of the OMZ increased from -4 % to +50 % in the most recent years while the DOC filtering capacity decreased from +6 % to +3 % (Fig. 3.6). The absolute DOC loss in the first two intervals is considerable (~50-60 µmol C L^{-1}, cf. Fig. 3.5B) if compared to the absolute POC loss (~0-20 µmol C L^{-1}, cf. Fig. 3.5A), but loses its significance when the system enters the recovered state. Considering the high DOC concentrations and the incomplete sewage treatment during the high pollution period it could be argued that heterotrophic respiration was mainly fuelled by labile DOC compounds and not by POC degradation. In the recovered system, clearly the POC loss dominates the total loss of organic carbon in the estuary (last two periods, Fig. 3.6). Approximately 160 and 175 µmol L^{-1} POC were lost in the OMZ, matching closely the above mentioned increase of phytoplankton biomass, supporting the finding of Wolfstein and Kies (1995) that consumption of fresh phytoplankton is most probably causing the OMZ in the Elbe estuary. This hypothesis was also supported by Kerner (2007), who suggested that the degradability of POC in the freshwater part, expressed as the biological oxygen demand in seven days (BOD_7), and POC concentrations were linearly correlated (Kerner, 2007; $r^2 = 0.81$; Fig. 4; p. 496). Further downstream, in the MTZ, the correlation disappeared, reflecting the loss of degradability during the transport through the freshwater part of the estuary. This observation has also been described for the river Rhine by Kempe (1982a), who showed a significant (>99.9 %)

positive correlation for BOD and TOC content at two stations (Lobith and Braubach, years 1963-1978).

Nitrification as a factor raising the BOD can be neglected in the recovered system, since concentrations of NH_4 entering in the Elbe estuary are sufficiently low not to dominate the oxygen consumption since the early 1990s (see Fig. 3.2 and Kerner et al., 1995). However, during times of high NH_4 concentrations up to 50 % of the DO was consumed by nitrification (Kerner et al., 1995).

If the above finding is put in context of the POC filtering capacity of 38 % as calculated by Abril et al. (2002), it is clear that during the summer months the freshwater part is as important for the POC removal as the MTZ. In the freshwater part 50 % of the POC which enters the estuary are already removed before it enters the MTZ. The OMZ filtering capacity has, despite shorter water residence times, the same magnitude as the filtering capacity of the commonly studied MTZ. This finding emphasises the potential importance of estuarine freshwater zones in the estuarine carbon cycle. The changes in the organic carbon filtering capacity due to changes in the water quality furthermore show that changes in water quality should be taken into account if data from recovering systems are applied in regional or global estimates for carbon processing in estuaries.

3.3.4 Oxygen dynamics during summer

Despite already declining NH_4 concentrations, the temporal development of annual mean summer DO concentrations and saturation values showed no clear increase in the pre-OMZ and in the OMZ between 1985 and 1989 (Fig. 3.3). The DO concentrations averaged over the five years were 212 $\mu mol\ O_2\ L^{-1}$ (76 % saturation) and 132 $\mu mol\ O_2\ L^{-1}$ (46 % saturation), respectively. Rising NO_3 concentrations together with declining NH_4 (Fig. 3.1) suggest that nitrification started to play a role in oxygen diminishing processes counterbalancing increasing DO values, potentially masking DO production by increased photoautotrophic activity.

From 1989 onwards, the absolute concentrations as well as the oxygen saturation started to increase in both zones (Fig. 3.3). The role of nitrification in DO drawdown became less important, accounting for maximally 15 % of the DO loss (Kerner et al., 1995; Kerner, 2000). In the pre-OMZ, atmospheric equilibrium is reached in 1993. After this year, the concentration increase slowed down and eventually levelled out, indicating that the system in the pre-OMZ has reached a temporary steady state with respect to DO concentrations. The development of oxygen levels is comparable to other estuarine systems with similar geographic and hydrodynamic settings. Increasing oxygen concentrations in the tidal freshwater part were also reported from estuaries which were subject to management efforts to improve the water quality. In the Delaware estuary minimum oxygen concentrations in the urban river section increased from <100 µmol L^{-1} in the 1960s to atmospheric equilibrium in 1990 (Sharp, 2010). Thereafter, the DO summer mean concentrations stayed constantly above the atmospheric equilibrium. The improvement of DO concentrations was attributed to the improvement of water quality due to upgrades of the large major sewage treatment plants in the greater Philadelphia area (Sharp, 2010). Nevertheless, the formation of an OMZ was still observed in June or late July when nitrification rates and respiration rates were potentially high (Sharp et al., 2009). For the Thames estuary, severe hypoxia or even anoxia was reported in the urban river section in the 1960s and 1970s which recovered in the 1980s also due to effective sewage management (Tinsley, 1998). In the former hypereutrophic Scheldt estuary (Cox et al., 2009) oxygen concentrations improved in the 1980s (Soetaert et al., 2006) but still remained at very low levels in the freshwater part during summer in 1993-1994 (Herman and Heip, 1999).

After 1996 there is a weak decreasing trend of oxygen concentrations in the Elbe-OMZ. The coupling of algal POC and oxygen demand in the Elbe estuary led to the phenomenon that despite better water quality, oxygen consumption increases in the OMZ due to increased algal growth upstream. Elevated POC concentrations in the pre-OMZ that mirror algal growth are described in section 3.3.2. Increased phytoplankton biomass due to improved water quality, thus could have a negative effect on the oxygen concentrations in the OMZ. Another factor that affected the DO concentrations in the OMZ was the deepening of the shipping channel in 1999. Kerner (2007) argued that decreased flow velocities in shallow branches of the estuary lowered the physical aeration capacity. In the “Hahnöfer Seitenelbe” branch (see map, Fig. 2.1C), DO concentrations were 2.3 mg L^{-1} (≙ 71.9 µmol L^{-1}) above the values in the main channel before this anthropogenic intervention. After the deepening, the difference decreased to 1.3 mg L^{-1} (≙ 40.6 µmol L^{-1}) (Kerner, 2007), which is equivalent to a loss of the aeration capacity of 76 %.

3.3.5 Impact on the inorganic carbon system during summer

The improvement of the water quality in the upper catchment area of the Elbe did not only affect the organic carbon processing in the estuary but also the inorganic carbon dynamics. DIC concentrations fluctuated over the whole study period (Fig. 3.7A) ranging between 1350 and 2150 µmol L^{-1}, with generally higher values during the early years of the dataset. Maximum concentrations were observed in 1989, 1998, 2002, and 2007 and minimum concentrations occurred in the years 1997, 2000, and 2005. These variations in general cannot be traced back to dilution effects due to variations in discharge (Fig. 3.7A). The correlation coefficient of a linear regression between discharge and DIC is 0.13 for the OMZ and 0.05 for the pre-OMZ (respective data can be found in the electronic supplement). In the first decade DIC concentrations in the pre-OMZ and the OMZ did not show strong differences. From 1995 onwards, summer DIC concentrations started to diverge slightly between the zones, with lower values in the pre-OMZ. Diverging development of DIC concentrations is most probably an effect of increasing autotrophic activity in the pre-OMZ in combination with enhanced remineralisation in the downstream areas (see section 3.3.3 and 3.3.4). While the autotrophic activity in the pre-OMZ decreases the DIC concentrations due to uptake of CO_2, the CO_2 which is released during the remineralisation of organic matter increases DIC in the OMZ. In the OMZ, calcium carbonate dissolution may be enhanced due to higher pCO_2 as modelled by Kempe (1982b) for the outer estuary, adding even more DIC to the system. Long-term trends of increasing bicarbonate species, as described in Raymond and Cole (2003) and Raymond et al. (2008), could not be identified in our data. These trends could however be masked by short-term variations caused by biological activity as we are looking at summer mean data only.

The aforementioned increase of autotrophic and heterotrophic processes also affected the pH. While from 1985 to 1989 the pH values in both zones fluctuated between 7.2 and 7.6 (Fig. 3.7B), there was a strong increase after the reunification of Germany in 1989. It can be hypothesised that from 1989 on significantly reduced NH_4 inputs lead to a reduction of nitrification, which in the years before was responsible for low pH values. Vanderborght et al. (2002) and Hofmann et al. (2009) showed in models for the Scheldt estuary that nitrification is a dominant factor governing the pH. With its decrease, less NH_4 is oxidised and less protons are set free. The significant decrease of nitrification in the Elbe is described in Kerner et al. (1995). In the OMZ the pH reached its maximum of 8.2 in summer of 1994. Thereafter, it fluctuated slightly around pH 7.9, with the exception of 2003 (pH 7.7). After recovery, the pre-OMZ exhibits a first pH maximum in 1993 (pH 8.7). In this zone the pH fluctuation was greater and in the range of 8.3-9.0. Between 1993 and 2007 the pH in the pre-OMZ was on average 0.5 pH units higher than in the OMZ, again this is attributed to an enhanced primary production and concomitant dissolved CO_2 consumption in the upstream areas.

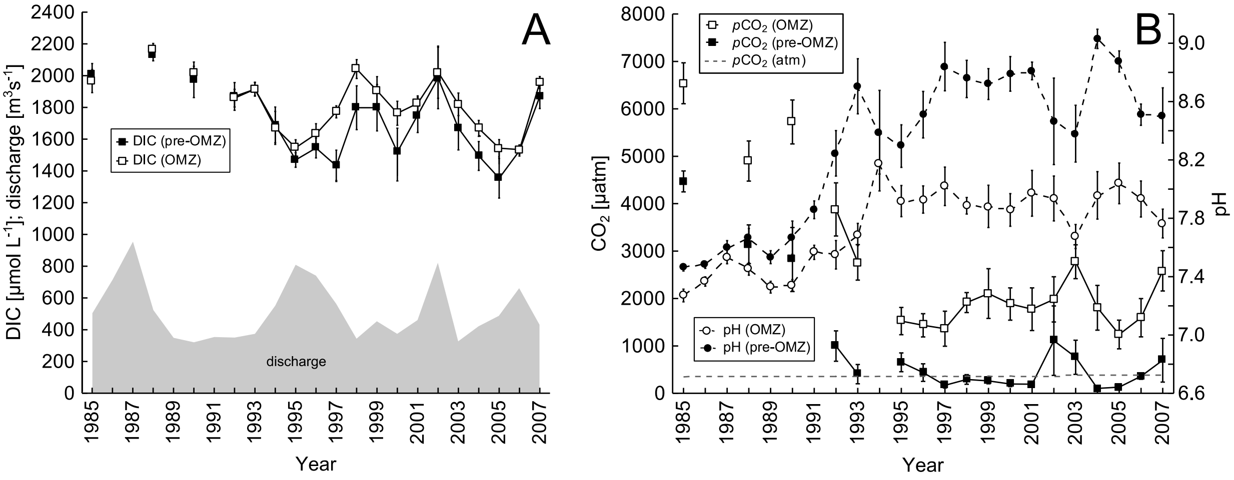

Fig. 3.7: (A) Temporal development of annual mean summer values of DIC (squares) and pH (circles) in the pre-OMZ (filled) and OMZ (open). Whiskers indicate confidence intervals (95 %). The grey area shows the temporal development of discharge (summer means) at the last non-tidal gauge Neu Darchau (Elbe-km 536). (B) Temporal development of annual mean summer values of $p\mathrm{CO}_2$ in the pre-OMZ (black filled squares) and OMZ (open squares) as well the atmospheric $p\mathrm{CO}_2$ values (grey dashed line) derived from GLOBALVIEW-CO_2 (2011). Whiskers indicate confidence intervals (95 %).

Fig. 3.7B shows the temporal development of the annual mean summer $p\mathrm{CO}_2$ in the two zones of the tidal freshwater part of the estuary. In 1985 the $p\mathrm{CO}_2$ in both zones was more than 12 times higher than the respective summer mean atmospheric partial pressure of about 345 µatm for the latitudinal band at 53.2° (GLOBALVIEW-CO_2, 2011). The pre-OMZ exhibited seasonal summer average $p\mathrm{CO}_2$ values of 4,470 µatm. In the OMZ, the $p\mathrm{CO}_2$ was even higher with 6,540 µatm. These values are in the same order of magnitude as values for the years 1954-1977 (Kempe, 1982a), indicating the Elbe's long history of high $p\mathrm{CO}_2$ and supported by data from an Elbe cruise in 1981 showing a $p\mathrm{CO}_2$ of about 4000 µatm at the freshwater station, Elbe-km 619 (Kempe, 1982b). Until 1990, the $p\mathrm{CO}_2$ in both zones stayed on high levels of above 2,000 and 4,000 µatm in pre-OMZ and the OMZ, respectively. The high values could be a reaction to the nitrification processes described previously. The pH is lowered and rising proton concentrations are buffered by CO_2 degassing. After 1990, the $p\mathrm{CO}_2$ in the OMZ dropped to values between 1,000 and 2,000 µatm with temporary maxima in 2003 (2,770 µatm) and 2007 (2,580 µatm). Values in the pre-OMZ follow that trend, but on much lower levels (difference: 1,000-2,000 µatm). In summer 1997, values decreased below atmospheric equilibrium and stayed mostly in this range - with exceptions in 2002, 2003, and 2007. This could be an indicator that nitrification is not any longer a main factor influencing $p\mathrm{CO}_2$ via pH. Aerobic mineralisation became the driving factor for $p\mathrm{CO}_2$ in the upper water column.

The values described here are well within the range of European estuaries as collected by Frankignoulle et al. (1998). However, to compare these values it is important to look at the individual definitions of estuaries the authors used to assess the CO_2 flux in the estuary. Most studies focussed on the mixing zone between river water and seawater. The estuarine freshwater part was not taken into account or was only represented by a small number of samples (cf. Frankignoulle et al., 1998 for examples). This approach omits the contribution of the freshwater part to the estuarine CO_2 budget, despite increasing evidence that in this zone high pCO_2 concentrations exist due to intense microbial respiration (Vanderborght et al., 2007). As for the Elbe estuary, the most recent study showed highest pCO_2 values of 1,100 µatm in the MTZ, for 1997 (Brasse et al., 2002).

The data used here (Fig. 3.7B) show pCO_2 values for areas that have not been investigated before in terms of the inorganic carbon system to this extent. The freshwater part was clearly highly oversaturated in the first decade of this analysis (1985-1995). With a noticeable improvement of water quality, the summer pCO_2 in the pre-OMZ dropped below atmospheric values. In consequence, the upstream freshwater part of the Elbe estuary could act as a sink for CO_2 during summer. In the OMZ, however, the pCO_2 values during summer remain elevated compared to the pre-OMZ. Values can pass 2,500 µatm, indicating that a recovery in terms of water quality does not necessarily lead to a low pCO_2. Compared to the maximum value of 1,100 µatm (Brasse et al., 2002) measured in the MTZ, the pCO_2 in the OMZ was even higher throughout the last decade.

The pCO_2 is one of the factors determining sea-air CO_2 fluxes. The contribution to the total efflux of carbon from the MTZ or the freshwater part not only depends on the differences in pCO_2, but also on other factors such as the surface area. For the Elbe estuary system, through its funnel shaped morphology, opening towards the sea, the freshwater areas cover a longer distance (~60 %), but a smaller area (~30 %). However, the calculated freshwater pCO_2 is twice as high as the MTZ value in 1996 (Brasse et al., 2002). Thus one third of the estuarine area could contribute above average to the sea-air CO_2 fluxes. Therefore, the estuarine freshwater part should be considered in future carbon budget studies due to the potentially high pCO_2 fluxes in this zone.

3.4 Conclusions

The Elbe estuary is, as many European estuaries, heavily influenced by anthropogenic activities and was subject to strong pollution, targeted by restoration efforts of authorities. The improvement of the water quality due to structural improvements in the catchment affected the biogeochemical cycling of organic carbon in the tidal freshwater part of the estuary. The tidal freshwater part became as important as the MTZ as a POC filter, removing about 50 % of the POC that enters the estuary (on average since 1993). Minor changes in DIC and CO_2 concentrations (Appendix C) suggest that up to 50 % of this POC are transformed and lost to the atmosphere. Thus, the freshwater part of the estuary should be considered as a significant source of CO_2 to the atmosphere despite its small areal proportion. Global extrapolations of estuarine carbon budgets applied scarce data, gained mostly in the 1990s for Elbe-like systems (e.g. Chen and Borges, 2009; Laruelle et al., 2010). However, the carbon cycling changes due to improved water quality presented here show that it is important to account for temporal variation of water quality. To refine our knowledge on estuarine carbon cycling and water-atmosphere CO_2 fluxes, the complete inner estuary including the tidal freshwater areas should be considered as well as temporal water quality changes.

4 The inorganic carbon system of the inner Elbe estuary

4.1 Introduction

The global carbon cycle is a key research topic in earth system sciences, with particularly high importance for climate change studies (IPCC, 2007). The carbon budget of the ocean as one of the main reservoirs in the global carbon cycle is of special attention. Kempe (1996) introduced the coastal ocean as a new area of interest and raised the question if it is a net source or sink for carbon dioxide (CO_2). Since then, many studies have emphasised the role of the continental shelf sea, although it covers only a small part of the total surface. Borges (2005) estimated that coastal ecosystems without marshes and estuaries act as a sink for CO_2 (0.37 Pg a^{-1}), which is mainly caused by intense primary production and subsequent sedimentation of organic matter (Smith and Hollibaugh, 1993).

The oceanic carbon cycle is coupled to terrestrial carbon fluxes by rivers that deliver dissolved and particulate inorganic and organic carbon to the sea. On this way, estuaries form the transition from land to ocean. Estuaries are very often strongly influenced by anthropogenic activities. During the last ten years, estuaries were in the focus as a potentially important part of biogeochemical matter cycling in the coastal zone. They are regarded as sources for CO_2, because long residence times allow intense respiration of organic matter (Frankignoulle et al., 1998), which is brought into the estuary via rivers. This leads to a global emission of 0.43 Pg C a^{-1} (Borges, 2005), which outweighs the estimated uptake, leading to a net heterotrophic state of coastal ecosystems. A re-estimate of global coastal ocean CO_2 fluxes relied on a refined coastal typology and yielded lower values for CO_2 emissions from estuaries, leading to a close to neutral budget (+0.06 Pg C a^{-1}, Laruelle et al. (2010)). Cai (2011) argued that carbon export from marshes fuel respiration in estuarine systems and that riverine carbon is bypassed and transported to the coastal ocean, yet concluding that sinks and sources are balanced. Many studies have shown that due to this intense respiration the partial pressure of CO_2 (pCO_2) in waters of outer estuaries is very often above atmospheric levels (i.e. Brasse et al., 2002; Zhai et al., 2005). The latest estimate by Chen et al. (2012) differentiated inner, middle and outer estuaries and states that inner estuaries (at salinities 0-2) are a stronger source for $CO_{2,}$, with an average pCO_2 of 3,033 ± 1,078 µatm, than outer estuaries, not considering river plumes at salinities >25, with an average pCO_2 of 692 ± 178 µatm.

The inorganic carbon system is furthermore influenced by processes like carbonate formation/dissolution, nitrification/denitrification, and sulphate reduction/oxidation. Kempe (1982b) reported very high pCO_2 in the Elbe estuary in 1981. The, at that time, strongly acidified system led to dissolution of imported marine carbonates, which significantly increased the sum of inorganic carbon anions, denominated as dissolved inorganic carbon:

$$DIC = [CO_2]+[HCO_3]+[CO_3]. \qquad \text{Eq. 4.1}$$

At the same time, the total alkalinity (TA), defined by Dickson (1981) as

$$\begin{aligned} TA = {} & [HCO_3]+2[CO_3]+[B(OH)_4]+[OH]+[HPO_4]+2[PO_4]+[SiO(OH)_3]+[HS] \\ & +2[S]+[NH_3]-[H]-[HSO_4]-[HF]-[H_3PO_4], \end{aligned} \qquad \text{Eq. 4.2}$$

is increased, because $CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$. TA increase by dissolution of carbonates in fluid mud bottom sediments of the Loire estuary was described by Abril et al. (2003). In addition to these processes, (de)nitrification can play an important role in the consumption and generation of alkalinity. For each mole ammonia (NH_4) that is consumed by bacterial nitrification, alkalinity decreases by two moles (Brewer and Goldman, 1976). Ammonia can be highly abundant in polluted estuarine systems and nitrification consecutively strongly affects alkalinity (Abril and Frankignoulle, 2001). In eutrophied systems, nitrate (NO_3) often poses an oxygen source in oxygen depleted waters, which commonly occur (cf. Chapter 3 and Vanderborght et al., 2007). Bacterial denitrification then leads to a TA increase of one mole per mole N (Brewer and Goldman, 1976).

Besides changes by chemical and biological processes, DIC concentrations can be influenced by water input from adjacent marshes (e.g. Cai and Wang, 1998), groundwater discharge (Johannes, 1980; Kempe et al., 1991), tributaries lining the inner estuary, and sewage effluents.

The majority of published studies focusses on the parts of estuaries, where seawater mixes with riverine water, following the estuary definition by Pritchard (1967). However, some studies have included the freshwater tidal river (Chapter 3 and e.g. Cadée and Laane, 1983; Hellings et al., 2001; Sharp et al., 2009). It was hypothesised in chapter 3 that the innermost parts of estuaries, the tidally influenced, but non-saline waters, are also very important in matter turnover processes and can contribute significantly to CO_2 fluxes. This, however, is dependent on the magnitude of fluxes and, moreover, on the surface water area, which represents the interface of water-air gas exchange. These factors will, amongst others, be evaluated to test the hypothesis.

Furthermore, it is important to look at the ecological state of the system, because highly polluted systems are characterised by high bacterial respiration rates and subsequent CO_2 flux to the atmosphere (e.g. Frankignoulle et al., 1996). Many of the well-studied systems are situated within highly industrialised regions (Hellings et al., 2001) that gained some environmental awareness and improved water quality management during the last 20 years. With economy in Asia and especially China bursting with productivity, it is conceivable, that riverine and estuarine as well as coastal systems will undergo a similar development of high pollution through agriculture, industrial activity, and population concentrated around these waters (i.e. Wang et al., 2008 and references therein). It is, therefore, necessary to evaluate recent studies and historical monitoring data of estuarine systems in the temperate climate zone to enable impact estimates of water quality changes in less well studied systems.

Many CO_2 related estuary studies rely on data from a few cruises (a detailed table is given in Raymond et al., 2000). This study aims at a more comprehensive dataset, covering all seasons within a 3-year campaign, on the carbon cycling in the inner Elbe estuary. Gas exchange with the atmosphere is a key aspect to answer the question, which processes govern the carbon cycling in the Elbe inner estuary. The use of $\delta^{13}C_{DIC}$ data will help to identify major influences on carbon transformation. The CO_2 system of the Elbe was evaluated before (Kempe, 1982b; Brasse et al., 2002), but it is hypothesised by the author of this thesis that the improvement of water quality during the last decades has impacted not only CO_2 fluxes but the inorganic carbon system in general. The amount of DIC fluxes from rivers through estuaries to the coastal zone is still poorly constrained (Hossler and Bauer, 2013). In a tentative budget, this study will evaluate the magnitude of CO_2 degassing, the influence of DIC export from marshes, and benthic exchange processes. Through inclusion of seasonally and spatially differentiated data, it will be possible to calculate a more constrained Elbe export of DIC to the coastal zone, which was, until now, a mere estimate based on discrete samplings.

4.2 Methods

A detailed overview over the study area is given in chapter 2. All samples were taken from about one meter below the surface with a NISKIN type vertical water sampler. Aliquots were drawn in the following order: DIC/TA – $\delta^{13}C_{DIC}$ - pH, temperature, conductivity, DO, PC/POC, SPM, nutrients.

4.2.1 Particulate carbon, nitrogen, SPM

A well-mixed aliquot was drawn from the water sampler and filtered through pre-combusted and pre-weighted GF/F glass fibre filters. Filters were dried at 40°C for two days and then weighted and summed to derive weight of suspended matter per litre. Aliquots of these filters were analysed for particulate carbon (PC) and particulate organic carbon (POC) with a Carlo Erba NA-1500 elemental analyser following the method by Nieuwenhuize et al. (1994). Particulate inorganic carbon (PIC) is considered as the difference between PC and POC.

4.2.2 Temperature, conductivity, pH

The pH values were measured with a Metrohm pH 827 mobile meter and Primatrode (6.0228.020) on cruises 1-13 and Aquatrode (6.0257.000) on cruises 14-18. Values are reported in the NBS scale. Three NBS buffers were used for calibration; the reported precision for measurements was 0.01 pH units. For mean calculations, pH values were transformed to H^+ activities, averaged and converted back to pH. Temperature, conductivity, and dissolved oxygen were determined with a WTW 350i and ConOx combination probe. All probes were checked and calibrated in the morning of every cruise day.

Salinity was calculated from conductivity, with an empirical formula developed by Bergemann (2005), valid for Elbe riverine and estuarine waters.

4.2.3 Dissolved inorganic carbon, total alkalinity

Analysis of DIC and TA (as defined by Dickson, 1981) was done according to Dickson et al. (2007). Samples were drawn before all others. Triplicates of glass bottles with a volume of 250-500 mL and ground stoppers (greased) were taken and preserved with mercury chloride. Samples were stored in a cool and dark place until analysis. DIC samples were drawn first from each bottle and analysed coulometrically with a Marianda VINDTA 3D automated DIC analyser. Samples were afterwards filtered through polycarbonate filters (0.2 µm) and analysed for TA with an automated potentiometric endpoint titration (VINDTA 3S) and results were evaluated using nonlinear curve fitting to determine equivalence points. DIC as well as TA measurements were calibrated with certified reference seawater by A. Dickson. Coefficients of variation of standard measurements were on average within 0.15 %.

4.2.4 Major ions

Major ions, Na^+, K^+, Ca^{2+}, Mg^{2+}, F^-, Cl^-, Br^- and SO_4^{2-}, were determined chromatographically (Metrohm 881 Compact IC Pro system). Coefficients of variation of multiple determinations were in order of the listing above: 1.9 ± 1.1 %, 3.0 ± 3.0 %, 5.7 ± 1.7 %, 1.8 ± 1.7%, 9.3 ± 9.4 %, 1.6 ± 0.7 %, 3.8 ± 2.9 % and 0.9 ± 0.6 %.

4.2.5 Nutrients

Samples for nutrient determination were filtered immediately through polycarbonate filters (0.45 µm), stored in acid-washed polyethylene bottles and kept at +6°C until further processing. Nitrate (NO_3) was measured via reduction to nitrite. Nitrite (NO_2), ammonia (NH_4), and phosphate (PO_4) were determined photometrically by a Technicon AutoAnalyzer System III. The applied methods are given in Grasshoff et al. (1999). Relative precisions of measurements were 1.8±2.5 % (NO_3), 2.5±4.7 % (NO_2), 6.0±11.1 % (NH_4), and 1.9±3.6 % (PO_4). Analysis of DSi was done via manual spectrophotometric determination of blue silicomolybdic acid at 810 nm wavelength (Grasshoff et al., 1999). The relative precision of measurements was 1.6±3.1 %.

4.2.6 DIC isotopes

Samples for $\delta^{13}C_{DIC}$ analysis were drawn into 12 mL acid pre-washed *Labco Exetainers* and preserved with mercury chloride. Samples were stored in a cool and dark place until analysis. Stable carbon isotope ratios were determined using a Finnigan™ MAT 253 isotope ratio mass spectrometer coupled to a Finnigan™ GasBench II via Thermo Scientific ConFlo IV. Ratios of $^{13}C/^{12}C$ are reported as δ values relative to the VPDB (Vienna Peedee Belemnite) international reference (Craig, 1957), expressed as $\delta^{13}C_{DIC}$ in parts per thousand (‰). Accuracy was within ± 0.06 ‰.

To evaluate the behaviour of $\delta^{13}C_{DIC}$ along the salinity gradient, a theoretical mixing line was constructed, which depends on the isotopic compositions and DIC concentrations of the marine and riverine endmembers (Spiker, 1980), denoted with *m* and *r* respectively:

$$\delta^{13}C_{mix} = \frac{f * \delta^{13}C_r * DIC_r + (1-f)\delta^{13}C_m * DIC_m}{DIC_{mix}}. \quad \text{Eq. 4.3}$$

With f as the freshwater fraction, calculated from relative salinity contribution as follows:

$$f = \frac{Sal_{max} - Sal_{mix}}{Sal_{max}}. \quad \text{Eq. 4.4}$$

The maximum measured salinity (Sal_{max}) during each survey was used as a virtual endmember because the salinity gradient was not sampled to up to the actual salinity endmember of 31. Data on $\delta^{13}C_{DIC}$ were gathered during four cruises in late summer and autumn of 2010 (Fig. 4.5)

4.2.7 Calculation of pCO$_2$

The pCO$_2$ values were calculated from measured DIC values, temperature, pH and others. Two different approaches were used. An often used approach in marine sciences is to use a program called *CO2SYS*, published by the USGS (Lewis and Wallace, 1998). This program incorporates the most commonly used carbon dissociation constants used for calculations of the carbonate system in marine environments, such as Cai and Wang (1998) or Millero et al. (2006).

In riverine research, the program *PHREEQC* (Parkhurst and Appelo, 1999) is often used to calculate pCO$_2$ data from given databases of monitoring programmes (i.e. Humborg et al., 2010; Lauerwald et al., 2013). In this program, the ionic strength can be taken into account by adding the major ions and nutrient data to the calculations. River waters have differing ionic compositions and this can be credited in the calculations. *CO2SYS* and formulas therein use the salinity for an approach on ionic strength, because seawater has an overall very slightly varying major ion composition.

Calculated pCO$_2$ values from *PHREEQC* (using the phreeqc.dat database) are, for a salinity <1, up to 23.6 % higher if compared to values from *CO2SYS*, applying the popular constants by Millero et al. (2006). Differences become smaller with increasing salinity (averaged relative difference: 7.0 ± 10 %), indicating the influence of marine waters, for which the latter constants are optimised. Values at salinities <1 fall strictly below the hypothetical 1:1 ratio and values from the salinity gradient approach the 1:1 ratio (Fig. 4.1A).

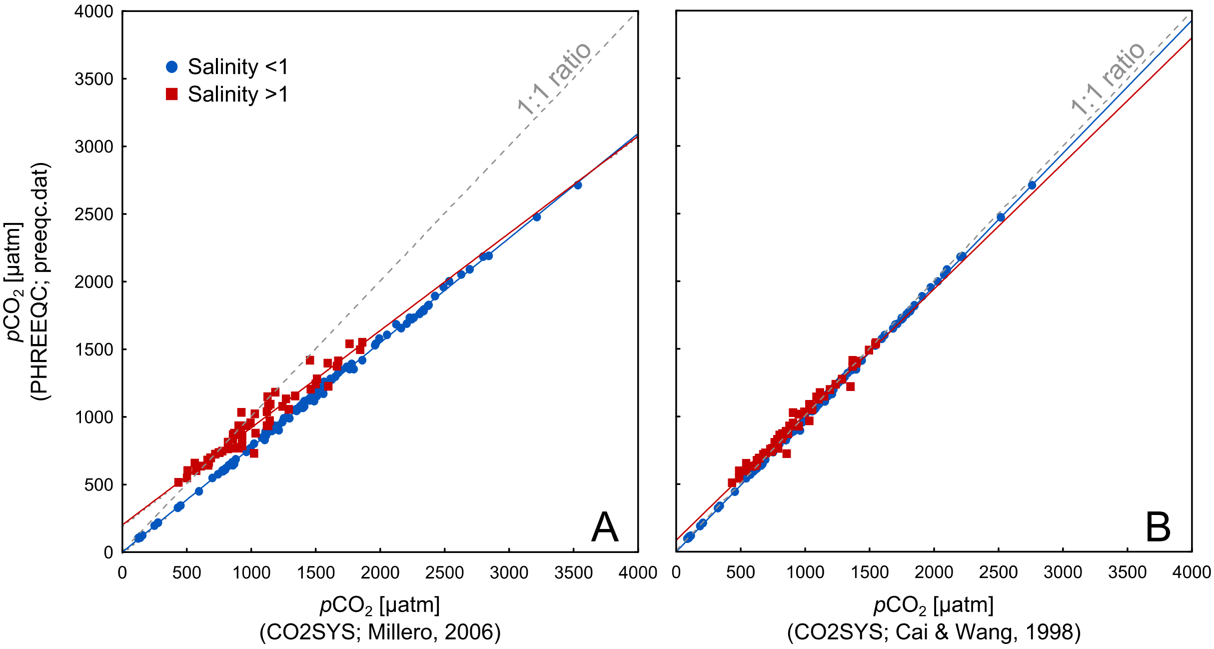

Fig. 4.1: Comparison of calculated pCO2 values. Results from PHREEQC plotted versus data from CO2SYS with constants by Millero et al. (2006) (A) and with constants by Cai and Wang (1998) (B). The lines indicate linear regression lines of measurements with salinity <1 (blue circles) and >1 (red squares). The dashed line marks a theoretical 1:1 ratio.

Interestingly, *PHREEQC* results are relatively similar over the whole data range if compared to the constants by Cai and Wang (1998) (1.3 ± 4.2 % difference), probably owing the fact, that they used a set of different constants for different salinity ranges to compile a comprehensive formula. Fig. 4.1B shows how values approach the 1:1 line.

On the basis of this finding, it seems invaluable to incorporate data of major ions into calculations of $p\mathrm{CO}_2$ from DIC and pH if no direct $p\mathrm{CO}_2$ measurements are available. In this study, *PHREEQC* calculations were used with the exception in cases where no ion data were available (complete cruise of July 2011 and three more single samples); here, *CO2SYS* was used with constants by Cai and Wang (1998).

4.2.8 Calculation of air-water CO_2 exchange

The flux of CO_2 between water and atmosphere (F in mmol $\mathrm{m}^{-2}\ \mathrm{d}^{-1}$) is estimated by the equation

$$F = k \times \alpha \times \left(pCO_{2_{(\mathrm{water})}} - pCO_{2_{(\mathrm{atmosphere})}}\right), \qquad \text{Eq. 4.5}$$

with k as the gas transfer velocity ($\mathrm{m\ s}^{-1}$ x 86,400 to convert from seconds to days), α as the solubility coefficient of CO_2 ($\mathrm{mmol\ m}^{-3}\ \mathrm{atm}^{-1}$) and $p\mathrm{CO}_{2(\mathrm{water})}$ as the calculated $p\mathrm{CO}_2$ from the samples and $p\mathrm{CO}_2$ of the atmosphere ($p\mathrm{CO}_{2(\mathrm{atmosphere})}$), according Dickson et al. (2007) derived by

$$pCO_{2_{(atmosphere)}} = xCO_{2(atm)} \times (P_{ATM} - pH_2O). \qquad \text{Eq. 4.6}$$

Here, xCO_2 is the molar fraction of CO_2 in dry air obtained from GLOBALVIEW-CO_2 (2011) data. It was shown that the 52.17° band shows good agreement with data from the nearest monitoring station in Westerland (cf. chapter 3). Daily mean ambient air pressure (P_{ATM}) at the measuring station Hamburg-Fuhlsbüttel was obtained from the DWD (German Weather Agency). Additionally, $p\mathrm{H_2O}$ was estimated to account for an assumed 100 % humidity on the water surface (after Weiss and Price, 1980):

$$\ln pH_2O = 24.4543 - 67.4509\left(\frac{100}{T}\right) - 4.8489\ln\left(\frac{T}{100}\right) - 0.000544\,S. \qquad \text{Eq. 4.7}$$

In this equation T denotes the water temperature and S denotes the salinity of the sample.

Determining the gas transfer velocity is an issue of persistent discussions. It is one of the key factors determining the magnitude of CO_2 exchange with the atmosphere and probably the most problematic term in the equation (Raymond and Cole, 2001). It is mainly controlled by wind stress (e.g. Broecker and Peng, 1974; Wanninkhof, 1992) but also influenced by water currents (Zappa et al., 2003), rainfall (Ho et al., 1997), turbidity (Abril et al., 2009) and any other processes affecting the turbulence of the water body. As heterogeneous systems, estuaries feature a pronounced variability of all these factors. Most of the published k values refer to in situ measurements with flux chambers or gas tracers (e.g. Frankignoulle, 1988; Borges et al., 2004; Ho et al., 2006). While these k values should represent the referenced systems, their general applicability is doubtful because of inter-site variability of geographical, climatic, and physical settings. In a more generic approach, Abril et al. (2009) incorporated wind speed (u, in m s^{-1}), SPM concentration (in g L^{-1}), surface area (S, in km^2) of the estuary and water current velocity (v, in m s^{-1}) to derive k:

$$k = (1.8 \times e^{-0.0165v} + [1.23 + \log(S)] \times [1 - 0.44SPM] \times u) \times (\tfrac{600}{Sc})^{0.5}. \qquad \text{Eq. 4.8}$$

As one approach that integrates as many variables as possible, Eq. 4.8 is used in this thesis. A mean of all current measurements published by the Wasser- und Schiffahrtsamt Hamburg (2012; Tab. III.2.1.1-1 a-d) of 13 stations along the estuary was used (0.663 m s^{-1}), along with a GIS derived total area of 276.6 km^2 including only permanently flooded regions between Geesthacht and Cuxhaven (refer to Tab. 2.1 for a detailed distribution of areas). Please note that previous estimates used a larger area for the Elbe estuary (327 km^2; Borges, 2005). Abril et al. (2009) introduced the surface area in Eq. 4.8 to account for the wind fetch influence on k. While relying on data by Borges et al. (2004), who studied the whole estuarine gradient, including the plume and excluding the freshwater parts, it is assumed that the dependency is still true for the much smaller inner Elbe estuary with respect to the wind fetch effect.

The Schmidt number (Sc) for CO_2 in freshwater is calculated according to Wilke and Chang (1955) in Wanninkhof (1992) as an empirical function of the water temperature (t):

$$Sc = 1911.1 - 118.11t + 3.4527t^2 - 0.04132t^3. \qquad \text{Eq. 4.9}$$

The approach with Eq. 4.8 yields relatively high k values for the Elbe estuary (mean of all measurements: 20.1±5.6 cm h^{-1}) if compared to the average k (8 cm h^{-1}) used to estimate CO_2 flux in European estuaries by Frankignoulle et al. (1998). However, the generic approach reproduces one value for the Elbe by published by Abril and Borges (2004; Fig. 7.2: 31 cm h^{-1} at a wind speed of 8 m s^{-1}) and is therefore considered feasible.

Because the determination of k is subject to errors, an additional approach was used to calculate k for the Elbe in order to bracket the flux estimates. Jiang et al. (2008) analysed literature data on the wind speed to k dependence, adding more recent data to the regression analysis conducted by Raymond and Cole (2001) to derive the following empirical equation:

$$k = (0.314u^2 - 0.436u + 3.99) \times (\frac{600}{Sc})^{0.5}. \qquad \text{Eq. 4.10}$$

This k calculation leads to generally lower flux estimates if compared to Eq. Eq. 4.8. If a flux is described with a range, it refers to both of the aforementioned calculations with results from Eq. 4.10 named first and from Eq. 4.8 named second, unless stated otherwise or marked with J08 for Jiang et al. (2008) and A09 for Abril et al. (2009) respectively.

4.2.9 General data handling

To give an overview over the spatial and temporal distribution of basic components of the carbonate system, data from all ESTUCARB cruises are averaged. Averaged data are split into the four zones along the inner Elbe estuary during the four seasons. Season time frames refer to the meteorological seasons.

To evaluate concentration data of dissolved material in the salinity gradient, mixing with marine waters has to be accounted for. To analyse the riverine contribution and identify possible sources along the gradient, mixing lines were constructed to interpret the development of concentration changes as shown e.g. in Officer (1979). If a linear regression can describe the observed concentration, mixing is considered to be linear and with no concentration changes along the gradient. If values appear below a linear mixing line, the estuarine part of the salinity gradient is considered a sink while values above this line would indicate a source of the regarded parameter. To analyse concentration changes that are not traced back to mixing with seawater, the calculation of effective DIC concentrations is necessary. The method described in section 5.2.2 was used here. Mixing curves for DIC concentrations could be constructed using mainly second and third order polynomial equations. A detailed list of equations and coefficients of determination is given in Tab. 4.1.

Tab. 4.1: Fitting equations for the modeled DIC and TA concentration distribution in the salinity gradient on the basis of available transect data. (n.d. = not determined)

dissolved inorganic carbon

month	year	discharge	fit	equation	r^2
9	2009	327	2. order polynomial	$-1.3\ S^2 + 39.9\ S + 1720.4$	0.87
10		390	linear		0.99
3	2010	1,353	linear		
4		2,015	n.d.		
5		726	2. order polynomial	$0.1\ S^2 - 4.9\ S + 2088.4$	0.99
7		400	4. order polynomial	$-0.002\ S^4 + 0.2\ S^3 - 4.3\ S^2 + 41.3\ S + 2086.9$	1.00
8		666	3. order polynomial	$0.1\ S^3 - 3.9\ S^2 + 59.6\ S + 1843.2$	1.00
9		1,030	2. order polynomial	$2.4\ S^2 - 33.2\ S + 2073.9$	1.00
10		2,229	2. order polynomial	$0.4\ S^2 - 7.9\ S + 2158.3$	0.91
11		1,797	n.d.		
2	2011	1,899	n.d.		
4		793	linear		0.98
7		580	n.d.		
9		698	2. order polynomial	$1.04\ S^2 - 26\ S + 2321$	0.98
10		718	2. order polynomial	$0.3\ S^2 - 17.6\ S + 2530.8$	0.99
12		758	2. order polynomial	$0.7\ S^2 - 25.6\ S + 2493.9$	0.97

total alkalinity

month	year	discharge	fit	equation	r^2
9	2009	327	2. order polynomial	$-1.7\ S^2 + 59.4\ S + 1647$	0.91
10		390	linear		0.82
3	2010	1,353	n.d.		
4		2,015	n.d.		
5		726	2. order polynomial	$0.7\ S^2 - 1.2\ S + 2037.6$	0.98
7		400	2. order polynomial	$-0.4\ S^2 + 18.6\ S + 2081.9$	1.00
8		666	2. order polynomial	$-2.02\ S^2 + 57.3\ S + 1783.7$	1.00
9		1,030	3. order polynomial	$0.3\ S^3 - 1.8\ S^2 - 7.2 \times S + 2004.4$	1.00
10		2,229	3. order polynomial	$-0.1\ S^3 + 2.4\ S^2 - 16.9 \times S + 2140.3$	0.99
11		1,797	n.d.		
2	2011	1,899	linear		
4		793	2. order polynomial	$-0.7\ S^2 + 12.5\ S + 2343.1$	0.97
7		580	n.d.		
9		698	3. order polynomial	$-0.04\ S^3 + 2.1\ S^2 - 25.1\ S + 2282.2$	0.99
10		718	linear		0.99
12		758	2. order polynomial	$0.9\ S^2 - 24.4\ S + 2506.4$	0.98

4.3 Results

4.3.1 Concentrations

TA and DIC concentrations as well as $p\mathrm{CO_2}$ show a clear seasonal pattern in all zones but the post-MTZ (Fig. 4.2). In the inner three zones, TA and DIC are lowest during summer and highest during winter. Highest $p\mathrm{CO_2}$ is observed during summer in the OMZ and MTZ (up to ~2,200 µatm), while the pre-OMZ features the lowest measured values (~380 µatm) during spring. It is assumed this value would be even lower if the full first section was fully covered, but it has a significantly lower number of measurements due to survey constraints (refer to Appendix B-3 for individual data).

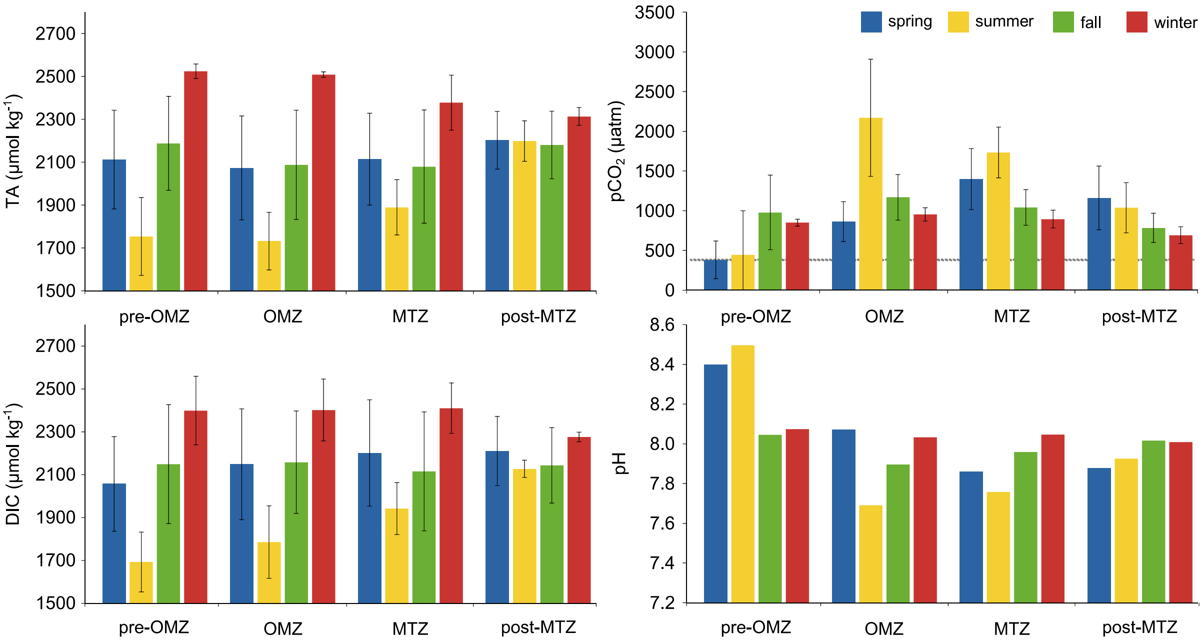

Fig. 4.2: Seasonal mean TA and DIC concentrations, $p\mathrm{CO_2}$, and pH values, grouped by 4 distinguished zones. The dashed grey line in the $p\mathrm{CO_2}$ plot indicates the annual mean atmospheric $p\mathrm{CO_2}$. The black bars show the standard deviation of the mean.

While seasonality is observed in the freshwater part of the estuary and parts of the inner salinity gradient, TA as well as DIC concentrations in the post-MTZ fluctuate little throughout the year (Fig. 4.2), with an annual average of 2,223.7 ± 60.4 µmol $\mathrm{kg^{-1}}$ and 2,189.2 ± 68.1 µmol $\mathrm{kg^{-1}}$ respectively. The $p\mathrm{CO_2}$ is less constant and declines from 1,160 µatm in spring to about half the value in winter.

Individual transects reveal linear conservative mixing with seawater, as well as addition and removal of inorganic carbon (Fig. 4.3; Fig. 4.4). Linear mixing was not observed during summer. However, excursions from linear mixing are minor and when averaged over a season, these differences seem to level out (refer to flux description).

Besides temporal and spatial characteristics, DIC concentrations exceed TA concentrations in the larger parts of the OMZ and MTZ. Changes in this ratio towards higher TA values are observed in the upstream parts of the OMZ and in the pre-OMZ, as well as the seaward samples (Appendix D-1). Development of concentrations is often nearly parallel, with notable deviation only in some summer months.

Observed pH values mirror the seasonality as well. Low *p*CO_2 in the pre-OMZ are reflected in exceptionally high pH values, on average between 8.4 and 8.5 in spring and summer. During winter, all zones feature a relatively homogenous pH ranging from 8.01 to 8.07. The lowest pH was observed in the OMZ during summer (pH 7.69). The MTZ is featured by pH values around 8 throughout the year.

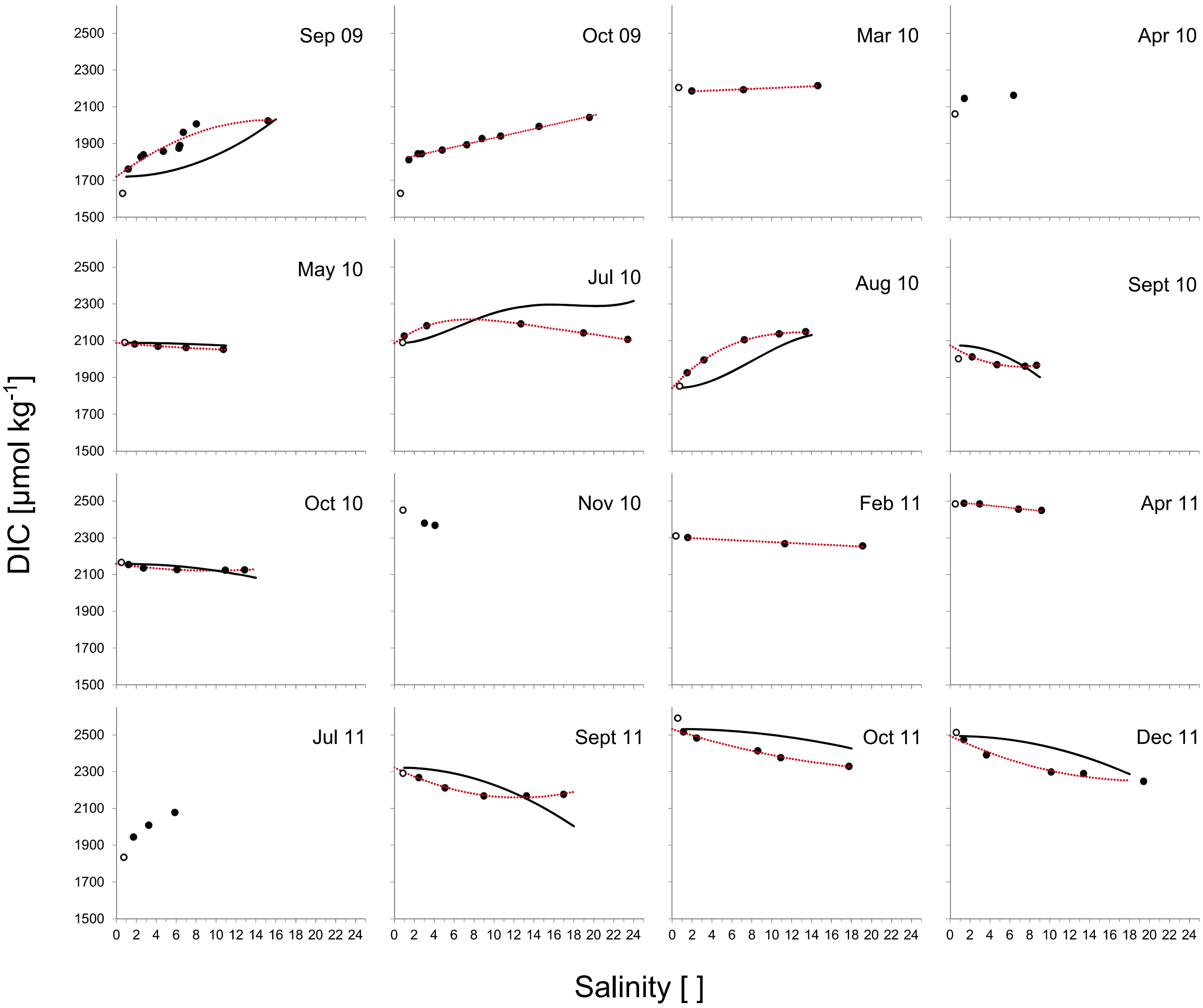

Fig. 4.3: DIC concentration versus salinity plots for the modeling of effective DIC concentrations. Filled circles mark actually measured values, open circles mark the last measurement at salinities <1. The dotted red line shows an individually determined regression, which is used to calculate effective concentrations of DIC (solid line).

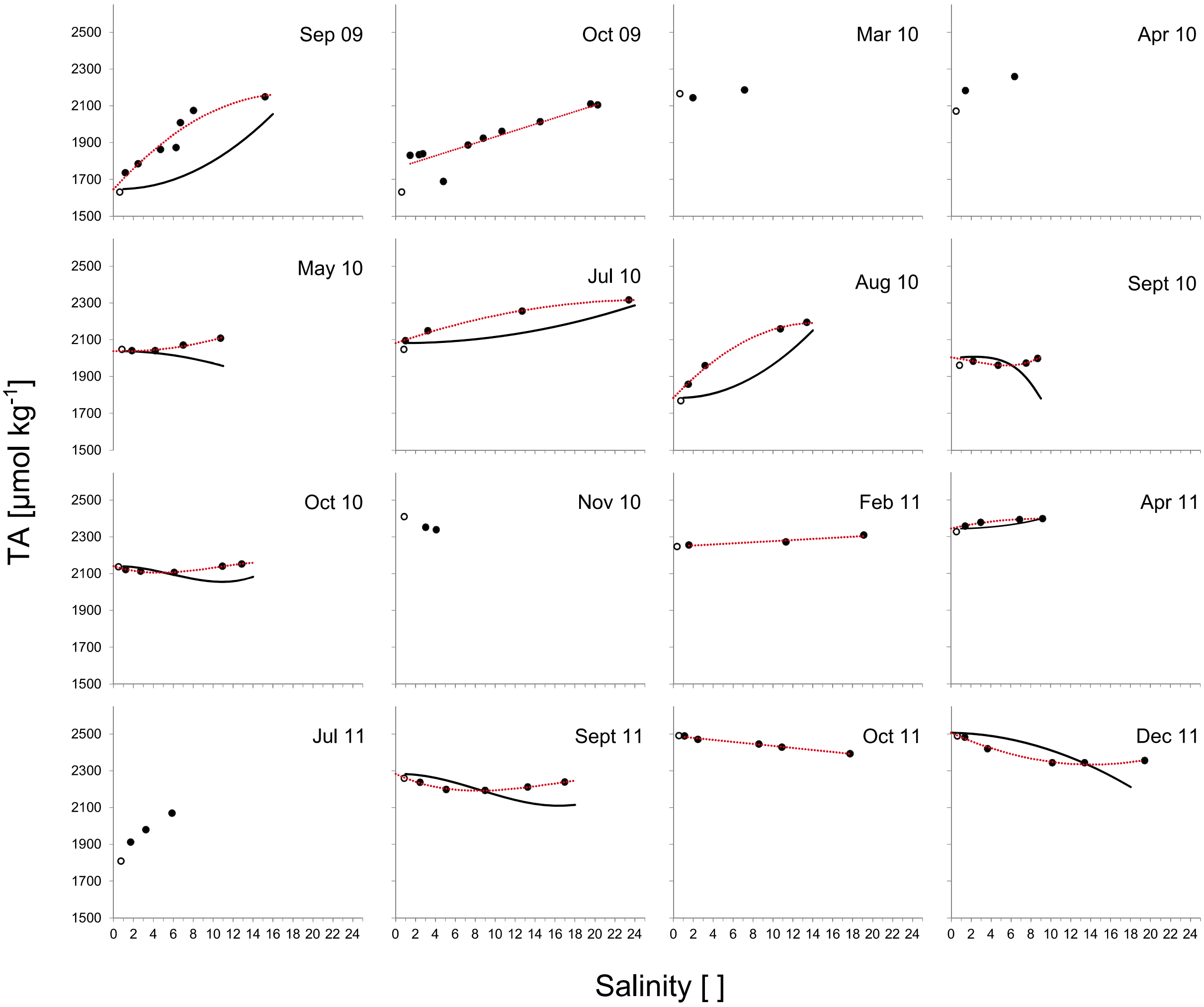

Fig. 4.4: TA concentration versus salinity plots for the modeling of effective TA concentrations. Filled circles mark actually measured values, open circles mark the last measurement at salinities <1. The dotted red line shows an individually determined regression, which is used to calculate effective concentrations of TA (solid line).

4.3.2 DIC isotopic data

The upstream parts are characterised by $\delta^{13}C_{DIC}$ values from about -9 ‰ in August to -13 ‰ in October (Fig. 4.5). In August, values decrease towards the OMZ while October values increase. The area of the OMZ is characterised by little change in the $\delta^{13}C_{DIC}$ ratio and values increase steeply from the outer end of the MTZ seawards indicating mixing with seawater (Fig. 4.5). A calculation of expected conservative mixing lines according to Eq. 4.3 reveals a minor source of DIC depleted in ^{13}C in July and August, while September and October data show near congruency between observed and modelled values (Fig. 4.6).

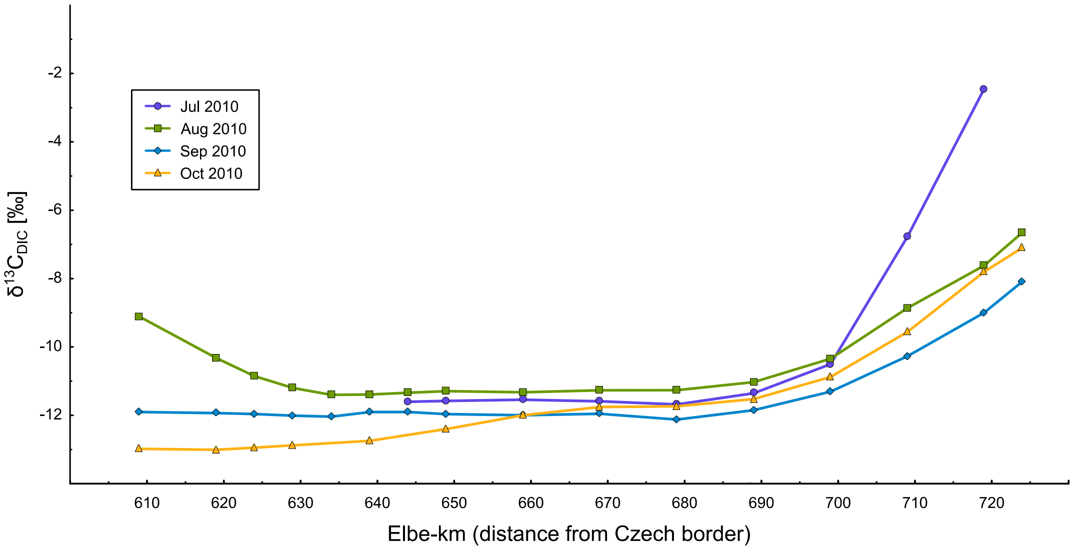

Fig. 4.5: Distribution of $\delta^{13}C_{DIC}$ values along the inner Elbe estuary in summer and fall 2010.

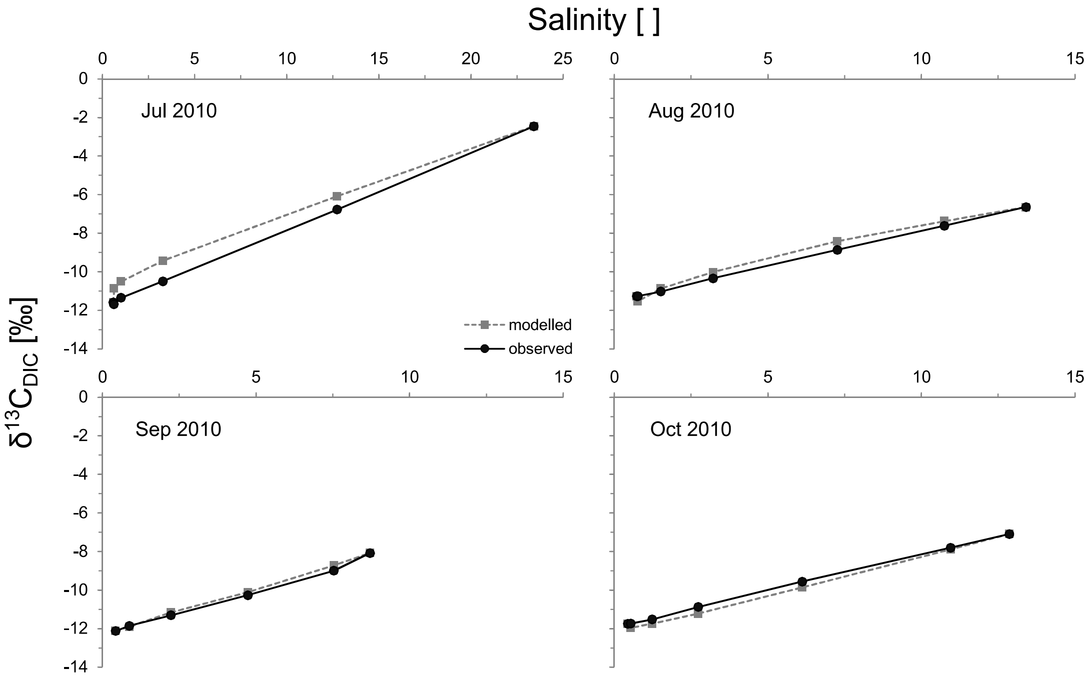

Fig. 4.6: Modeled (dashed line) versus observed (solid line) distribution of $\delta^{13}C_{DIC}$ along the salinity gradient of the inner Elbe estuary.

4.3.3 Fluxes

The calculated fluxes of DIC and TA through the inner estuary (Fig. 4.7) show a pronounced seasonality as well. Highest fluxes occur in winter and spring from all zones. During summer the flux increases strongly between OMZ and MTZ, while fluxes increase steadily from the pre-OMZ seawards during the rest of the year (Fig. 4.7).

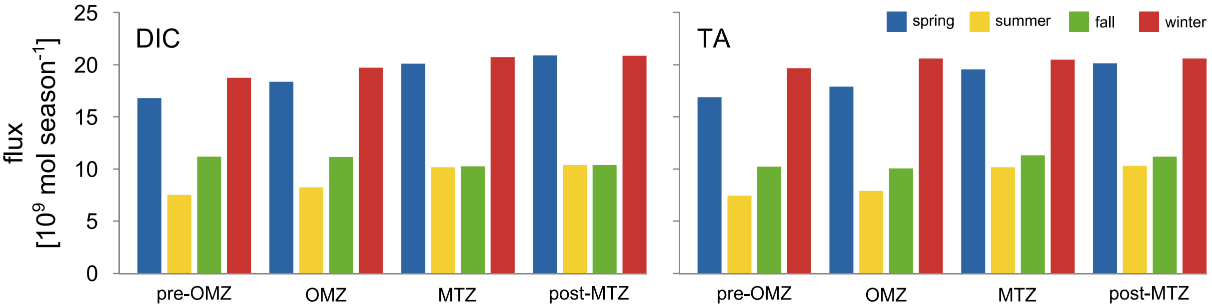

Fig. 4.7: Seasonal fluxes of DIC and TA from the four distinguished zones.

The larger part of the inner estuary is characterised by CO_2 effluxes during the whole year. Uptake of CO_2 is observed only in the pre-OMZ during spring, with -0.01 mol m^{-2} d^{-1} (both approaches; Fig. 4.8). Maximum fluxes to the atmosphere occur in the OMZ during summer (0.21-0.39 mol C m^{-2} d^{-1}). The MTZ is characterised by elevated CO_2 effluxes as well, while the post-MTZ features decreased effluxes compared the upstream parts. This spatial heterogeneity disappears in winter, when fluxes are relatively homogeneous throughout the inner estuary, with values between 0.06-0.10 / 0.07-0.12 mol m^{-2} d^{-1} (J08/A09; Fig. 4.8).

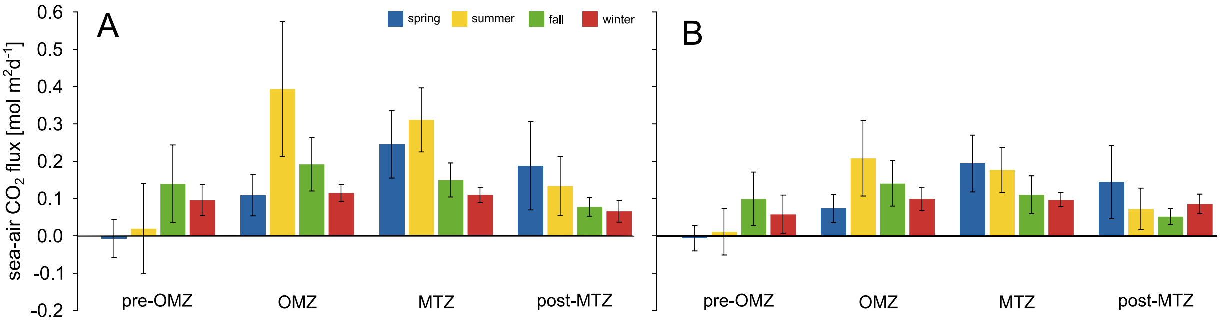

Fig. 4.8: Mean sea-air CO_2 flux per area, grouped by season and zone. Whiskers indicate the standard deviation of the mean. A – values are based on calculations after Abril et al. (2009); B – values are based on calculations after Jiang et al. (2008).

4.4 Discussion

4.4.1 Discharge as major driver of DIC fluxes towards the coast

While there are significant fluctuations in the DIC and TA concentrations between the different seasons, they cannot explain the strong differences in the seasonal fluxes of these parameters. Discharge is the main factor determining the carbon fluxes towards the North Sea. Fig. 4.9 shows the monthly mean discharge at km 619. For the discussed fluxes, the mean discharge of 10 years was chosen to rule out short term fluctuations. Compared to a long term century mean, fluxes are slightly lower during summer and slightly higher during the all other seasons. Overall, it shows that the flux pattern is governed by the discharge. The relatively steady increase from the pre-OMZ to the post-MTZ during winter might be explained by the gradual addition of water by tributaries, which line the inner estuary and contribute on a long term about 15 % of the water delivered to the North Sea (Bergemann, pers. comm.).

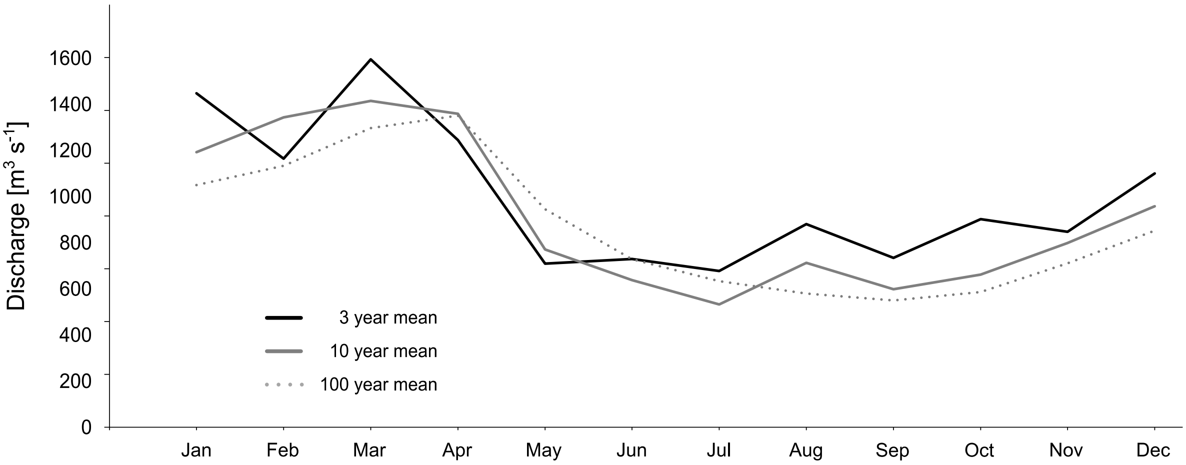

Fig. 4.9: Monthly mean discharge rates at Elbe-km 619, split into a 3-year mean (black line), 10-year mean (grey line), and 100-year mean (dashed line).

During winter, increased DIC mobilisation in the catchment due to rainfall and snowmelt is reflected in relatively high TA and DIC concentrations in the upper estuary, a region where waters are considered to represent the riverine signal. As carbonates contribute more than silicates to the mobilisation of TA in the form of bicarbonate (HCO_3^-) (Meybeck, 1987), the Elbe waters should carry elevated TA loads, because about 8.6 % of the Elbe river catchment are comprised of sedimentary carbonates and 13.5 % are mixed sediments that are likely to contain carbonates transported via glaciers from cretaceous marine carbonates situated North. These numbers are derived from watershed data by Lehner et al. (2008) in conjunction with data from the global lithological map GLiM by Hartmann and Moosdorf (2012).

4.4.2 Primary productivity in the pre-OMZ

The highest spatial fluctuations in the inorganic carbon system occur during times of increased temperature, i.e. spring, summer and early fall. The most characteristic observation is that DIC and TA are lowest in the freshwater area during these times. In the pre-OMZ, this is traced back to primary production, occurring in situ and in the upstream river. This is reflected in increased POC loads which are delivered to the estuary (cf. chapter 3). In the same area, low $p\mathrm{CO}_2$ values below atmospheric pressure and pH values of 8.4 and higher support this. During spring $p\mathrm{CO}_2$ in the water is below atmospheric values, resulting in a net uptake of 6-8 x 10^6 mol CO_2 during this season. This zone is also characterised by increased dissolved oxygen levels, which was shown in chapter 3 as a development over the past 25 years. Additionally, the $\delta^{13}C_{DIC}$ signal from a cruise in late summer shows a value near -9 ‰ (Fig. 4.5), a heavier signal than an average riverine value of -12 ‰ observed by Mook and Tan (1990) for Dutch rivers. Similar values are expected in the Elbe, because they are considered a mixed signal between C from bacterial respiration of organic matter (-25 ‰) and C from weathering of marine carbonates (0 ‰) (Spiker, 1980), which are abundant in the Elbe catchment. Hellings et al. (2001) observed similar values in the upstream part of the Scheldt estuary. A signal depleted in ^{12}C, as determined here, indicates primary production, supported by a strong correlation between oxygen saturation and $\delta^{13}C_{DIC}$ (r^2=0.985 for data of the freshwater part; Fig. 4.10). Heavier values in this plot are also characterised by high pH values above 8. This correlation was not observed in the July data, probably due to a shortened transect, which started at the outer end of the OMZ and did not cover the most upstream areas of the estuary. The September situation featured no particular changes in $\delta^{13}C_{DIC}$, while in October a correlation was well observed. In contradiction to the August situation, the heaviest values were observed in the MTZ. It is conceivable that the increase of $\delta^{13}C_{DIC}$ and oxygenation is an effect of extended residence times in the MTZ in combination with less bacterial activity due to decreased temperature, leading to dominance of physical re-aeration in this zone. CO_2 evasion leads to a heavier signal and reduced respiration rates may not be able to counterbalance this effect.

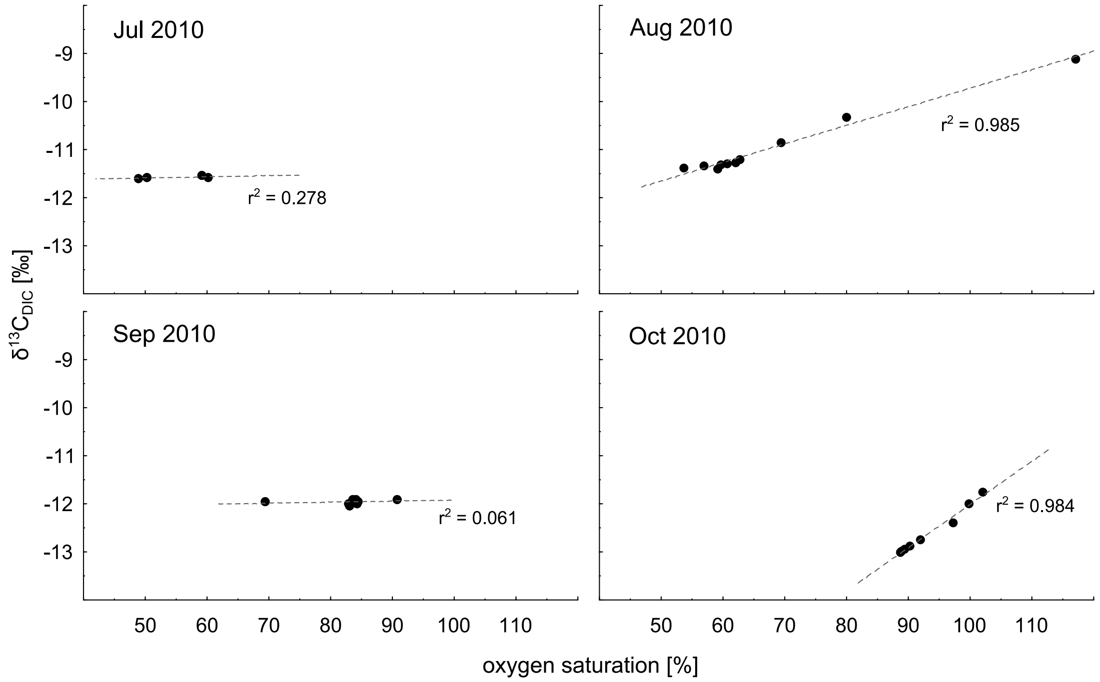

Fig. 4.10: Correlation between $\delta^{13}C_{DIC}$ and oxygen saturation for data from the freshwater part of the estuary.

4.4.3 CO_2 evasion hotspot OMZ

It was described in chapter 3 that the OMZ as a major hotspot for respirational processes, leading to a characteristic oxygen sag giving the zone its name. From here on downstream, primary production is inhibited by reduced light availability due to increased SPM (Goosen et al., 1995; Wolfstein and Kies, 1999). With DIC data from the most recent years, it is possible to confirm that this zone is dominated by respiratory consumption of POC, which produces CO_2. This is reflected in the maximum observed values of pCO_2 in the OMZ during summer together with a steep decline of pH from values near 9 to around 7.8. In the OMZ, $\delta^{13}C_{DIC}$ signals seem to converge at -11 to -13 ‰ (Fig. 4.5), an additional indicator for domination of respirational processes leading to lighter values. Strongly decreasing POC concentrations support the finding. Fig. 4.11 shows the seasonal mean POC part of SPM along the inner estuary in comparison to the CO_2 concentrations. In the OMZ, the POC part is reduced to about half of the input, concomitantly, CO_2 concentrations increase strongly. The major in- and outputs of CO_2 to and from this zone (river load and atmospheric exchange) can explain the loss of POC to a large extent during summer: 0.30 mol POC m^{-2} d^{-1} are lost while 0.32-0.50 mol CO_2 m^{-2} d^{-1} (J08/A09) are produced.

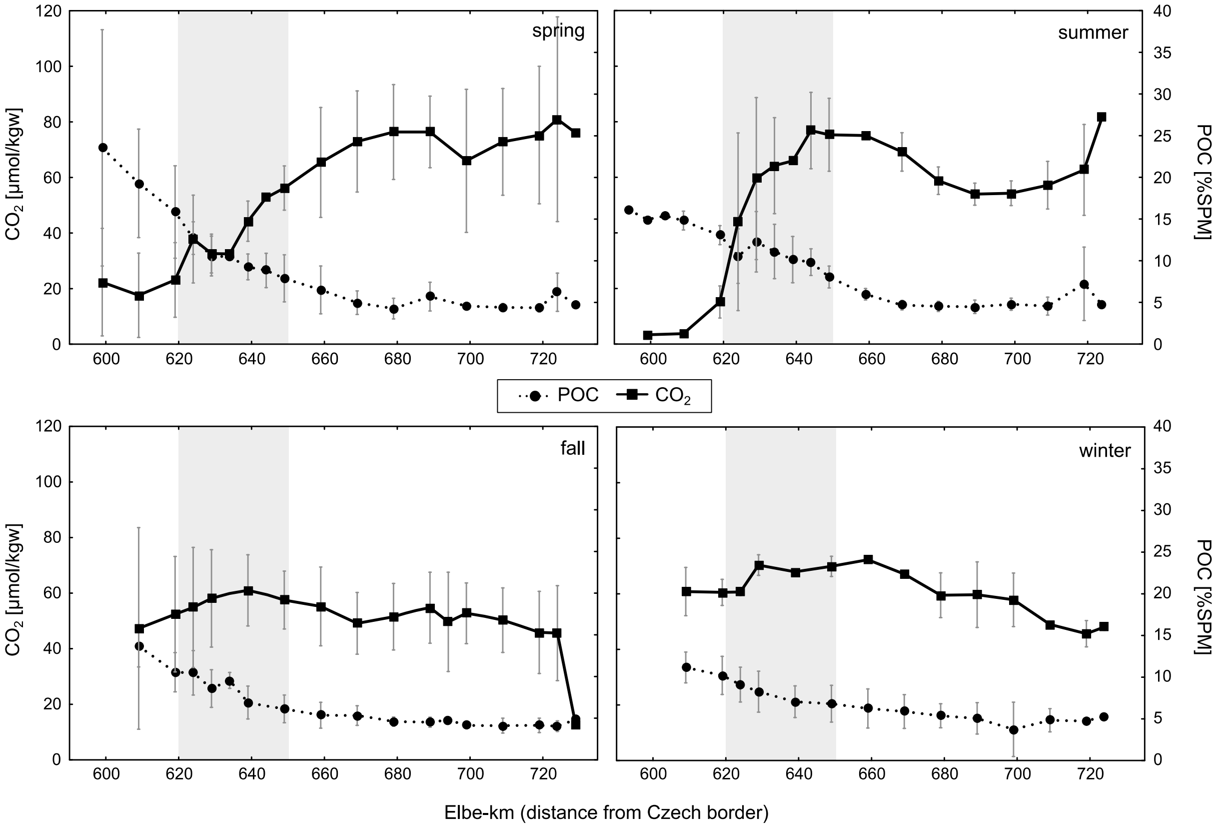

Fig. 4.11: Seasonally averaged concentrations of CO_2 (solid line; data in the salinity gradient corrected for dilution with sea water) and POC fraction of SPM (dashed line) along the inner Elbe estuary. The grey area marks the region of the OMZ.

The decrease of POC and increase of CO_2 is less pronounced in the MTZ, which is in many estuaries the region where *p*CO_2 maxima occur (Frankignoulle et al., 1998). In the Elbe estuary, observed maxima are found in the freshwater bearing OMZ, before the MTZ. The freshwater part is often omitted in studies and has a significant CO_2 contribution to the atmosphere. The overall annual emission of CO_2 from the OMZ is $1.3 – 2.0 \times 10^9$ mol a^{-1}, which makes up about 12-13 % of the total annual CO_2 emissions of the inner Elbe estuary (Tab. 4.2). This may not be the largest share of estuarine CO_2 emissions, but the high net emission of the MTZ is caused by its much greater extent (41 % of the inner estuary; Tab. 2.1). Emissions in the MTZ are most likely not only traced back to in situ production of CO_2, but also ascribed to advected dissolved CO_2 from the OMZ, which was not equilibrated due to shorter residence times here, compared to MTZ and post-MTZ.

Tab. 4.2: Sea-air fluxes of CO_2 in the different zones, divided into seasons. Fluxes are given in 10^6 per given period. Negative values indicate influx of CO_2. The second value gives the relative fraction of the total flux of the inner estuary during the respective period.

	sea-air CO_2 flux (calculation after Abril et al. (2009))				
	pre-OMZ [10^9 mol] / [%]	OMZ [10^9 mol] / [%]	MTZ [10^9 mol] / [%]	post-MTZ [10^9 mol] / [%]	Inner estuary [10^9 mol] / [%]
spring	-0.08 / -0.2	0.27 / 5.5	2.50 / 51.3	2.10 / 43.3	4.86 / 100
summer	0.02 / 0.4	0.97 / 17.2	3.16 / 55.9	1.50 / 26.4	5.66 / 100
fall	0.15 / 4.9	0.47 / 15.7	1.52 / 50.5	0.87 / 28.9	3.02 / 100
winter	0.10 / 4.5	0.29 / 12.7	1.12 / 49.8	0.74 / 33.0	2.24 / 100
annually	0.26 / 1.7	2.00 / 12.7	8.30 / 52.6	5.21 / 33.0	15.77 / 100

	sea-air CO_2 flux (calculation after Jiang et al. (2008))				
	pre-OMZ [10^9 mol] / [%]	OMZ [10^9 mol] / [%]	MTZ [10^9 mol] / [%]	post-MTZ [10^9 mol] / [%]	Inner estuary [10^9 mol] / [%]
spring	-0.01 / -0.2	0.18 / 4.8	1.97 / 52.4	1.61 / 42.9	3.76 / 100
summer	0.01 / 0.4	0.52 / 16.4	1.80 / 57.4	0.81 / 25.8	3.13 / 100
fall	0.11 / 4.9	0.35 / 16.1	1.12 / 52.1	0.58 / 26.9	2.16 / 100
winter	0.09 / 4.6	0.24 / 12.0	1.01 / 50.8	0.65 / 32.6	2.00 / 100
annually	0.20 / 1.8	1.28 / 11.6	5.90 / 53.5	3.66 / 33.1	11.04 / 100

4.4.4 CO_2 evasion in the seawater mixing stretch

The MTZ and post-MTZ are characterised by enhanced respiratory processes due to long residence times, leading to an increase of DIC as proven by positive excursions from a linear mixing line for DIC during summer and early fall (cf. Fig. 4.3). The observed depletion of $\delta^{13}C_{DIC}$ over the modelled conservative mixing corroborates that the non-conservative behaviour of DIC concentrations in July and August 2010 can be traced back to CO_2 production by respiration, which favours light C. This effect may be less pronounced than expected because consecutive evasion of CO_2 increases the ratio (Mook et al., 1974), thereby counterbalancing the $\delta^{13}C_{DIC}$ signal. Due to its large area and extended residence times, the inner salinity gradient is the largest CO_2 source to the atmosphere. At mean seasonal pCO_2 between 691–1,732 µatm (depending on season and location) 5.9–8.3 x 10^9 mol CO_2 (J08/A09) are degassed annually. Data on pCO_2 published by Brasse et al. (2002) from a cruise in spring 1997 falls within the observed pCO_2 range of this study. In the innermost sampling point of their cruise, they measured the lowest pCO_2 (650 µatm at about km 660) which is in the observed range of two surveys conducted in April 2010 and 2011. The decline towards the sea matches results from the April 1997 cruise. However, this does not represent a typical summer situation, which is characterised by the highest pCO_2 in the OMZ (2,170.5±736.3 µatm; Fig. 4.2).

Overall, this leads to a CO_2 efflux of 39.8-56.9 mol m^{-2} a^{-1} for the full inner Elbe estuary. This observation fits in the range of assessed CO_2 exchange rates for a comparable climatic setting, being higher than the estimate by Laruelle et al. (2010), but lower than the spatially more confined value by Chen et al. (2012) (Tab. 4.3). This confirms, that generalised models provide a suitable estimate of sea-air CO_2 fluxes, at least for the Elbe estuary, but it was already pointed out that data on European estuaries, which are polluted above average, is overrepresented (Laruelle et al., 2010).

Tab. 4.3: Compilation of literature data of sea-air CO_2 fluxes per area in comparison with data from this study. *lower value: calculation after Abril et al. (2009), higher value: calculation after Jiang et al. (2008).

type	CO_2 flux [mol m^{-2} a^{-1}]	reference
inner estuaries, 30°-60° latitude	46.00	Borges (2005)
tidal systems and embayments	28.5±24.9	Laruelle et al. (2010)
inner estuary (sal. 0-2)	68.5±25.6	Chen et al. (2012)
middle estuary (sal. 2-25)	37.7±16.5	
Elbe inner estuary (= tidal river + inner salinity gradient)	39.79-56.94*	this study

4.4.5 CO_2 fluxes through the inner estuary

The comparison of pCO_2 with data from the past proves the potential degradation of the system hypothesised in chapter 3, i.e. higher CO_2 evasion in the freshwater region with improvement of water quality. This is supported by the calculated total CO_2 production, including CO_2 that is evaded as well as transported further in dissolved form (Tab. 4.4).

Tab. 4.4: Estimated CO_2 production rates within the zones. These are derived by the difference between inflow and outflow of CO_2 in one zone, including the CO_2 flux from or to the atmosphere. The smaller number is derived by calculation of CO_2 fluxes based on Jiang et al. (2008) the higher number refers to calculations based on Abril et al. (2009).

	OMZ		MTZ		post-MTZ	
	CO_2 production		CO_2 production		CO_2 production	
	[10^9 mol $interval^{-1}$]	[mol m^{-2} d^{-1}]	[10^9 mol $interval^{-1}$]	[mol m^{-2} d^{-1}]	[10^9 mol $interval^{-1}$]	[mol m^{-2} d^{-1}]
spring	0.47-0.56	0.19-0.22	2.16-2.68	0.21-0.26	1.70-2.19	0.15-0.20
summer	0.79-1.25	0.32-0.50	1.73-3.10	0.17-0.30	0.94-1.62	0.08-0.14
fall	0.38-0.51	0.15-0.20	1.11-1.50	0.11-0.15	0.56-0.85	0.05-0.08
winter	0.34-0.38	0.13-0.15	0.87-0.98	0.09-0.10	0.65-0.74	0.06-0.07
annually	1.98-2.69	0.20-0.27	5.94-8.34	0.14-0.20	3.85-5.40	0.08-0.12

The absolute values are highest in the MTZ but the production per area is highest from summer to winter in the OMZ, with nearly twice the values of the MTZ. Being four times larger, the MTZ produces only twice the amount of CO_2. The OMZ can, therefore, be considered a hotspot for CO_2 fluxes.

Calculated CO_2 fluxes are possibly underestimated because diel fluctuations of CO_2 production were generally not considered in flux calculations. Primary production, which can counterbalance CO_2 production by heterotrophy, does not occur during night-time, so CO_2 levels can be elevated (Raymond et al., 1997). This process can be further enhanced by autotrophic dark respiration (Cole et al., 1992). However, both effects are considered to be of minor importance in large parts of the Elbe inner estuary due to the overall high CO_2 levels.

4.4.6 Diminished influence of carbonate dissolution on DIC

CO_2 is only a small fraction of the DIC, ranging from 0.2-5.7 % over the study period, and cannot account for the overall DIC increase. The major part of DIC production is traced back to alkalinity generation. Alkalinity is considered a rather conservative component in the carbon system, but it is in estuaries likely affected by processes like calcium carbonate dissolution/formation, (de)nitrification, sulphate reduction and others.

Kempe (1982b) observed a strong increase of TA in the low salinity region, i.e. the region comparable to the inner salinity gradient of this study. He traced the increase back to dissolution of imported marine carbonates that undergo a strong corrosion due to the high $p\mathrm{CO_2}$ and acidity of the discharged waters. This process was not observed in the study at hand. The data do not show strong changes in the relative carbonate bearing fraction of SPM in the low salinity area (Appendix D-2). Additionally, saturation indices of $CaCO_3$ are with one exception above zero, indicating oversaturation in contradiction to observations made by Kempe (1982b). This effect is strongly governed by the pH, which was below 7.6 on the cruise in 1985 and rarely dropped below 7.8 on the recent surveys. While carbonate dissolution may play a role in modern day estuaries, as observed in the Gironde (Abril et al., 1999) and the Loire (Abril et al., 2003), no significant effects were observed for the Elbe estuary.

4.4.7 Sulphate reduction effects on DIC counterbalanced by oxidation

It is assumed that sulphate reduction, which produces 2 moles of TA and DIC per mole S reduced (Krumins et al., 2012), plays no important role for alkalinity generation in the Elbe inner estuary in contradiction to other estuaries like the York river estuary, where reduction rates of 12 mmol S m^{-2} d^{-1} are proposed to balance a large part of excess DIC (Raymond et al., 2000). The coarse nature of sediments in the Elbe estuary in conjunction with oxygenated bottom waters due to constant mixing, leads to oxidation of any reduced species leaving the sediment, as was shown for rapid oxidation of ammonia in Elbe sediment cores by Neumann et al. (in prep).

4.4.8 Marsh export of DIC

Marshes a known to contribute to the DIC budget of the adjacent estuary (Cai et al., 1999). Wang and Cai (2004) estimated that 35.6 mmol C m^{-2} d^{-1} are exported as DIC from a marsh-dominated estuary in North America (Duplin River, Georgia). Observations for freshwater marshes at the York river estuary are with 44.9±22.5 mmol C m^{-2} d^{-1} in the same order of magnitude (Neubauer and Anderson, 2003). Most recent estimates by Weiss et al. (in prep.) show higher DIC export rates of up to 84.4 mmol C m^{-2} d^{-1} (annually integrated data from three marshes along the inner Elbe estuary). With roughly 95 % of the DIC being HCO_3^-, the high rates can explain a large part of the addition of TA to the Elbe salinity gradient during transects where a positive excursion from linear mixing was observed. In comparison, the "missing" TA in the York river adds up to 9 mmol m^{-2} d^{-1}(Raymond et al., 2000). This is an order of magnitude lower than estimated here, with a source of 120 mmol m^{-2} d^{-1} in the low salinity area MTZ.

4.4.9 Influence of the nitrogen cycle on DIC fluxes

TA can be drawn down by nitrification, a process which lowers TA by two moles per mole NO_3 produced. A data compilation by Berounsky and Nixon (1993) shows pelagic nitrification rates from <0.1 to 32 µmol N L^{-1} d^{-1}. If applied to the area of the Elbe MTZ, this process could decrease the TA by about 77 x 10^6 mol d^{-1}. Nitrification rates depend primarily on the availability of NH_4 and on temperature but are also governed by other environmental variables (Berounsky and Nixon, 1993 and references therein), so that a direct comparison gives an upper limit that is not met because NH_4 concentrations are rarely exceeding 10 µmol kg^{-1} (Appendix D-3). In the Scheldt, NH_4 levels were much higher and a direct relationship between NH_4 decrease and TA increase was observed on a cruise in 1993 (Frankignoulle et al., 1996).

On a contradicting side, denitrification is a source for TA and it is estimated that about 50 % of global DIN river inputs are removed in estuaries by denitrification (Seitzinger and Kroeze, 1998). In this context, Dähnke et al. (2008) revealed a change from a sink to a source for NO_3 in the low salinity stretch of the Elbe estuary, postulating a transition from a denitrification to a nitrification spot. The observation on nitrate sources could explain the observed sink of TA in this area during a few months, mainly during summer and early fall as shown in Fig. 4.4. Positive TA concentration excursions from conservative mixing in the salinity gradient are more pronounced than negative excursions, making the inner Elbe estuary an annual net source for TA. Yet, considering individual concentration changes during the 18 conducted campaigns, it is remarkable, that there is no general trend towards removal or addition of TA in any zone. The observed non-steady behaviour of nitrogen species NH_4 and NO_3 along the inner estuary (Dähnke et al., 2008) shows that different processes influence the nitrogen cycle in the Elbe estuary. Because (de)nitrification and TA production/consumption are coupled, impacts on the nitrogen cycle directly influence the carbon cycle. With the loss of its natural denitrification capacity, the inner Elbe loses a source for TA.

4.4.10 A tentative inorganic carbon budget

A tentative budget for the DIC fluxes in the inner Elbe estuary was constructed to evaluate the impact of sinks and sources on fluxes to the coastal ocean (Fig. 4.12). Annually, 53.6 x 10^9 mol C are brought to the OMZ from upstream and 18 % are added along the inner estuary on the way downstream. The largest part of DIC, 97 %, is in the form of alkalinity, because at pH values around 8, as observed in the study, the major component of DIC is HCO_3^- which contributes most of the TA at the given pH environment.

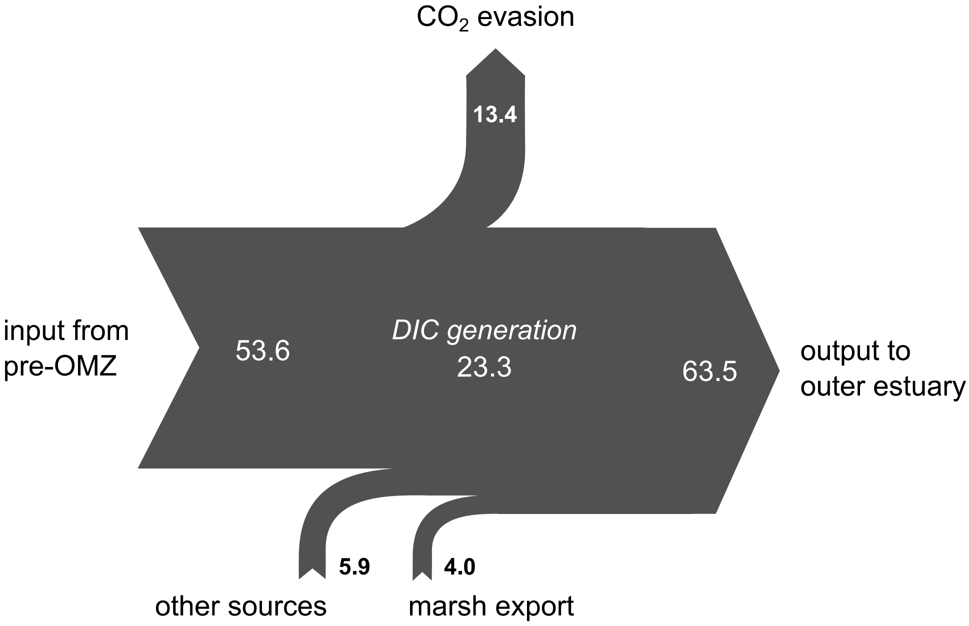

Fig. 4.12: A tentative budget for DIC fluxes (given in 10^9 mol a^{-1}) in the inner Elbe estuary. CO_2 evasion was calculated in this study, marsh export was estimated from data by Weiss (in prep.). Combined other sources are assumed to close the gap in the budget. To simplify the budget calculations, CO_2 fluxes, derived from two different equations, were averaged (cf. method section 5.2.2).

At least 23 x 10^9 mol DIC a^{-1} are produced between the OMZ and the post-MTZ. Although most of the added DIC is lost through CO_2 evasion, the estuary is a source for DIC. About 57 % of excess DIC are attributed to evasion (13 x 10^9 mol a^{-1}) and 43 % (10 x 10^9 mol a^{-1}) are transported seawards. Of the total estuarine DIC export, 17 % are released to the atmosphere and 83 % are discharged to the outer estuary. In comparison, Cai and Wang (1998) calculated for the Satilla river estuary that the total export of 1.98 x 10^9 mol DIC a^{-1} splits into 90 % CO_2 evasion and 10 % export to the adjacent ocean. In contrast, only a maximum of 4.6 % of the DIC delivery from the Changjiang River estuary (subtropical climate) is lost to the atmosphere (Zhai et al., 2007).

The Elbe estuary is characterised by average residence time of 3 weeks (Tab. 2.1), while the Satilla is characterised by longer residence times of about 8 weeks (Cai and Wang, 1998), and the Changjiang features fairly short residence times of a week or less (Qi et al., 2003 in Zhai et al., 2007). On the basis of this comparison, it is hypothesised that the water residence time in estuaries influences not only the remineralisation rate (Herman and Heip, 1999; Abril et al., 2002), but also the ratio between DIC export to the atmosphere and to the coastal zone.

The relationship shows further, that the Elbe although being heterotrophic and transferring high amounts of CO_2 to the atmosphere due to extended residence times, is still delivering a significant amount of DIC to the adjacent coastal zone. The importance of the DIC input from rivers to the coastal carbon cycle is highlighted by a study of the North Sea budget (Thomas et al., 2005). They point out that rivers are part of the major carbon sources to the North Sea. The authors rely on river DIC loads scaled up from data of BIOGEST programme, single measurements at the limit of tidal influence or further upstream. As stated, spatially heterogeneous distributions of DIC concentrations had to be ignored due to scarcity of data, and it was assumed that the riverine signal represents the loads that enter the German Bight (Pätsch and Lenhart, 2011). The study at hand is able to prove that mixing is not linear throughout time, and areas before the salinity gradient have the potential to alter the riverine DIC signal. A comparison with annual DIC fluxes from this study (average of three years of survey) and data from 2009 by Pätsch and Lenhart (2011) shows that their fluxes were underestimated by 30 % with respect to DIC (62.3 vs. 44.0 x 10^9 mol a^{-1}). This is an important finding, since the quality of model results of the North Sea carbon cycle depend, amongst others, strongly on well constrained riverine DIC sources (Kühn et al., 2010).

A comparison with the latest estimate annual global DIC exports via rivers to the oceans (0.325 Pg C a^{-1}; Hartmann et al., 2009) shows that 0.23 % are contributed by the Elbe. That is 1.5 % of the European river DIC export if data by Kempe (1979) are used. To put in a local perspective, the CO_2 release from the inner estuary amounts to 3-4 % of the annual CO_2 emissions of the city of Hamburg in 2010 (Statistikamt Nord, 2011),.

Advected CO_2 accounts for only a small part of the CO_2 release. It is a general observation that river waters are enriched in DIC on estuarine pathways due to their net heterotrophic nature (i.e. Smith and Hollibaugh, 1993). This excess DIC is to a large part released to the atmosphere due to extended residence times of the waters in the downstream region of the inner estuary. The data support the notion that estuarine filtering of POC (Abril et al., 2002; Amann et al., 2012) and DIC production are closely connected.

Other major DIC contributors are marshes. Most recent data from Weiss et al. (in prep.) show that marshes along the inner Elbe estuary (including the freshwater part) are responsible for about 17 % of the annual excess DIC produced in the estuary (4.0×10^9 mol DIC a^{-1}). In comparison, Neubauer and Anderson (2003) observed a much higher marsh contribution: About 47 % of excess DIC in the salinity gradient of the York estuary can be explained by export from adjacent marshes.

To close the gap in the budget, sources other than marsh export and estuarine respiration contribute 5.8×10^9 mol C a^{-1}. That is about 59.9 mmol m^{-2} d^{-1}. This rate falls within the observed range of benthic fluxes in three estuaries in Northern Spain (Ortega et al., 2005) and other coastal ecosystems, compiled in the same source. Benthic exchange is, consequently, considered the main contributor to the unexplained addition in the budget. Additional potential sources were discussed in the previous sections and cannot be determined due to the lack of data on DIC or TA derived by tributaries (which have been shown to be important to the silica budget as described in section 5), groundwater, and pelagic processes.

4.5 Summary & conclusion

1. The postulated importance of seasonality on CO_2 flux estimates, as most recently pointed out by Chen et al. (2012), was confirmed. Many studies on global upscaling of CO_2 fluxes base on a limited number of cruises, which did not consider all seasons. Estimates, which include data from the Elbe estuary (Frankignoulle et al., 1998; e.g. Borges, 2005), refer to a cruise in April. It is expected that upscaling on the basis of season specific data is leading to an underestimation if estuarine systems are comparable to the Elbe, which features the lowest observed pCO_2 in spring in the freshwater part.

2. It was hypothesised in chapter 3, on the basis of monitoring data, that the OMZ is a hotspot for CO_2 production. Now, this could be confirmed by more precise data from the ESTUCARB cruises. The prominence of the freshwater part was highlighted. It should be included in future estuarine carbon cycle estimates. 14 % of the inner Elbe estuary were omitted in previous studies. The most upstream part represents 4 % of the total area, is autotrophic and, therefore, a sink for CO_2 during spring, and a relatively weak source during the rest of the year. In contrast, the remaining 10 % are net heterotrophic throughout the year and contribute 12 % of the annual CO_2 flux to the atmosphere and 82 % of the dissolved CO_2, which is transported seawards. This implies generally that estimates of carbon fluxes may be erroneous, when an oxygen depleted area, present in most anthropogenically disturbed estuaries, is not located within the salinity gradient or when the freshwater part covers a significant portion of the total area. This is also a problem of the estuary definition. It is proposed to regard the full extent of the tidal influence as part of the estuary to cover areas of potentially high matter turnover.

3. On an annual timescale, the inner Elbe estuary is net heterotrophic and acts as a source for CO_2: 13.2×10^9 mol a^{-1} (47.8 mol m^{-2} a^{-1}) are released to the atmosphere. This high amount proves that an improvement of water quality does not necessarily imply a strong decrease in CO_2 emissions.

4. Additionally, the system is a source for DIC and TA, because the major component of DIC is bicarbonate. 23×10^9 mol DIC a^{-1} are produced. About half of the excess production is derived from marshes, benthic exchange, and other undetermined sources. Adding DIC to the riverine delivery, the inner Elbe estuary may pose a relevant factor in North Sea budgets.

5. Although an annually averaged addition of DIC and TA was observed, a comparison of individual transects did not show a clear trend towards removal or addition of DIC or TA. As the nitrogen cycling impacts the carbonate system, findings of increased nitrification processes (Dähnke et al., 2008) directly implicate a potential TA removal in the Elbe estuary. Thus, nitrification rates are needed to assess the impact on TA fluxes in the estuary.

6. For the first time, isotopic data of DIC were shown for the Elbe estuary. They provided further evidence for the dominance of respirational processes. Hotspots are the OMZ and the MTZ. Because of the much greater area of the MTZ it is the main contributor of CO_2, although pCO_2 and exchange rates are higher in the OMZ.

7. Dredging of the navigational channel has been shown to influence the shallow water areas that are important for the oxygen budget of the estuary (Kerner, 2007). The sediment removal also impacts the benthic exchange and supposedly an important TA supply to the estuarine waters. Therefore, anthropogenic changes have to be evaluated not only with respect to hydrodynamical impacts, but also to biogeochemical repercussions. The direct intervention by humans could lead to a significant decrease of TA delivery to the North Sea in the future.

8. Borges et al. (2006) postulated that the current approach of CO_2 flux upscaling suffered from inadequate surface area estimates. For a more constrained CO_2 budget, the surface of the inner Elbe estuary was determined via GIS approach. A comparison with surface area data given by Borges et al. (2005) shows that the area could, in fact, be overestimated by 18 %. This overestimation is relatively low considering it was a rough approach. The question remains: When and why are simple approaches good enough global upscaling analysis?

9. When calculating pCO_2 from pH and DIC or TA, the use of equilibrium constants and means of calculation have to be chosen with care. Salinity plays an important role in the estimation of ion activity of the sample. In estuarine studies, calculations often rely on salinity measurements via conductivity or other methods derived from oceanic research, referring to the ion composition of marine waters. In the Elbe estuary, the low salinities do not merely reflect diluted marine waters, but represent the ionic composition based on catchment lithology. Hence, it is necessary to calculate the ion activity product based on the actual ion data from each sample to derive a reliable pCO_2 value in the end. For the obtained

samples, a common approach with *CO2SYS* (Lewis and Wallace, 1998) leads to an overestimation of more than 20 %.

5 Silica dynamics of the inner Elbe estuary

5.1 Introduction

Silicon (Si) accounts for one quarter of the earth's crust as silicon dioxide (SiO_2). Many rock types consist of silicate minerals, which incorporate SiO_2. Through weathering of silicates, Si is dissolved and mobilised in the form of silicic acid (H_4SiO_4). This dissolved Si (DSi) is transported via rivers to the ocean. Along the way, it is utilised by organisms that transform DSi into particulate biogenic silica (BSi) (Lauerwald et al., 2012; Struyf and Conley, 2012 and references therein). DSi is an essential nutrient for aquatic organisms like diatoms, radiolaria and sponges, which need the element to build their skeletons and spicules. Higher plants can build up siliceous structures called phytoliths.

Diatoms are the most important aquatic organisms in the silica cycle and can be found all over the globe. They reproduce extensively during spring and summer and form algal blooms, which consume DSi from the water column, leading to the formation of BSi. This BSi is found in the water column and sediment of lakes, rivers, and the ocean. For this reason, it is considered an important component of the silica budget (Conley, 1997). Solubility of BSi increases in the presence of seawater and bacteria (Roubeix et al., 2008), and it becomes available again for organisms as DSi. Inorganic processes, on the other hand, contribute to the drawdown of DSi in the water column of estuaries and coastal zones. Reverse weathering processes and the formation of authigenic clay minerals have been proposed as a sink (Michalopoulos and Aller, 1995), as well as the adsorption of DSi onto suspended particles (Bien et al., 1958).

On their way to the coastal zone, fluxes of DSi and BSi have to pass estuaries, the transition from land to ocean. These estuaries can act as filters and may add, retain, and alter silica components (e.g. Arndt et al., 2009). Thus, estuaries play an important role in land-ocean silica fluxes. Estuaries are highly diverse ecosystems and often anthropogenically disturbed. In the Elbe estuary, population densities are high and industrial activities abundant. Due to the tidal influence, the residence time of the water body is prolonged, making it an efficient biogeochemical reactor. While many studies on estuaries around the globe follow the estuary definition by Pritchard (1967), which doesn’t include the tidally influenced freshwater areas, this study refers to the inner estuary as defined by Fairbridge (1980; in Elliot and McLusky, 2002) as consisting of two parts: “a middle estuary subject to strong salt and freshwater mixing; and an upper or fluvial estuary, characterized by freshwater but subject to strong tidal action. The limits between these sectors are variable and subject to constant changes in the river discharges.”

The watersides of estuaries are often lined with marshes that diurnally exchange water with the estuary. Struyf et al. (2006) showed for the Scheldt estuary that DSi is exported from marshes into the adjacent estuary and BSi is imported with the estuarine flooding water during summer. Similar findings were shown recently for the Elbe estuary by Weiss et al. (2012), who suggested that during summer, the adjacent marshes along the salinity gradient are able to replenish DSi depleted estuarine waters.

River damming and intensified input of nitrogen (N) and phosphorus (P) led to a decrease of DSi concentrations in river water that is delivered to the ocean (Conley et al., 1993; Humborg et al., 1997; Beusen et al., 2009). The excess of N and P in the river water through agriculture, industry, and domestic wastewater inputs, has led to a shift in nutrient ratios. The nutrient ratios needed for diatom growth vary strongly, depending on the species and habitat (Brzezinski, 1985; Dortch and Whitledge, 1992, and references therein). Billen and Garnier (2007) use a C:N:P:Si ratio of 106:16:1:20 as an average value for their nutrient flux studies to the coastal zone. If the Si:N value drops significantly below 0.8 and Si:P shifts to values below 20, development of dinoflagellates, which do not need Si for their growth, is promoted. This can cause extensive harmful algal blooms (e.g. Officer and Ryther, 1980; Smayda, 1990; Hallegraeff, 1993) which may even exert a certain pressure on public health (Morris Jr., 1999). With DSi potentially depleted in estuarine and coastal waters, it is important to examine BSi as another silicon source in the coastal zone (Conley, 1997).

It is estimated that around 1.1×10^{12} mol BSi a^{-1} (Conley, 1997; Laruelle et al., 2009) are delivered via rivers to the ocean. Estimates for the export of DSi range from 5.6 (Tréguer et al., 1995) - 6.2×10^{12} mol a^{-1} (Dürr et al., 2011). Beusen et al. (2009) modelled an export of 5.2 Tmol DSi yr^{-1}, taking retention by river damming into consideration. Overall, that indicates that a significant part of the total silicon export by rivers, about 15 %, is BSi. Based on data compiled by Tréguer and De La Rocha (2013), globally about 20 % of all Si, delivered by rivers, is retained in estuaries. However, BSi was rarely measured in estuaries if compared to studies of DSi distributions (Chou and Wollast, 2006, and references therein).

Global estimates of BSi fluxes may be biased due to the fact that most data come from river dominated systems with rather short residence times in the inner estuary. Although some of the investigated rivers/estuaries feature above average discharges (e.g. the Amazon) and contribute the largest part of silica fluxes to the ocean, based solely on the sheer volume of discharge, it remains uncertain how systems with much longer residences and less discharge behave in terms of silicon dynamics. Anderson (1986) and recently Carbonnel et al. (2012) pointed out that BSi is not necessarily coupled to DSi uptake. BSi is preferentially settled in the Scheldt estuary, leading to a decreased export of BSi (Carbonnel et al., 2012).

Si budget studies have to rely on datasets of only a few estuarine systems around the globe. In this study, DSi and BSi data are presented from 18 transects along the inner estuary during all seasons from 2009-2011. In addition, DSi data of the past 20 years from governmental water quality monitoring are analysed, as well as supporting suspended matter (SPM) and macro nutrient data. Historical BSi data were calculated from a BSi/POC relationship. The extent of spatial and temporal Si dynamics covered by data in an inner estuary, comparable to the Elbe, is only met by the Scheldt (Carbonnel et al., 2009; Carbonnel et al., 2012). In this chapter, spatial analysis was performed to identify key areas for silicon production and consumption. Annual fluxes from the Elbe River, the tidal freshwater part and the inner salinity gradient are investigated in an attempt to unravel the Si filtering function of the inner Elbe estuary.

5.2 Methods

For a better differentiation of the spatial patterns of Si dynamics, the inner estuary was divided into four distinct zones with differing major biogeochemical processes, as described in chapter 2.

5.2.1 Sampling and analysis

Surface water samples (~0.5 m depth) were obtained with a NISKIN type vertical water sampler. Subsamples for silica analysis were drawn after shaking the sampler for a homogeneous aliquot. The sample was filtered on a polypropylene Millipore filtration unit, using 0.45 µm pre-weighted polycarbonate filters (Sartorius®, ∅ = 47 mm). The filtrate was stored until analysis in polyethylene bottles at darkness and 4°C. Filters were stored frozen and subsequently dried at 40°C within 24 h after sampling.

Analysis of DSi was done via spectrophotometric determination of blue silicomolybdic acid, described in Grasshoff et al. (1999). BSi was analysed basically following the sequential wet chemical extraction method described by DeMaster (1979, 1981) to correct for mineral contribution during dissolution of suspended matter. Filters were put into flat bottom plastic vials containing 1 % reagent grade Na_2CO_3 solution and left for digestion in a shaker bath at 85°C. After three, four, and five hours, subsamples were taken from each bottles, neutralised with 0.021N HCl and analysed as described above for DSi. Resulting concentrations were plotted against digestion time and the y-intercept of a least squares regression line determined the concentration of BSi in the sample. If a significant slope could not be identified, a mean value of all digestion steps was used to calculate the BSi content of the sample (Conley, 1998). Due to the complications that arise in digestion because of the potential interference of silicate minerals (Ragueneau and Treguer, 1994), analytical precision varies (Conley, 1998).

The Elbe estuary has been intensively monitored in terms of water quality by local authorities. Earliest available data are from the 1950s (Kempe, 1982a). For DSi and POC, data exist from 1990-2010. Longitudinal profiles along the estuary with on average one sampling station every ten kilometres were sampled nearly monthly with a focus on the summer months, while several fixed stations along the gradient delivered monthly data (on average; used stations are marked in Fig. 2.1) (FGG Elbe, 2012). DSi has been analysed spectrophotometrically, similar to the method described above. Data from the FGG Elbe (2012) for particulate organic carbon (POC) were derived from analysis of total and dissolved organic carbon. These were determined via catalytic high-temperature oxidation and CO_2 detection via infrared detector (DIN 38409-H3-1/ EN 1484-H3). POC data determined from samples within the ESTUCARB project were determined with a Carlo Erba NA-1500 elemental analyser following the method by Nieuwenhuize et al. (1994). Nitrogen species and phosphate were analysed photometrically by a Technicon AutoAnalyzer System III. Details are given in section 4.2.5.

All available data were compiled into one single database. For this reason, averaged data contain all three types of samples where available, (i.e. ESTUCARB profiles, monitoring profiles and fixed stations), unless stated otherwise.

5.2.2 Silica mixing models

To evaluate these DSi additions along the salinity gradient and the consequent DSi export from the inner estuary to the North Sea, an estuarine mixing model was applied to account for dilution effects from seawater. This was done according to the standard estuarine mixing model (Boyle et al., 1974; Liss, 1976; Officer, 1979; Kaul and Froelich, 1984), which assumes a steady-state of the system. With prolonged residence times and fluctuating discharge in the Elbe estuary, deviations from the steady state introduce errors. In consequence, given calculations can only provide a first estimate.

Non-linear regression functions were calculated to fit the measured data of four cruises, for which enough data were available from the salinity gradient to construct a model (Fig. 5.1). Third order polynomials were suitable to describe the distribution convincingly in three cases. In July 2010, the scarcity of samples leads to misrepresentative equations, so that data were added, assuming a linear mixing between the last two data points. The added data led to a well fit by a 5-degree polynomial (Tab. 5.1; Fig. 5.1). The fitted DSi concentration curve includes concentration changes due to release from discussed sources along the gradient as well as from tidal mixing with seawater. To determine the magnitude of additions apart from the mixing, it is necessary to factor out the influence of seawater, deriving an effective concentration (c*) (Liss, 1976) that is corrected for seawater dilution:

$$c^* = c_y - S_y \frac{c_y - c_x}{S_y - S_x}. \qquad \text{Eq. 5.1}$$

This is done based on a partition of the area covered by the salinity gradient in multiple compartments. Each compartment represents one salinity unit up to the maximum measured salinity of the cruise. c_x and S_x represent DSi concentration and salinity in the upstream preceding compartment. c_y and S_y represent DSi and salinity in the downstream following compartment. Through the determination of the effective concentration, the flux of DSi can be calculated:

$$F_{DSi} = Q \times c^*. \qquad \text{Eq. 5.2}$$

Q is the discharge, which is adapted in downstream direction to account for additions from tributaries. With this equation, flux calculations were made for the delivery from the freshwater zone as well as for the output to the outer estuary. The difference between those fluxes is the total addition along the gradient (calculation 1 in Tab. 5.1). The addition flux can be separately calculated as

$$F_{add} = Q \times ({c^*}_{max} - {c^*}_{tidalriver}), \qquad \text{Eq. 5.3}$$

where c^*_{max} is the maximum effective concentration observed and $c^*_{tidalriver}$ is the DSi concentration at the last non-saline sampling point (calculation 2 in Tab. 5.1).

Calculations 1 and 2 yield different results that range from 3 % underestimation to 21 % overestimation of fluxes (Tab. 5.2). This is due to the fact that a real data point was chosen for the input flux from the tidal river, while the effective concentration bases solely on a constructed concentration curve that is not overly precise, especially for low salinities. Because sampling was terminated at the outmost point of the inner estuary (i.e. river-km 724, near the city of Cuxhaven), the addition up to this point was calculated by assuming a “virtual” endmember at the maximum sampled salinity. The total amount of added DSi could only be determined by sampling the full gradient up to a salinity of 30-33 (North Sea endmember, Schott, 1966 in Scheurle et al., 2005).

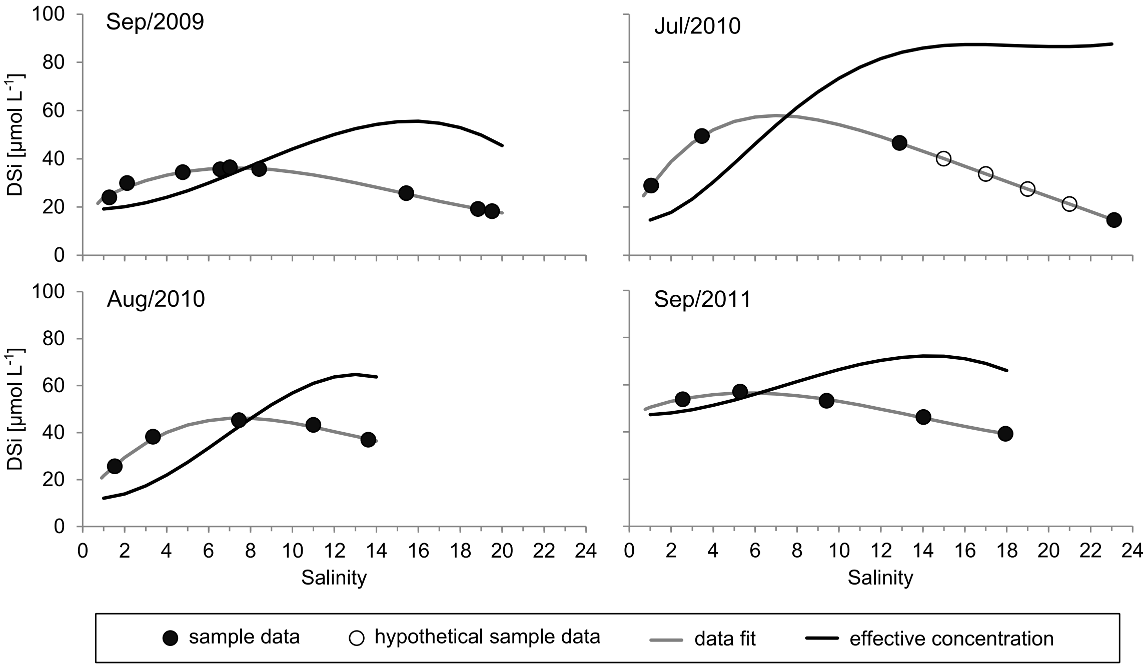

Fig. 5.1: Measured DSi concentrations along the salinity gradient during four cruises of the ESTUCARB project (filled circles). The dotted line shows the polynomial fit (3rd order, except Jul/2010: 5th order) that represents the DSi distribution best. The solid line shows the effective DSi concentration after correcting for the mixing with seawater. The open circles are assumed concentrations based on linear mixing between the last two sampling points to force a reasonable fit.

Tab. 5.1: Parameters of the modeled DSi development dependent on salinity. Third-order polynomials need b-parameters 0-3: $DSi = b0 + b1 \times Sal + b2 \times Sal^2 + b3 \times Sal^3$; DSi distribution in July 2010 was best described by a fifth-order polynomial: $DSi = b0 + b1 \times Sal + b2 \times Sal^2 + b3 \times Sal^3 + b4 \times Sal^4 + b5 \times Sal^5$.

Month/year	b0	b1	b2	b3	b4	b5	r^2
Sep/2009	19.238	5.214	-0.471	0.010	-	-	0.990
Jul/2010	15.160	14.801	-1.883	0.093	-0.002	2.049×10^{-5}	1.000
Aug/2010	12.079	10.601	-1.008	0.027	-	-	0.988
Sep/2011	47.356	3.527	-0.391	0.009	-	-	0.996

Tab. 5.2: Calculated addition fluxes from the estuarine mixing model. Calc. 1 and calc. 2 refer to the two different calculation methods as described in section 5.2.2.

Month/ year	DSi flux from tidal river	DSi flux from km 724	Addition (Calc. 1)	Addition (Calc. 2)	Deviation calc. 1 and 2
		10^6 mol d^{-1} / 10^6 mol mo^{-1}			%
Sep/2009	0.24 /7.19	1.31 / 39.41	1.07 / 32.22	1.03 / 30.80	4.6
Jul/2010	0.54 / 16.68	3.10 / 96.07	2.56 / 79.39	2.29 / 71.09	11.7
Aug/2010	0.82 / 25.29	3.76 / 116.51	2.94 / 91.22	3.03 / 93.93	-2.9
Sep/2011	2.28 / 68.43	4.10 / 123.03	1.82 / 54.60	1.51 / 45.16	20.9

5.2.3 Silica flux calculation

DSi and BSi loads were calculated by multiplying discharge (Q) and Si concentration (c_{Si}):

$$load = Q \times c_{Si} \, . \qquad \text{Eq. 5.4}$$

DSi and BSi data from the years 2000 to 2011 were taken into account to calculate monthly mean values for the discharge and Si concentrations (Tab. 5.3), as only this period is believed to represent a reasonably constant ecosystem state (cf. chapter 3). The river input and the estuarine freshwater input were calculated by averaging the DSi concentrations of all sampling points between Elbe-km 585-595 and Elbe km 649-661, respectively (Tab. 5.3; black bars in Fig. 2.1C). Discharge was recorded at a gauging station at km 536 (located near Neu Darchau, operated by the Waterways and Shipping Administration of the Federal Government) and had to be corrected for inflows from tributaries and diffuse sources on the way downstream. Data from August of 2002 were omitted in the mean calculation because of an extraordinary rainfall event in the upper catchment area during this month, leading to a discharge of 3,410 $m^3 s^{-1}$. In comparison, the calculated long term mean discharge in August is 464±291 $m^3 s^{-1}$ (n=3,472). DSi and BSi concentrations were monthly averaged before calculating the load to account for the fact that three compared zones have not always been sampled on the same day or week. Strong temporal and spatial fluctuations would lead to large error bars in the estimation of addition or removal of Si (Fig. 5.5). Calculated loads are given in 10^6 mol $month^{-1}$ and error bars indicate the standard deviations of the product:

$$\sigma_{load} = \sqrt{(\frac{\sigma_{c_{DSi}}}{c_{DSi}})^2 \times (\frac{\sigma_Q}{Q})^2} \times load \, . \qquad \text{Eq. 5.5}$$

Load differences are calculated by subtracting the load of the upstream zone from the load of the downstream zone ($\Delta load = load_{EFI} - load_{RI}$). The calculated differences are also given in 10^6 mol $month^{-1}$ with negative values indicating a loss and positive values a gain in the given zone (Fig. 5.6). Error bars indicate the standard deviations (σ) of the difference:

$$\sigma_{load\Delta} = \sqrt{{\sigma_{load_{EFI}}}^2 + {\sigma_{load_{RI}}}^2}. \qquad \text{Eq. 5.6}$$

Tab. 5.3: Monthly averaged discharge, DSi, and BSi concentrations calculated for the river input and the estuarine freshwater input. Monthly load calculation is based on this data.

	month	**discharge [m^3 s^{-1}]**			**DSi [µmol L^{-1}]**			**BSi [µmol L^{-1}]**		
		mean	*n*	*stddev*	*mean*	*n*	*stddev*	*mean*	*n*	*stddev*
River input	1	905.3	372	701.4	205.2	8	23.8	-	-	-
	2	1076.0	339	499.0	183.8	16	13.4	19.0	13	12.4
	3	1200.7	372	498.3	154.6	12	47.2	31.6	1	-
	4	1163.0	360	574.1	88.0	9	50.4	-	-	-
	5	633.4	372	217.9	28.5	18	69.5	56.4	17	28.7
	6	507.7	360	230.2	18.0	16	28.0	41.9	16	21.4
	7	428.6	372	154.5	28.0	19	35.8	51.4	18	25.1
	8	462.7	341	277.6	28.5	14	47.8	40.0	14	26.0
	9	495.1	360	293.6	97.2	8	80.2	-	-	-
	10	541.5	372	338.5	122.3	7	76.7	-	-	-
	11	629.1	360	416.6	158.3	17	45.2	8.2	15	5.2
	12	764.5	372	463.5	192.7	8	30.3	-	-	-
Estuarine freshwater input	1	994.0	372	770.1	197.9	21	17.9	126.2	4	29.3
	2	1181.5	339	547.9	188.6	24	8.9	65.4	38	42.6
	3	1318.4	372	547.1	171.3	22	18.6	102.0	5	63.5
	4	1277.0	360	630.4	109.0	22	37.2	48.9	8	26.5
	5	695.5	372	239.3	31.4	27	21.3	36.5	37	16.1
	6	557.4	360	252.8	13.0	27	11.2	43.7	35	19.2
	7	470.6	372	169.6	12.5	31	11.5	42.3	38	13.2
	8	508.0	341	304.8	12.4	35	11.3	55.6	32	28.2
	9	543.7	360	322.4	41.2	24	51.1	75.8	9	48.3
	10	594.6	372	371.7	70.4	20	54.9	-	-	-
	11	690.8	360	457.5	137.5	26	45.8	56.6	36	31.0
	12	839.4	372	508.9	180.0	19	18.9	99.8	5	51.5

5.3 Results

The results in section 5.3.1 and 5.3.2 refer only to data gained from ESTUCARB cruises (Tab. 2.2) and exclude monitoring data, to allow the direct comparison of BSi and DSi concentration development along the inner Elbe estuary. Data from the monitoring programme and the recent cruises are used to calculate monthly mean fluxes in section 5.3.3 - 5.3.5.

5.3.1 Winter silica concentrations

DSi winter concentrations show a relatively homogeneous distribution throughout the freshwater part of the estuary (Fig. 5.2, for larger figures of individual cruises refer to Appendix D-4). Four surveys were conducted during winter season, which is characterised by river discharge, ranging from about 600 $m^3 s^{-1}$ in December 2011 to about 1600 $m^3 s^{-1}$ in February 2011 (Tab. 2.2). The freshwater boundary is located between Elbe km 690-700 during these times. In summer, the freshwater boundary shifts to Elbe km 670-680 due to lower discharge. There is a slight increase in DSi concentrations in downward direction from about 180 µmol L^{-1} in the pre-OMZ to around 190 µmol L^{-1} at the last freshwater station in the MTZ. As soon as seawater is mixed in, the concentrations decline linearly, indicating conservative mixing (post-MTZ; Fig. 5.2). This is confirmed by a mean winter DSi concentration of ~50 µmol L^{-1} at Elbe-km 757 more downstream, at a salinity of ~26 (FGG Elbe, 2012). BSi concentrations are very low during winter in the pre-OMZ (~15 µmol L^{-1}) and rise downstream to a maximum of ~100 µmol L^{-1} in the MTZ, afterwards decreasing to 80 µmol L^{-1} and less (Fig. 5.2). The particulate form of Si behaves similarly to the total SPM concentrations. The fraction of BSi relative to total SPM fluctuates over the transect with values around 6 %, while BSi varies significantly between the cruises because of the natural system variability in space and time.

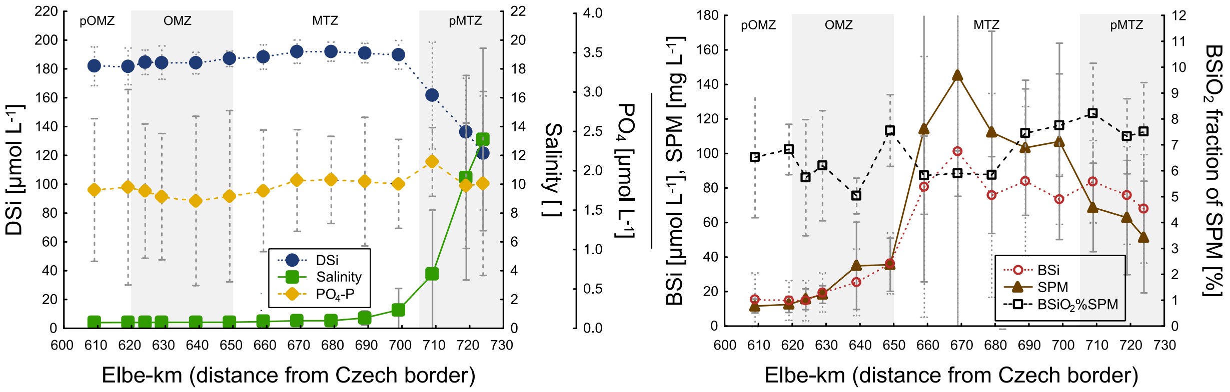

Fig. 5.2: Winter development of mean DSi (filled blue circles) and PO4 (filled yellow diamonds) concentrations, Salinity (filled green squares), BSi (open red circles), SPM (filled brown triangles) concentrations, as well as the BSi fraction of SPM (open black squares) along the inner estuary from the weir in Geesthacht (km 585.5) seawards to Cuxhaven (km 724). All data points are averages of data collected during several months in the respective season. Bars mark the standard deviation of the mean.

5.3.2 Summer silica concentrations

During summer, low levels of DSi concentrations are observed in the water column (Fig. 5.3). Already low DSi concentrations in the pre-OMZ (<10 % of the winter value) decline further downstream to less than 5 % of what is observed during winter, while increasing again in the MTZ. BSi concentrations follow the SPM concentrations with maxima in the MTZ, and the relative part of BSi declines from the river value (~18 %) to the post-MTZ (~6 %).

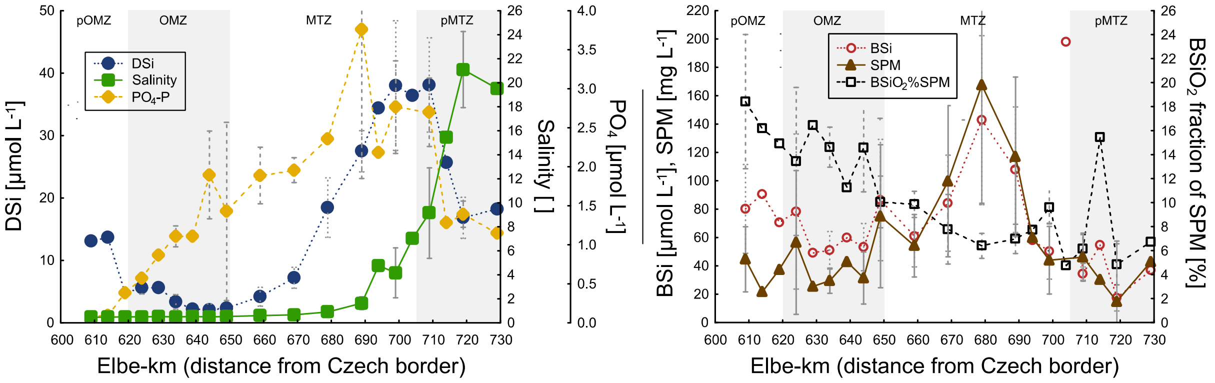

Fig. 5.3: Typical summer development of mean DSi (filled blue circles) and PO_4 (filled yellow diamonds) concentrations, Salinity (filled green squares), BSi (open red circles), SPM (filled brown triangles) concentrations, as well as the BSi fraction of SPM (open black squares) along the inner estuary from the weir in Geesthacht (km 585.5) seawards to Cuxhaven (km 724). All data points are averages of data collected during several months in the respective season. Bars mark the standard deviation of the mean.

In contrast to the near DSi depletion situation - especially in the upstream areas – a characteristic DSi elevation was observed in the area of the pre-OMZ and parts of the OMZ during four cruises (July/October 2009, August 2010 September 2011) (Fig. 5.4), with DSi concentrations of 60-90 µmol L^{-1}, which drop throughout the OMZ to a mean DSi concentration of 12 µmol L^{-1}. In contrast to the “depleted DSi situation”, BSi concentrations do not mirror the SPM distribution exactly. In the pre-OMZ and beginning of OMZ, BSi concentrations are fairly constant around 70 µmol L^{-1} and rise in the MTZ until values decline from the MTZ seawards, where levels stabilise at BSi concentrations around 30 µmol L^{-1}.

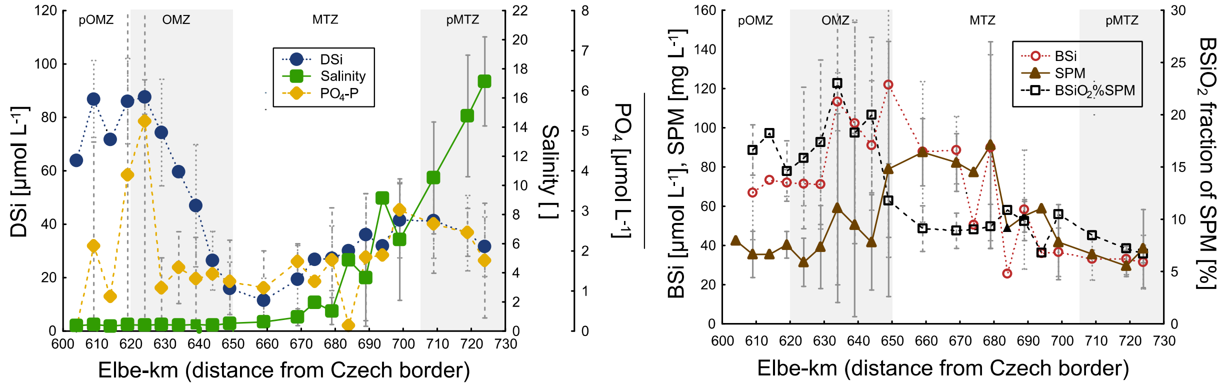

Fig. 5.4: A different summer development of mean DSi, PO_4 concentrations, BSi, and SPM concentrations. Compare for Fig. 5.3 for more information on plotted data.

5.3.3 Seasonal DSi fluxes using monthly averaged data

Discharge controls the seasonal pattern of fluxes from the river to the freshwater part and out of it (Fig. 5.5). Fluxes into the freshwater part are around 500 x 10^6 mol month^{-1} during winter and drop about 95 % towards summer (Fig. 5.5A). Due to tributaries and other sources, fluxes leaving the freshwater part are elevated in winter (~550 x 10^6 mol month^{-1}), if compared to the river input, and they decrease towards summer to 3 % of the winter value (Fig. 5.5B). During March, the largest absolute additions of DSi to the freshwater area are observed (Fig. 5.6A), while the largest relative gain is observed in April (~35 %, Fig. 5.6B). The difference can be explained by the onset of increased DSi consumption in the upstream fluvial system, while discharge is still high. Yet, tributaries lining the freshwater area of the estuary still have higher DSi concentrations, so that the relative contribution, compared to the river DSi input, is higher.

The absolute losses of DSi during the warm months (June- October) are small compared to winter fluxes, but the relative loss of DSi with up to 50 % highest (cf. discussion of nutrient limitation below).

During winter and transition time, losses and additions lead to a net gain of about 100 x 10^6 mol DSi which represents 7 % of the riverine input, while a net loss of about 9 % is estimated for spring, summer and autumn (Tab. 5.4). This loss is strongly attenuated by a high positive value in April. November and March are considered transitional months and add an overall 96 x 10^6 mol DSi to the equation (Fig. 5.6A). Overall, this leads to a net addition of 130 x 10^6 mol DSi per year in the tidal freshwater part of the Elbe estuary. This value represents 4 % of the DSi that is annually delivered to the estuary by the Elbe River (Tab. 5.4).

Tab. 5.4: Seasonal fluxes of Si. Winter refers to December-February, transition season includes early March and November and spring, summer and autumn refer to April-October.

	DSi (10^6 mol season^{-1})	**DSi** (% of river input)	**BSi** (10^6 mol season^{-1})	**BSi** (% of river input)
winter	100.0	7.3	337.6	301.5
transition	95.9	12.7	288.0	33.7
spring, summer, autumn	-66.2	-9.4	-49.2	-7.2
annually	129.6	4.4	576.4	55.1

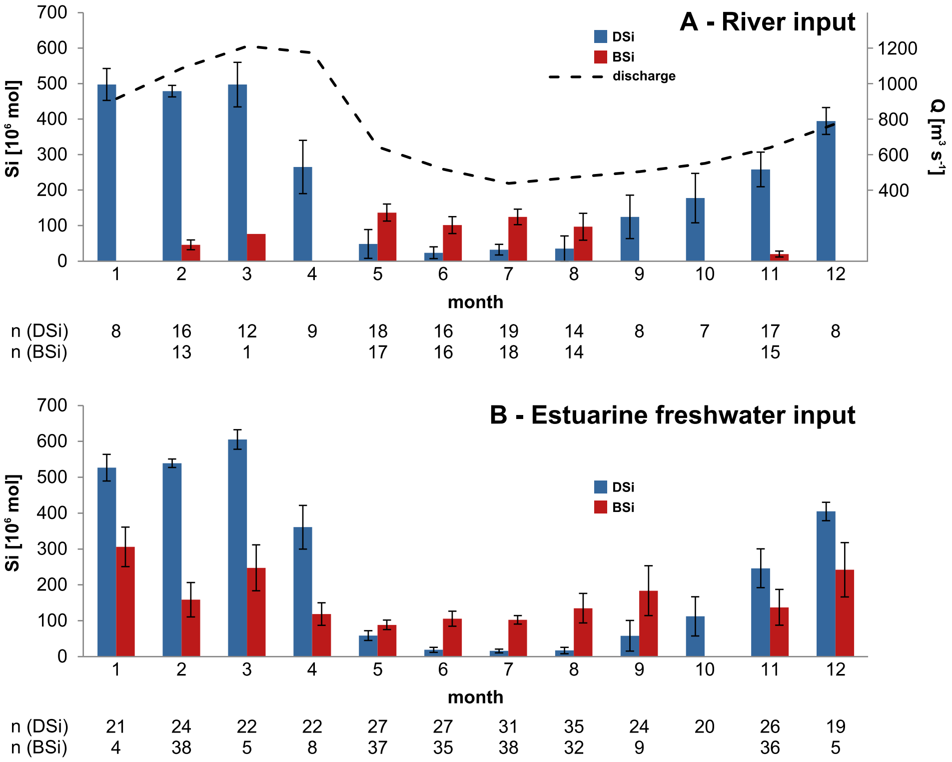

Fig. 5.5: Monthly mean loads of DSi and BSi discharged from the Elbe river (A) and the freshwater part of the estuary (B). Error bars indicate standard deviations. Number of measurements (n) taken into account for the calculation are given below the graphs. The dashed line in A shows the long term monthly mean discharge (Q).

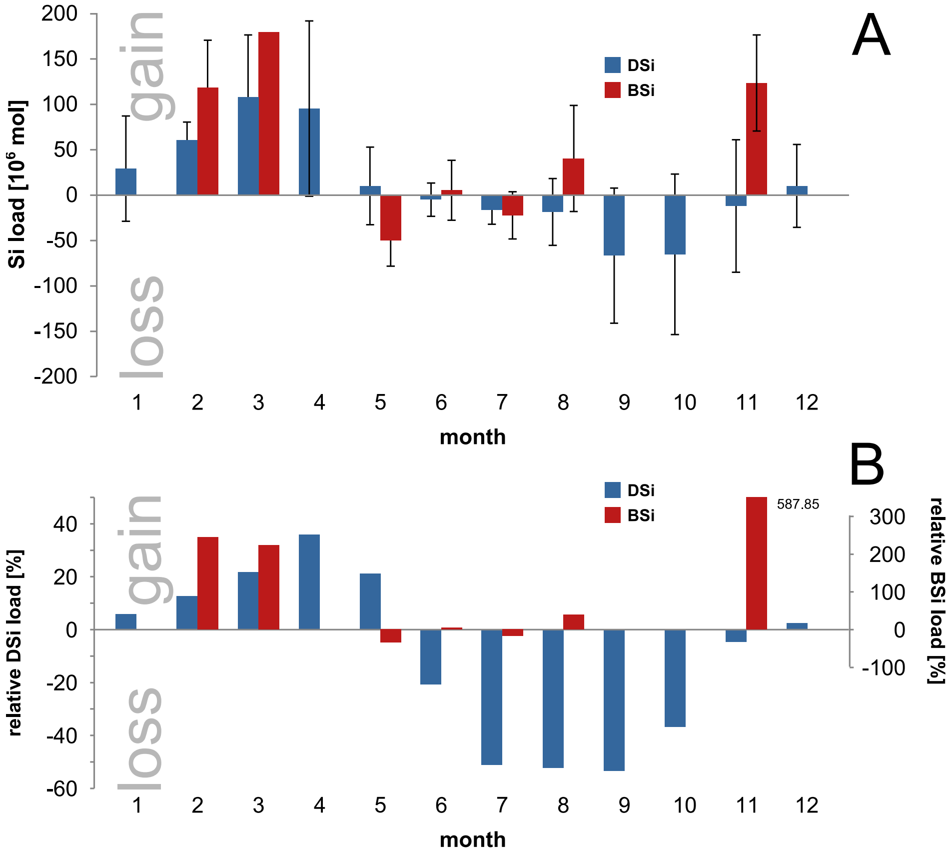

Fig. 5.6: A – Monthly DSi and BSi loads that are gained (positive values) or lost (negative values) along the tidal river between the river input (km 585.5 and the end of the freshwater part (km 661). Error bars indicate the standard deviations derived from error propagation. B – Relative loss or gain of monthly BSi and DSi loads compared to the river input (RI). Please note that values for DSi refer to the left y-axis and values for BSi refer to the right axis.

5.3.4 Reconstruction of historical BSi data from POC monitoring data

Compared to the amount of DSi studies in estuaries around the world, investigations on BSi are relatively rare. This holds true for the Elbe estuary, where BSi was not measured before, and the ESTUCARB surveys cover a relatively short time period with regard to a historical development.

Therefore, a method to estimate past and future BSi trends was needed: The analysis of recent POC and BSi data revealed a good correlation between the parameters. A large part of the ESTUCARB measurements are from the MTZ, defined by SPM accumulation, thus, a correlation of two particulate substances is implicated. This fact made it necessary to distinguish zones and seasons (Tab. 5.5). Zones were chosen as described in chapter 2. Seasons were split into cold (November-March) and warm (April-September), while October was omitted due to strongly fluctuating values. The overall linear relationship between BSi and POC holds true for the specified zones and seasons with the exception of data from the post-MTZ, which show no correlation ($r^2 = 0.06$; Tab. 5.5). Values in the pre-OMZ during the warm season are only linearly correlated up to POC values of about 500 µmol L^{-1} (Fig. 5.7).

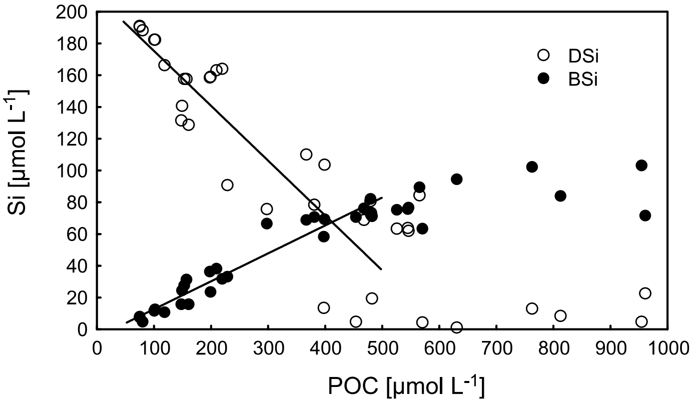

Fig. 5.7: Relationship of BSi (filled circles) and DSi (open circles) with regard to POC during the warm season (April-September) in the pre-OMZ. The regression lines show a linear relationship with POC for both fractions up to POC concentrations of 500 µmol L^{-1}. BSi trend: p=0.0000; $r^2 = 0.76$; DSi trend: p=0.000; $r^2 = 0.80$.

At higher POC concentrations, the BSi concentrations level out on values of around 80 µmol L^{-1}. This relates directly to decreasing DSi concentrations in this time and zone, which reach depletion at POC concentrations of about 500 µmol L^{-1}. The consumption of DSi is higher than the formation of BSi, indicated by the slope of the linear regression of DSi concentrations, which is steeper than the BSi regression line. This indicates that consumption of DSi is not directly connected to the BSi formation in the water column. The limited linear relationship between DSi and BSi could not be observed to this extent for the other zones and seasons.

As a result of the observed POC:BSi relationship (Tab. 5.5), BSi concentrations were calculated from POC monitoring data. This method certainly introduces errors, but still poses a chance to analyse overall BSi fluxes, which have never been shown to this extent before. To get a reasonable estimate of the monthly mean fluxes, data from the years 2000-2011 were included in the calculation. Data are available from 1985 onwards, but dominating processes especially regarding POC transformation and primary production in the Elbe estuary differed strongly in the earlier years due to intensive pollution (cf. chapter 3) and were consequently not taken into account.

Tab. 5.5: Regression parameters of the dependency between BSi and POC, divided by zone and season. Warm season = April-September, cold season = November-March.

zone	season	r^2	p-value	regression equation	remarks
pre-OMZ	warm	0.9083	0.0000	BSi = 0.15*POC – 0.50	true for POC < 600 µmol L^{-1}
	cold	0.9040	0.00008	BSi = 0.20*POC - 8.31	
OMZ	warm	0.7804	0.0000	BSi = 0.26*POC - 5.85	
	cold	0.8112	0.00000	BSi = 0.20*POC - 9.15	
MTZ	warm	0.6943	0.0000	BSi = 0.18*POC + 17.87	
	cold	0.7652	0.0001	BSi = 0.17*POC + 6.91	
post-MTZ	warm	0.0618	0.0958	BSi = 0.06*POC + 38.29	
	cold	0.0616	0.4366	BSi = -0.05*POC + 95.54	

5.3.5 Seasonal BSi fluxes using monthly averaged data

During winter, the BSi flux from the Elbe river was lowest (46±14 x 10^6 mol BSi $month^{-1}$; Fig. 5.5A), while the BSi fluxes from the freshwater part downstream are higher during winter with loads up to 310 x 10^6 mol $month^{-1}$. River input fluxes increase towards summer up to 3-fold relative to the winter flux, while fluxes from the freshwater part decrease about 3-fold relative to the winter values (Fig. 5.5B). Load differences between the input to and output from the freshwater part of the Elbe estuary reveal that there is a strong addition of BSi during transition and winter times (Fig. 5.5), which cannot be interpreted due to SPM accumulation at the end of the freshwater area. Therefore, BSi load data are considered to be biased by the MTZ and omitted in the discussion.

5.3.6 Nutrient ratios

Nutrient concentrations oscillate seasonally and this is reflected in the pattern of the Si:N ratios (Fig. 5.8). During winter, elemental ratios are highest and during summer lowest. The maxima seem to increase slightly in the course of time, from 0.4 in winter of 1989 to values near 0.8 in the late 2000s. This is observed in all zones. The minima approach 0 during summer in the pre-OMZ and OMZ. In comparison, the MTZ and post-MTZ, minimum ratios are slightly elevated and fluctuate between near 0 and 0.3. In the post-MTZ there seems to be an increasing trend for the minima, which reach values <0.1 in the early nineties and increase to 0.2 and more in the recent years (Fig. 5.8).

The relationship of Si:P is also characterised by seasonal variation in all zones (Fig. 5.8). During summer, the ratio can drop below 20 down to values <1. This drop is observed along the pre-OMZ in the summer of every examined year from 1989 to 1995. Afterwards, the drop becomes less frequent with continuously increasing Si:P ratios. In the downstream following three zones, Si:P sinks below the threshold of 20 in every summer season since 1989. Maximum values of 80-100 with peaks up to 450 occur in zones pre-OMZ to MTZ during winter. In the post-MTZ, maximum ratio increases over time from around 40 in the early 1990s to around 80 in the late 2000s.

Data for nutrient concentrations, on which ratios are based, are given in Appendix E. Generally, input of DIN and P declined significantly during the last decades (c.f. Chapter 3 and Adams et al., 2001).

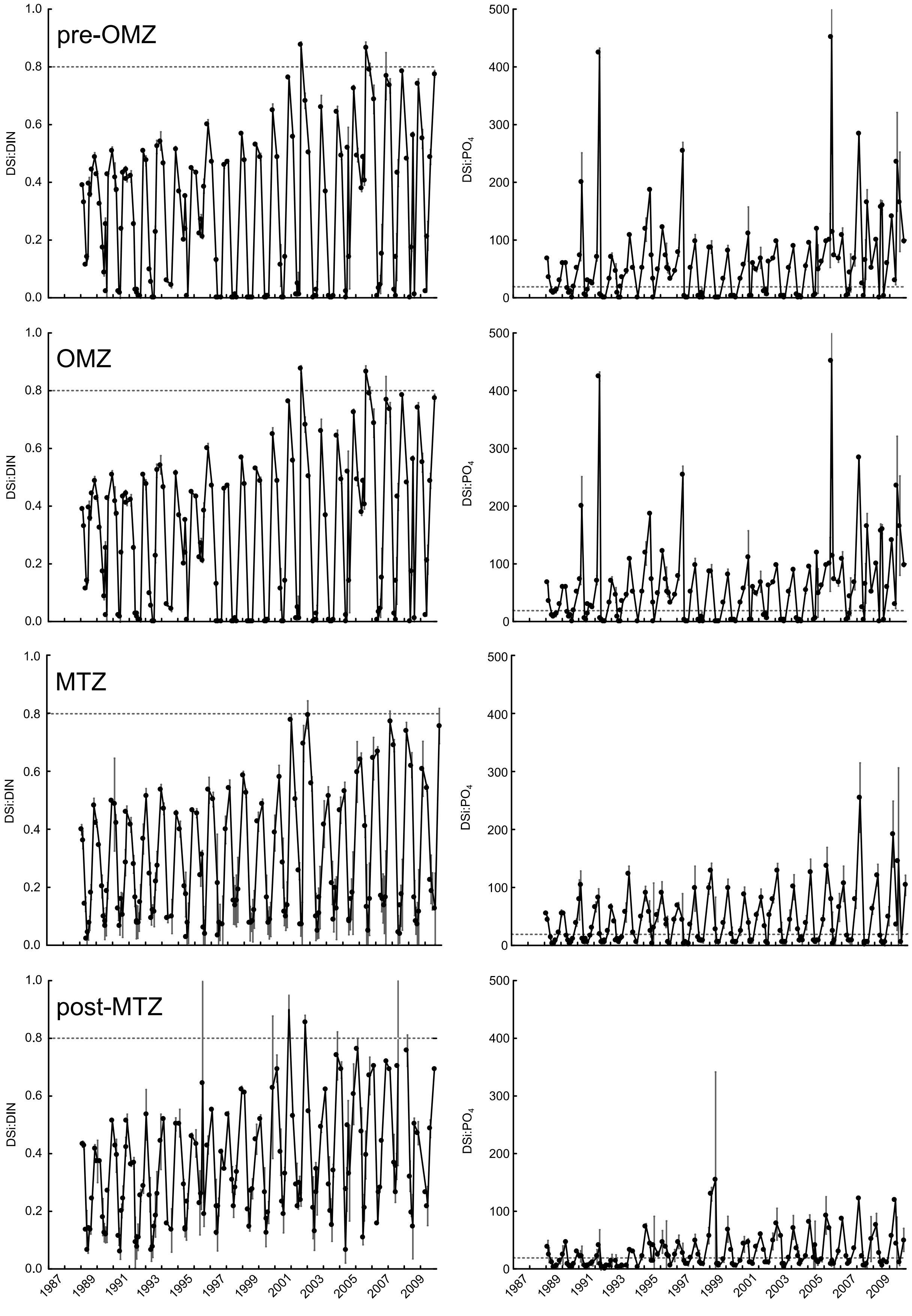

Fig. 5.8: Temporal development ratios DSi:DIN and DSi:PO$_4$ in the inner Elbe estuary, divided by zones. Error bars indicate the standard deviation, where the data point represents a monthly average due to occurrence of multiple values during one month. Dashed lines indicate limiting ratio according to (Redfield, 1958).

5.3.7 Silica budget calculations

Annually, 2,833 x 10^6 mol DSi a^{-1} are delivered from the river. In the freshwater part, 130 x 10^6 mol a^{-1} are added (increase of ~5 %), leading to a flux of 2,963 x 10^6 mol a^{-1} from the tidal river into the salinity gradient (Fig. 5.9). In total, 3,301 x 10^6 mol a^{-1} are exported as DSi to the North Sea, which is an increase of ~16 % over the river input. The major part of DSi export to the outer estuary is delivered during late autumn, winter and early spring, with an export of 2,794.6 x 10^6 mol DSi a^{-1} to the outer estuary. For late spring and summer, the export is calculated for May to August as the mean export at km 724 from the two examined cruises (July/August: 106.3 x 10^6 mol $month^{-1}$), which leads to an export of 425.2 x 10^6 mol a^{-1}. For September, the mean from two cruises yields 81.2 x 10^6 mol $month^{-1}$.

The annual BSi delivery from river to estuary amounts to 892 x 10^6 mol $month^{-1}$. BSi export to the North Sea was calculated on the basis of the Elbe SPM fraction in the German bight (Puls et al., 1997). This calculation yields 111.1 x 10^6 mol BSi export to the outer estuary, a reduction to 12 % of the river BSi load.

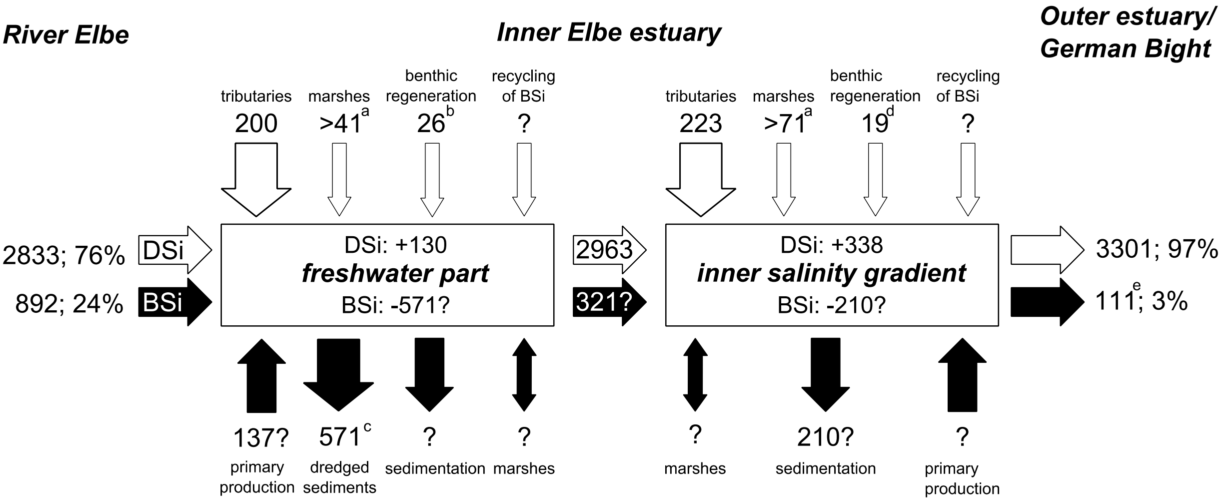

Fig. 5.9: Measured and calculated components of a preliminary Si budget for the inner Elbe estuary. All fluxes are given in 10^6 mol a^{-1}. Filled arrows symbolise BSi, outlined arrows DSi fluxes. Arrow direction indicates addition (towards compartment) or loss (away from compartment). Arrow widths are not to scale but indicate the tendency towards larger (wider arrows) or smaller (narrower arrows) fluxes. Question marks are assigned, where estimates are speculative or not possible. Percentages denote the fraction of TSi. [a] Weiss et al. (2012): freshwater marshes: 5.1 x 10^6 mol $month^{-1}$ (x2 for bulk and seepage phase), brackish + saline marshes: 8.9 x 10^6 mol $month^{-1}$ (x2 for bulk and seepage phase), both during summer (assumed here: May-August). [b] Ragueneau et al. (2006): mean of all max. values: 16 mmol m^{-2} d^{-1}. [c] Kappenberg and Fanger (2007): annual removal of 320,000 t SPM. [d] Ehrenhauss et al. (2004): 0.23 mmol m^{-2} d^{-1} minimum benthic flux from fine sediment of the Wadden Sea. [e] Puls et al. (1997): 0.09 Mt a^{-1} of riverine SPM delivered to the North Sea.

5.4 Discussion

5.4.1 A tentative silica budget for the inner Elbe estuary

On an annual basis, the inner Elbe estuary is a source for DSi and a sink for BSi. Compared to the river input, 16 % of DSi are added and 88 % of BSi are lost. This observation contradicts findings by Tréguer et al. (1995), who estimated that 25±25 % DSi are removed in temperate estuaries, arguing that biological DSi removal exceeds benthic resupply. However, they did not relate to a specific definition of estuaries, so that a comparison of the findings is impractical. Carbonnel et al. (2009) calculated for the freshwater part of the Scheldt estuary an annual net DSi retention of 14 % annually and 48 % in the productive season. In comparison, the same area in the Elbe estuary retains 9 % of the river DSi input during summer and adds 4 % annually (cf. Tab. 5.4). It is to conclude that two estuaries in a very similar geographical setting show a contradicting behaviour. This observation leads to the question whether the upscaling of data published to date, can represent estuarine behaviour on a global scale.

Globally, around 16 % of total Si fluxes from rivers are estimated to be comprised of BSi (Conley, 1997; Tréguer and De La Rocha, 2013). This relative value is exceeded by about 10 % for river delivery from the Elbe, but strongly decreased, if the estuarine output is considered. The sum of DSi and BSi entering the estuary from the river is decreased by 8 % along the inner Elbe estuary. This estimated retention is less than the global estimate of 21 % (Tréguer and De La Rocha, 2013), bearing in mind that in the global budget the retention of silica is determined by the drawdown of DSi, while in the Elbe, the removal of BSi is responsible for a decreased Si delivery to the coastal zone. Thus, processes in disturbed estuaries like the Elbe lead to a shift from DSi to BSi retention. This emphasises that estuaries significantly alter estimates from river data to the global Si budget.

The most important sources for DSi are tributaries, which contribute 90 % of excess DSi. Additional sources are benthic regeneration, bacterially aided dissolution, and marsh recycling of BSi. Estimates based on literature values are given in Fig. 5.9 and will be discussed in the subsequent sections. Primary production is assumed to be the single most DSi-consuming process. This is true for the most up and downstream stretches of the study area because strong turbidity inhibits photosynthesis in the areas between. DSi can be removed by abiotic processes, but is supposed to be negligible in estuaries (Chou and Wollast, 2006). The difference between inputs to the freshwater part and the net calculated addition is assumed to be the magnitude of primary production in this area (130×10^6 mol a^{-1}).

Sedimentation is hypothesised to explain the major BSi sink on the basis of observations for the Scheldt (Carbonnel et al., 2012). This process could pose a permanent sink of particulate material in managed estuaries. Large amounts of SPM settle in the harbour area of Hamburg, where it is continuously removed to keep the waterways and port basins navigable. Kappenberg and Fanger (2007) report on the settling behaviour of SPM in the Elbe estuary and show an increasing trend of sediment removal by dredging in the harbour area. They state that 800,000 tons of sediment were removed in 2005. 320,000 tons of which are attributed to Elbe river SPM. Considering an observed winter minimum value of about 5 % BSi fraction of SPM, this results in a direct anthropogenic removal of about 571 x 10^6 mol BSi via dredging in the tidal river. This is a conservative estimate because the BSi fraction of SPM triples during the warm season and preferential settling of BSi over the rest of SPM has been observed in the Scheldt (Carbonnel et al., 2009; Carbonnel et al., 2012). Yet, the largest deliveries of SPM from the river occur during times of the highest discharge in winter and spring. The amount of annually dredged material points to sedimentation as a major factor of BSi loss. However, the sedimentation rates are unclear and have to be investigated separately. The sedimentation regime may, to a large extent, be caused by ongoing changes in the waterway management. The amount of dredged material changes from year to year (Kappenberg and Fanger, 2007), so that the given estimate can only provide tentative estimate. Sediment dredging is typical for estuaries that are traditionally used as waterways, implying that globally, large amounts of BSi are removed artificially. The consequences of this displacement need to be explored further.

In addition to sedimentation and subsequent artificial extraction of BSi, the species is readily dissolved in the MTZ and post-MTZ due to the presence of seawater ions, bacteria and increased pH, but an estimate for the Elbe on the basis of literature values (i.e. Loucaides et al., 2008) seems unreasonable due to too many uncertainties, and was assigned a question mark in Fig. 5.9. Dissolution is also assumed to be important in the Scheldt by Carbonnel et al. (2012), but was not quantified. Furthermore, the salinity gradient of the Elbe is lined with marshes, which could import or export BSi from the estuary, as observed in the Scheldt by Struyf et al. (2006), but since there is no clear evidence for export or import and large uncertainties in the calculations, the estimation is left out in Fig. 5.9 for both zones.

5.4.2 Spatial patterns of silica concentrations

5.4.2.1 *Marshes and tributaries as major Si providers in winter*

DSi concentrations are high throughout the estuary and winter values are about twice as high as the average for European rivers with 93.2 µmol L^{-1} (Dürr et al., 2011). DSi concentrations remain relatively unchanged during winter, due to strongly reduced biological activity in the water body and sediments. The slight DSi increase between 619 and 699 might be attributed to input from tributaries, which contribute DSi enriched waters. 21 % of the river water discharge measured at Neu Darchau is added by tributaries along the inner Elbe estuary. These tributaries carry waters with DSi concentrations up to 35 % (mean: 12±22 %) above the main river (Fig. 5.5). Additionally, adjacent marshes potentially deliver DSi to the estuary. It was shown by Struyf et al. (2005) that freshwater marshes in the Scheldt estuary export DSi to the estuarine waters. BSi basically follows the SPM concentration development along the inner estuary. Minor changes in the relative parts of BSi show that only processes that affect all particles influence the concentration of BSi. It is expected that BSi is lost during transit by sedimentation but not through dissolution processes. A conservative mixing line of DSi in the salinity gradient indicates no addition of removal along the salinity gradient during winter.

Tab. 5.6: Discharge and mean DSi concentrations for the some of the main tributaries of the freshwater part of the Elbe estuary. Discharge data is taken from IKSE (2005). DSi means are calculated from data made available by FGG Elbe (2012). Values for the Elbe main stream are given for comparison. Fragmentary DSi concentration data for most of the larger tributaries is available from the 1990s. This is not the actually analysed time frame but the only data that are available. Comparison is believed to be feasible because the tributary catchments are small and not affected by the geopolitical and structural change of the Elbe catchment.

river	available time frame	annual mean discharge [$m^3 s^{-1}$]	summer DSi concentration (May-Sept) [µmol L^{-1}]			winter DSi concentration (Nov-March) [µmol L^{-1}]		
			mean	n	stddev	*mean*	*n*	*stddev*
Schwinge	1989-2002	2.6	183.8	66	42.9	221.9	69	40.8
Bille	1989-2005	4.0	78.0	24	44.5	229.9	19	30.8
Seeve	1989-2001	4.7	171.7	47	68.6	191.9	51	73.8
Este	1989-2002	3.2	194.5	66	32.1	225.3	69	27.9
Ilmenau	1989-2002	17.7	174.3	48	67.4	220.9	52	78.6
Pinnau	1989-2007	3.5	119.3	104	63.7	140.3	83	64.2
Krückau	1989-2007	2.4	148.0	103	64.6	140.9	83	73.7
Stör	1989-2007	21.7	55.2	103	65.9	167.2	81	73.5
Oste	1989-2002	17.7	66.0	80	73.2	237.4	68	43.9
Elbe	1990-2007	685.8	39.8	889	50.0	175.9	558	36.5

5.4.2.2 *Summer DSi consumption by primary production*

With increased temperature and light availability, biological activity is enhanced during late spring, summer and early autumn. Growth of diatoms in Elbe river (Muylaert and Sabbe, 1999) leads to a strong DSi decline from the high winter concentrations. It is expected that diatom blooms prevail and fully deplete DSi in the upstream area, but a depletion of phosphorus in the form of phosphate (PO_4) in this area may prevent a more intense DSi drawdown. In downstream direction, PO_4 concentrations fluctuate but rise up to 3 µmol L^{-1} at km 709. With declining DSi concentrations, DSi becomes the limiting component (Fig. 5.3). Its concentrations drop in the OMZ to 2 µmol L^{-1}.

5.4.2.3 Collapse of river plankton bloom increases estuarine DSi

For the second observed summer situation with elevated DSi concentrations in the upstream areas (cf. Fig. 5.4), it is hypothesised that the plankton bloom collapsed here, leading to decreased consumption of DSi. Bergemann et al. (1996) observed a bloom breakdown in the area of the weir at Geesthacht and traced it back to DSi limitation and poor weather conditions. This breakdown was also observed for the Rhine by Schöl et al. (2002), who identified low global radiation, high discharges through rain, and consecutive increased turbidity as factors for the reduction of photosynthetic activity. Grazing by planktonic metazoan was mentioned as an additional but not significant stress factor for diatom populations in the Rhine (Admiraal et al., 1994).

5.4.2.4 Non-conservative mixing of summer DSi

Mean DSi concentrations increase in the course of the MTZ (Fig. 5.3; Fig. 5.4). It is notable from the standard deviations that the values in the MTZ fluctuate more than in the upstream areas. This may be because this area is already affected by mixing with seawater, and sampling was not conducted at the synchronous tidal state. Inferring from the salinity curve that seawater mixing sets in at km 690 (riverine endmember) and a DSi value of 15 µmol L^{-1} at km 757 (marine endmember; FGG Elbe, 2012), the mixing line is below the measured values. This indicates addition of DSi in the MTZ and post-MTZ from other sources. These sources are likely to be the adjacent marshes, which are known to add significant amounts of DSi to estuaries, as shown for the Scheldt estuary by Struyf et al. (2006) and for the Elbe estuary (Weiss et al., 2012). Enhanced dissolution of BSi due to increased salinity could not be observed because of the masking influence of the MTZ (Fig. 5.3). Since the decline of BSi in the salinity gradient follows the same pattern as the SPM concentrations, dilution and sedimentation seem to be dominating processes. Mobilisation of small amounts of BSi from marshes is possible (Struyf et al., 2006) and a comparable process in the Elbe estuary may pose a counterbalance for in stream dissolution of BSi from other sources.

5.4.2.5 *Shallow waters are hotspots for DSi consumption*

The observed drawdown of DSi between OMZ and MTZ (Fig. 5.4) cannot be related to processes occurring in the main stem. It is hypothesised that benthic diatoms in shallow waters and periodically inundated mudflats of the side branches of the estuary consume the advected DSi from the main stem. There, primary production is strongly reduced due to light limitation through increased SPM and strong currents, which inhibit organisms from longer residence in light penetrated waters. Benthic microalgae need more silica per unit of chlorophyll than pelagic species, and they not only consume the regenerated nutrients from the sediment but can additionally feed from water column DSi (Sigmon and Cahoon, 1997; Leynaert et al., 2011). These microalgae can, therefore, significantly limit the benthic pelagic exchange of nutrients. Data on the spatial distribution of mudflats (Fig. 5.10) show that mudflats appear just after the drop of DSi concentrations. This also marks the border of the industrially used areas. The adjacent section is characterised by elongated islands that form natural barriers between the main stem, which is anthropogenically maintained and features high current velocities, and the side branches with calmer waters and a near-natural environment.

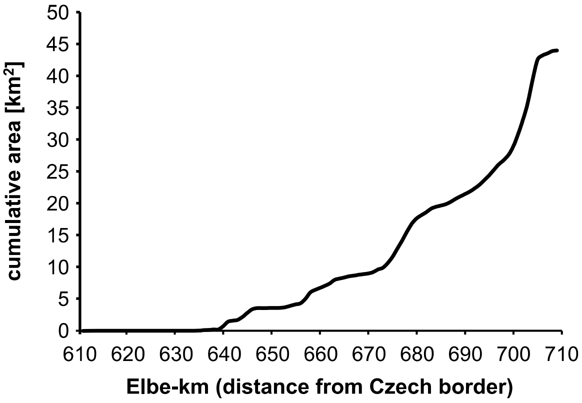

Fig. 5.10: Cumulative area of mudflat areas along the inner Elbe estuary excluding the areas before the harbour area (data start at km 611).

Through tidal currents, water is continuously interchanged between these areas. Kerner (2007) describes the side branches as zones with an aeration capacity for the main stem. Here, oxygen production through photosynthesis prevails, even during times of oxygen minima in the main stem. All these processes could be an indication for diatom production that draws down DSi. A spatial difference between the onset of mudflat areas and the area of observed DSi drop might be explained again by failure of sampling during synchronised tidal states, causing a mix of different sampled water bodies.

5.4.2.6 *Nutrient ratios and the effect on silica supply to the coastal zone*

The Si:N ratio shows that during times of biological activity, the inner Elbe estuary is permanently Si limited. The perpetuate decline of N inputs is visible in the ratios during winter but did not lead to a continuous shift in limitations during summer. Yet, the trend towards higher values shows that in the future, the ratio could rise even during declining N concentrations, since DSi concentrations seem to be stable in the respective seasons. The N excess is a widely observed phenomenon in coastal ecosystems as shown by Billen and Garnier (2007).

The development of the Si:P ratio indicates Si limitation in summer in the late 1980s and the early 1990s. Afterwards, the system in the pre-OMZ shifts to P limitation in 2006 and 2010. This would indicate that a reduced input of P from upstream sources could lead to increase in DSi delivery to the coastal zone. This trend was also observed by Hartmann et al. (2011) for the river Rhine. However, in the downstream following zones, the Si limitation prevails. This corroborates the annual net retention of Si in the inner estuary during summer and supports the findings from load difference calculations.

An on-going and intensified reduction of N and P inputs to the river and estuary could shift the limitation to P in the future. With still very high N values, a limitation of this element is less likely. The reduced nutrient input should be reflected in rising DSi exports to the coastal zone and a consecutive change in the coupled Si-C-cycle in the North Sea.

5.4.3 DSi fluxes through the inner Elbe estuary

5.4.3.1 DSi losses from primary production

The DSi loss between river input and output from the freshwater zone in summer and autumn is attributed to blooming diatoms, which consume the Si that is brought into the freshwater region of the Elbe estuary from upstream (Muylaert and Sabbe, 1999). Enhanced primary productivity leads to a maximum DSi loss of 50 % in July. This value is not exceeded but remains rather constant in the two following months (Fig. 5.6B). The build-up of biomass seems to stop or slow down significantly when DSi concentrations reach levels below 20 µmol L^{-1} (Fig. 5.7). It is hypothesised that P limitation inhibits further diatom growth (refer to section 5.3.6) The Si:P threshold of 15 is passed in the respective month and is responsible for a limitation of the DSi consumption. Additionally, the harbour area is situated in the tidal river, where high turbidity and stronger currents inhibit phytoplankton growth and pose another limiting factor.

5.4.3.2 Influence of benthic regeneration on fluxes

Benthic exchange can contribute to the DSi balance. Reported benthic regeneration rates of Si in estuaries have a very broad range between 0.1 and 113 mmol m^{-2} d^{-1} (Ragueneau et al., 2006 and references therein). Admiraal et al. (1993) used a rate of 0.36 mmol Si m^{-2} h^{-1} (8.6 mmol Si m^{-2} d^{-1}) for the DSi regeneration from freshwater sediments of the Rhine, which would yield 10.1 x 10^{6} mol Si month^{-1}, if applied to the freshwater part of the Elbe estuary (area: 56 km^{2}, including tidal flats). Assuming an averaged maximum of 16 mmol m^{-2} d^{-1}

from a compilation by Ragueneau et al. (2006), this yields 26 x 10^6 mol month^{-1}, which would be a significant part (20-30 %) of the calculated additions of DSi during the onset of spring. However, considering the observed large spread of observed regeneration rates, no certain export of DSi from sediments can be determined. The question on the dimension of benthic contribution on DSi fluxes in the Elbe estuary remains to be answered.

5.4.3.3 *Bacterially mediated BSi dissolution*

DSi can be regenerated by BSi dissolution through increased bacterial activity (Roubeix et al., 2008) and elevated temperatures (Kamatani, 1982; Yamada and D'Elia, 1984). During summer, the OMZ characterised by an oxygen sag that is induced by bacterial respiration (Kerner, 2000). Therefore, bacteria abundance in this area of intense remineralisation in the freshwater part of the study area likely leads to DSi regeneration in the water column. As the respective zone for which the Si loads were calculated already extends into the innermost part of the MTZ, it is likely that here the bacterial activity can affect BSi much more intensive because of prolonged residence times of the water body. Muylaert and Sabbe (1999) observed a change in the phytoplankton species composition occurring at very low salinities (<1) in the Elbe, because increasing salinity causes freshwater phytoplankton death. In addition, the observed intensified grazing has been hypothesised to enzymatically degrade the organic matrix of diatom frustules and enhance dissolution (Bidle and Azam, 2001; Roubeix et al., 2008).

However, this discussion is of qualitative nature and more data are needed on species distribution, the effect of temperature, and salinity, for a specific system like the Elbe, to derive plausible dissolution rates.

5.4.3.4 *Tributaries are major contributors of DSi*

Compared to the long term mean discharge of the Elbe, the examined tributaries make up about half of the discharge that is added in total to the freshwater area. During winter 15-30 x 10^6 mol month^{-1} of DSi are added to the Elbe (Fig. 5.11). This can explain 50-100 % of the calculated total DSi addition within the estuary. DSi concentrations in the tributaries remain very high during summer, relative to the Elbe tidal river (Tab. 5.6) and they are fairly constant throughout the seasons compared to the strong seasonal fluctuations of the main stem.

DSi loads leaving the freshwater part of the Elbe estuary during winter represent the actual DSi load that is delivered from the inner Elbe estuary to the German Bight. Here, conservative mixing with seawater is the major influence on DSi concentrations (Appendix

D-4 (A)). Significantly higher discharge during winter (cf. Fig. 5.5A) and a decreased concentration difference between tributaries and main stream (Tab. 5.6) weakens the influence of tributaries. They show mean DSi concentrations, which are slightly lower than in the main stem, except for data of the Oste, which is on average 26 % higher relative to the estuary. In total, the tributary contribution of DSi to the salinity gradient seems to be negligible during the cold season in contradiction to the freshwater zone, where tributaries are able to replenish up to 100 % of the added DSi in this time. This behaviour changes during summer: The Oste is the major tributary in the salinity gradient, and with mean DSi concentrations 66 % higher than in the main stem (Tab. 5.6), this tributary contributes during summer to increased addition fluxes.

Overall, these findings highlight the important role of tributaries in the study area. The Scheldt estuary shows a comparable influence on DSi fluxes. It was shown, that the Rupel tributaries contributed 63 % to the total DSi input to the Scheldt tidal river (Carbonnel et al., 2009). If other estuarine systems feature tributaries with a similar discharge, they should be incorporated into budget constructions. Thus, the sampling of tributaries should be considered as important as the investigation of all other surrounding environments.

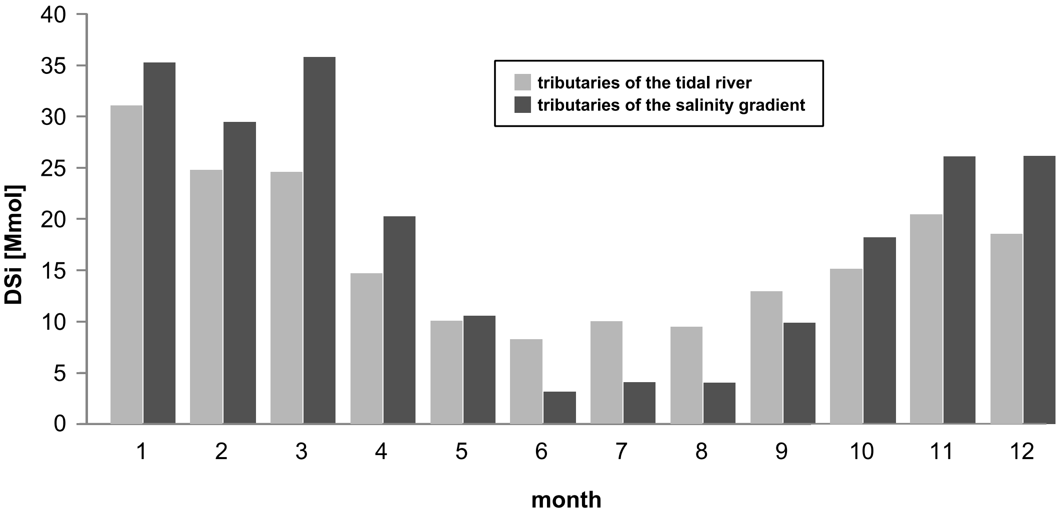

Fig. 5.11: Monthly DSi load discharged to the Elbe estuary along the tidal river (pre-OMZ, OMZ; grey bars) and the salinity gradient (MTZ, post-MTZ; black bars) from the main tributaries.

5.4.3.5 Marsh DSi export

Adjacent marshes are regarded as important for the DSi supply of estuaries. Struyf et al. (2005) estimated that freshwater marshes could replenish the depleted Scheldt waters within six tidal cycles during summer. During winter, the export is strongly reduced, due to smaller differences of DSi concentrations in inundating waters and marsh pore waters, but a slight export from a freshwater marsh between 0.2 and 3.2 mmol m^{-2} during one tidal cycle in January and February was still observed. These rates are used to estimate a potential DSi export from freshwater marshes of the Elbe estuary. The dyke foreland, i.e. the area between dyke and permanently flooded river bed, is taken from environmental impact study by Planungsgruppe Ökologie + Umwelt Nord (1997) for the area between km 585 and km 610 and for the area beyond Hamburg (km 638-680). The Hamburg area, from km 610 to 638, is left out intentionally, because dyke foreland means harbour area here. Based on this area data (13.5 km^2) and a diurnal tide, the winter marsh export yields 0.2-2.6 x 10^6 mol DSi $month^{-1}$. Extensive marshes appear in the area from km 700 downstream as represented in Fig. 5.10 as a steep increase of the cumulative area. Weiss et al. (2012) calculated that during summer, 8.9 x 10^6 mol DSi $month^{-1}$ are exported from marshes of the brackish and saline areas which are exactly the areas where a rising effective concentration of DSi is observed. This export is probably underestimated because it does not account for the seepage outflow from the marshes, which could contribute more than 50 % of the total DSi export (Weiss et al., 2012). This outflow would yield about 18 x 10^6 mol $month^{-1}$ from the marshes alone during summer and could explain a large part of the DSi additions observed in the salinity gradient, which range from 30 x 10^6 mol $month^{-1}$ to more than 90 x 10^6 mol $month^{-1}$ (Tab. 5.2).

5.4.4 BSi fluxes through the inner Elbe estuary

5.4.4.1 Reconstruction of BSi from POC monitoring data

Data of BSi are generally underrepresented in studies of estuaries. Thus, BSi fluxes through the estuarine realm are poorly constrained. Conley (1997) estimated on the basis of 11 rivers, highly different in discharge and geographical setting, that 16 % of the Si exported to the coastal ocean is in biogenic form. This estimate is still used in global budgets (Tréguer and De La Rocha, 2013). In attempt to tackle this issue, BSi data in conjunction with POC data were used to reconstruct historical BSi concentration data. This is based on the observation, made in chapter 3, that POC production in the Elbe increased in the last decade (cf. Fig. 3.5), due to more intense primary production. A linear regression between POC and BSi concentrations was possible, with p-values well below 0.1 % for pre-OMZ to MTZ (Tab.

5.5). The strong influence of seawater mixing disables the use of data in the post-MTZ. This method could, therefore, pose an opportunity to construct BSi values in systems that provide data on POC. A general applicability on estuaries around the globe remains to be shown. The reconstructed concentrations were incorporated in flux calculations to increase the data count for monthly averaged values.

5.4.4.2 Influences on BSi fluxes along the estuary

If the formation of a plankton bloom leads to a conversion of DSi to BSi, it is expected that DSi is transformed directly into BSi and can be found as such in the sample. Waters in the pre-OMZ are relatively undisturbed by industrial activities and shallow areas guarantee light availability, which should endorse BSi formation in this area. However, this is not always reflected in the data at hand. The calculated addition of BSi in June matches the loss of DSi perfectly, but in August the addition of BSi is twice as high as the loss of DSi. Furthermore, there is loss of BSi in May and July (Fig. 5.6). This non-proportional behaviour of DSi and BSi could be traced back to several factors: Benthic diatoms, which consume DSi from the water column, do not contribute to the BSi concentration in the sampled surface water (cf. Fig. 5.7 and description in section 5.3.2). Additionally, BSi that enters the estuary or is produced here may settle in the calmer basins of the harbour area. With increased temperature during the summer month, the dissolution of BSi is enhanced (Kamatani, 1982). This process is further promoted by prolonged residence times due to low summer discharge.

As an additional little noticed process, regular dredging to maintain the navigational channel leads to resuspension of large amounts of sediments, which are, in consequence, undergoing increased dissolution due to the increased surface area of SPM. However, these stirred up sediment clouds seem to vanish within a tidal cycle (pers. obs.), at least from the surface waters.

5.4.4.3 Export of BSi to the coastal zone

To estimate the potential BSi export from the inner Elbe estuary to the coastal zone, data of the annual SPM contribution by the Elbe to the Germany Bight area, calculated by Puls et al. (1997), is used in conjunction with the relative BSi fraction of SPM at the outmost sampled location, measured by the authors. Relative BSi contribution to SPM shows little variation throughout all seasons (Appendix D-4) with values of 6.3±1.3 % at salinities ≥16 (n = 9). Puls et al. (1997) estimated that 0.09 Mt a^{-1} of the SPM fraction <20 µm in the German Bight, which according to their findings represents 85 % of the total SPM, is delivered from the Elbe river. If scaled to 100 % SPM (0.11 Mt SPM a^{-1}), this yields an annual export of $111.1 \pm 23.8 \times 10^6$ mol BSi a^{-1}.

5.5 Summary & Conclusion

1. Contrary to the general idea of estuaries as a sink for silica delivered by the adjacent river, the inner Elbe estuary is a source for DSi: on an annual basis, 17 % are added. Major parts of this DSi are supplied by the adjacent tributaries, marshes, and by benthic regeneration. These processes are essential during summer, when the freshwater estuarine part acts as a sink for DSi and is potentially Si limited. The strong influence of tributary inputs of DSi may be an important feature, that should be further examined in the Elbe and other estuaries with a similar tributary setting.

2. With a total loss of 88 % of the BSi, received from the Elbe river, the inner estuary is considered to be a strong sink for BSi. A greater part of the BSi delivered from the river is trapped and settled in the harbor region of the freshwater area. By anthropogenic interference, sediment, and at the same time BSi is removed to keep the waterways navigable. This permanently draws BSi out of the estuarine Si cycle and inhibits the benthic transformation to DSi, increasing the potential of a Si limited system. Since waterway management is common in estuaries around the world, the global removal of BSi by dredging needs to be evaluated to better constrain land-ocean BSi fluxes.

3. The heterogeneous spatial characteristics of an estuary lead to complex patterns of Si distribution. While the upstream freshwater parts are able to sustain a plankton bloom, primary productivity is inhibited from the harbor area seawards. Thus, the estuarine Si filtering capacity depends on the extent of light limiting areas. This potential filtering leads to errors when estimating Si exports to the coastal zone from the river or the freshwater-seawater interface. It was shown that different processes along the inner salinity gradient add on average 10 % of DSi and remove 65 % of BSi on the way to the coastal zone.

4. Considering the matter fluxes to the North Sea, only 3 % of Si is exported in particulate form, which is low compared to a global estimate of 16 % (Conley, 1997). As it is a potentially important source for recycled Dsi, the absence of BSi could, together with slowly declining nutrients, pose a threat to diatom blooms in the German Bight.

5. Because data on BSi are, to date, underrepresented in estuarine studies, the reconstruction of BSi data from a BSi:POC relationship provides a good opportunity to increase the knowledge on temporal development of BSi fluxes and their potential variability.

6 Synthesis

The inner Elbe estuary was examined with regard to carbon and silica fluxes through distinguished compartments, from the freshwater-bearing limit of tidal influence to the estuarine mouth near Cuxhaven at intermediate salinities. Historical monitoring data were used to evaluate the impact of water quality changes on the carbon cycle in the Elbe estuary. 18 surveys were conducted to gain information on dissolved and biogenic silica as well as on the inorganic carbon system, to extend the given historical database.

In chapter 3 of the thesis, carbon fluxes were explored with a historical perspective. The strong pollution in the 1980s is mirrored in extensive data from authority monitoring. As a result from water contamination, high partial pressures of CO_2 (pCO_2) prevailed then, but they remained high with improved water quality in the recent years. A change in the quality of organic carbon was detected and the estuarine filter function for particulate organic carbon in the maximum turbidity zone (MTZ) (Abril et al., 2002) could be confirmed. Moreover, improved water quality led to the transformation of up to 50 % of upstream POC in the freshwater part including the harbour of Hamburg. A pronounced oxygen drawdown supported this, giving the zone its name: oxygen minimum zone (OMZ). It was hypothesised that this intense POC utilisation renders the OMZ a hotspot of CO_2 fluxes towards the atmosphere, which was rarely considered in other studies on estuaries. Overall, it was possible to demonstrate that a system, recovered from heavy pollution, can still be a strong source of CO_2, due to increased POC delivery from upstream primary production.

It was concluded that it is necessary to consider the full inner estuary including the tidal freshwater areas. Furthermore, in evaluation of an estuary and its future ecosystem development, it is important to assess temporal water quality variability, since less polluted waters do not necessarily restore naturally functioning estuarine ecosystems.

To test the hypothesis of the OMZ being a hotspot for carbon transformation, data from recent cruises were evaluated in chapter 4, using GIS derived surface areas, isotopic DIC data and modelled $p\mathrm{CO}_2$. In contrast to a common approach with formulas derived from the marine realm, considering a mixing of pure water with seawater (e.g. Millero et al., 2006), $p\mathrm{CO}_2$ was calculated with the software program *PHREEQC* (Parkhurst and Appelo, 1999), using the actual ionic composition of a sample. This revealed that the “classical” approach leads to a $p\mathrm{CO}_2$ overestimation of 20 % compared to *PHREEQC* results.
With this approach, it was confirmed that the OMZ is an important zone for carbon turnover. Highest $p\mathrm{CO}_2$ values and strongest CO_2 efflux per square meter compared to the rest of the inner Elbe estuary were observed here. The zone contributed above average to the total CO_2 efflux from the Elbe estuary, but based on the much larger surface area, the MTZ was still the largest source of CO_2, a finding, which is in accordance with other studies. Annually, about 13.2×10^9 mol CO_2 are released from the inner Elbe estuary. That is about 4 % of the annual CO_2 emissions of the city of Hamburg. The amount of CO_2 showed that an improvement of water quality does not necessarily imply a strong decrease of CO_2 emissions. In total, about 20 % of the DIC exports from the estuaries are attributed to CO_2 exchange with the atmosphere, while 80 % are transported seawards in dissolved form.

The refinement of surface area calculation, using a GIS based approach, showed that a previous assumption for the Elbe estuarine area was overestimated by 18 %, which could change global extrapolations significantly, if assumed that the same error applies to all examined systems.

Furthermore, it is revealed in chapter 4 that the Elbe estuary is a source for DIC as alkalinity (TA). The DIC flux to the coastal zone was increased by about 18 %, compared to the input flux from the zone before the OMZ. This DIC is likely to be derived from marshes, benthic regeneration, and other undetermined sources. About 40 % of the calculated excess DIC was attributed to these sources in the form of TA. The addition of DIC, and concomitant TA, to the riverine input of DIC, could be an important factor in North Sea budget calculations, which to date rely on an assumed conservative mixing of DIC, measured at a freshwater monitoring station.

The silica fluxes along the inner Elbe estuary were discussed in chapter 5. While estuaries in general are considered a sink for dissolved silica (DSi), the Elbe is a source. On an annual average, 17% were added along the inner estuary. This was mainly traced back to tributaries, which feature much higher DSi concentrations than the main stem. Additionally considered processes are benthic regeneration and the Si export from marshes. Biogenic silica (BSi), on the other hand, was found to be removed in the Elbe estuary. 88 % were lost on an annual average. Sedimentation was assumed the largest sink for BSi, and it was hypothesised that large amounts were excavated by sediment dredging and, thus, permanently removed from the estuarine Si cycle. Compared to global estimates on the BSi fraction of total Si exports to the ocean (16 %; Conley, 1997), the Elbe river contribution was higher, with 24 %, but this value decreases strongly to 3 % at the end of the inner estuary. This underlines the significance of BSi removal on the way downstream. Because dissolution of BSi is a valuable source process of DSi in the shelf sea, the strong retention of BSi is a potential threat to diatom blooms in the German Bight.

It was possible to reconstruct historical BSi concentrations via POC data from monitoring, because the increased POC, described in the first part, based on diatom primary production. This resulted in a positive correlation between POC and BSi.

As data on Si transformation in estuaries are scarce and widely underrepresented in global budgets, findings from this study are considered to be a valuable contribution, especially since the Elbe estuary seemed to act contradictory to observed systems so far.

A few specific questions arise from the findings presented in this thesis. Many sources and sinks of C and Si were discussed, but most of the quantities are poorly constrained due to scarcity of available data. For instance, a detailed survey on DSi and DIC fluxes from tributaries could significantly improve the knowledge on fluxes towards the estuary. The addition by subaquatic groundwater discharge needs to be evaluated, as there exist no data at all. Furthermore, although featuring well-mixed waters, it would be advisable to analyse vertical differences in the water column. It is possible, that fluid mud at the bottom of the Elbe estuary acts as a strong reactor, producing alkalinity by carbonate dissolution, as observed in the MTZ of the Loire (Abril et al., 2003). Also, due to the nature of monitoring programmes, effects of short-term weather events are rarely represented, so that special attention should be paid to infrequent weather related events in further studies. It was observed, that storm surges can be responsible for a larger part of imported BSi in salt marshes of the Wadden Sea (Müller, 2013). Furthermore, very rarely occurring ice drift could lead to perturbation of mudflats, releasing DIC enriched pore waters (Brasse et al., 1999). As these environments are also represented in the Elbe estuary, a similar effect is expected and could contribute above average to the addition or retention of matter.

A special focus should be put on the effects of waterway management. Findings from this thesis imply that the removal of sediment could have an impact on Si and C cycling that was not considered before. Countermeasures should factor in the effects of sediment dredging. In anticipation of continuously growing population in estuarine coastal areas, and subsequent intensified utilisation of the infrastructure, dredging actions are likely. This interference was for instance acknowledged in a comprehensive report on river catchment-coastal sea interaction in East Asian ecosystems (Hong et al., 2002) and was projected to increase. In addition, they reported that land reclamation activities are expected to increase in the future. This could alter the hydrodynamical character of estuaries as it changed the form of the Elbe estuary one century ago (Asmus et al., 1992). The potential decrease of shallow water areas could have a direct impact on the oxygen and carbon budget as observed in the Elbe estuary (described in chapter 3). Nitrogen dynamics are also likely to be influenced by waterway management (Dähnke et al., 2008).

While the population worldwide is constantly growing, it is of imminent importance to understand impacts from land-use change, increased nutrient input, wastewater effluent, increased atmospheric CO_2, and others. This global change is directly mirrored in changes of the fluxes through litho, bio, hydro, and atmosphere. The construction and improvement of budgets in these compartments is fundamental to predict future changes. The inclusion of estuaries in global carbon and silica budgets is still subject to high uncertainties, which are derived from their morphological and hydrodynamical heterogeneity. However, it was shown in the past that a relatively simple approach, e.g. for estuarine CO_2 flux estimates (Frankignoulle et al., 1998), yields a fairly good result if compared to the latest study (Chen et al., 2012). While the findings on CO_2 in this thesis fit right in the global average, they reveal a new view on the local scale, emphasising the significance of spatial differences and highlighting the change of fluxes to the adjacent coastal ocean, which is important on basin scale budgets, such as in this case the North Sea. Observations on DIC and TA fluxes towards the German Bight were already discussed and integrated in a model study on the impact of internal and external alkalinity fluxes on the carbonate system of the German Bight (contribution listed in Appendix A).

The observed direct link between carbon and silica, and the impact of changes in the nitrogen cycle on the alkalinity fluxes demonstrated once more how close biogeochemical cycles are connected in estuaries. Due to their unique position at the interface between land and ocean, the important role of estuaries on the alteration of matter fluxes will grow with ongoing global change. While the estuarine surface may be small compared to the shelf sea, this thesis has shown that the Elbe estuary is an important piece in the puzzle of land-ocean matter fluxes.

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Appendix

A Personal contributions to the listed publications

Amann, T., Weiss, A., Hartmann, J., 2012. Carbon dynamics in the freshwater part of the Elbe estuary, Germany: Implications of improving water quality. Estuarine, Coastal and Shelf Science 107, 112-121, DOI: 10.1016/j.ecss.2012.05.012.

Concept, introduction, and calculations, as well as the concluding remarks are the result of cooperation with Andreas Weiss. The collection of monitoring data and compilation of methods was done by the author of this thesis. Furthermore, the author created the discussion of subsections 3.3.4 and 3.3.5.

Weiss, A., Amann, T., Hartmann, J., 2012. Silica dynamics in tidal marshes along a salinity gradient in the Elbe estuary, Germany. Silicon, DOI: 10.1007/s12633-012-9131-1.

The author of this thesis contributed to the publication by helping to acquire field data.

Schwichtenberg, F., Pätsch, J., Amann, T., Schartau, M., Thomas, H., Winde, V., Dellwig, O., van Beusekom, J., Böttcher, M., Grashorn, S., Salt, L., in prep. Impact of internal and external Alkalinity fluxes on the carbonate system in the German Bight / SE North Sea - A model study for the years 2001-2009.

The author of this thesis contributed data on TA fluxes from the Elbe estuary to the North Sea, as discussed in chapter 4.

Amann, T., Weiss, A., Hartmann, J., in prep. A silica budget of the inner Elbe estuary, Germany.

Amann, T., Weiss, A., Hartmann, J., in prep. Inorganic carbon cycling and CO_2 fluxes in the inner Elbe estuary, Germany.

These publications are in preparation and base on chapter 4 and 5, respectively. They were created entirely by the author of this thesis.

Weiss, A., Amann, T., Hartmann, J., in prep. Sources and export of DIC and TA from tidal creeks along a salinity gradient in the Elbe estuary, Germany.

The author of this thesis contributed to this publication by the help in acquiring field data and by adding findings from the adjacent estuary.

B Results from ESTUCARB cruises (data tables)

1. Overview over sampled stations and general water chemistry parameters, part 1 of 3.

ID	DATE	UTC TIME	River km	long	lat	wind speed	$\sigma_{\text{wind speed}}$	ambient $p\mathrm{CO_2}$	Discharge (fac.corr.)	pH	temp-erature	Salinity	SPM	DO	DO saturation
	[dd.mm.yyyy]	[hh:mm]	[km]	[°]		[m s^{-1}]	[µatm]		[m^3 s^{-1}]	[ ]	[°C]	[ ]	[mg L^{-1}]	[µmol L^{-1}]	[%]
EC-01-589	29.07.2009	13:48	589	10.29	53.43	2.9	0.8	383.18	624.41	8.980	22.5	0.362	40.504	345.02	124.34
EC-01-592	29.07.2009	13:34	592	10.26	53.42	2.9	0.8	383.18	626.97	8.967	22.5	0.372		366.90	132.22
EC-01-594	29.07.2009	13:22	594	10.24	53.40	2.9	0.8	383.18	628.67	8.951	22.4	0.357	39.252	365.96	131.70
EC-01-597	29.07.2009	13:09	597	10.21	53.40	2.9	0.8	383.18	631.23	8.934	22.5	0.369			
EC-01-599	29.07.2009	12:55	599	10.17	53.40	3.7	1.7	383.18	632.93	8.948	22.4	0.357	43.844	354.40	127.53
EC-01-604	29.07.2009	12:25	604	10.12	53.42	3.7	1.7	383.18	637.20	8.935	22.5	0.348	42.516	287.83	103.72
EC-01-609	29.07.2009	11:55	609	10.07	53.46	5.3	0.8	383.18	641.46	8.888	22.9	0.341	35.652	256.58	92.96
EC-01-614	29.07.2009	11:26	614	10.05	53.50	5.3	0.8	383.18	645.72	8.821	22.3	0.362	35.464	255.64	91.85
EC-01-619	29.07.2009	10:58	619	10.02	53.53	5.5	0.9	383.18	649.99	8.447	22.4	0.324	45.604	261.58	94.12
EC-01-624	29.07.2009	10:34	624	9.95	53.54	5.5	0.9	383.18	654.25	8.003	22.4	0.337	22.380	207.51	74.67
EC-01-629	29.07.2009	10:08	629	9.87	53.54	5.5	0.9	383.18	658.51	7.947	22.1	0.335	20.476	197.51	70.77
EC-01-634	29.07.2009	09:38	634	9.80	53.55	5.4	0.9	383.18	662.77	7.981	21.7	0.332	24.980	207.51	73.93
EC-01-639	29.07.2009	09:11	639	9.72	53.56	5.4	0.9	383.18	667.04	8.059	21.5	0.323	23.276	212.20	75.38
EC-01-644	29.07.2009	08:48	644	9.65	53.57	5.1	1.1	383.18	671.30	7.892	21.4	0.353	24.360	194.39	68.95
EC-02-619	27.08.2009	11:30	619	10.02	53.53	5.7	0.9	378.89	367.15	8.136	22.2	0.416	44.076	189.07	67.69
EC-02-621	27.08.2009	11:15	621	9.95	53.54	5.7	0.9	378.89	368.11	7.733	22.3	0.422		151.26	54.23
EC-02-624	27.08.2009	11:00	624	9.87	53.54	5.7	0.9	378.89	369.56	7.632	22.2	0.425	41.076	142.82	51.13
EC-02-629	27.08.2009	10:30	629	9.80	53.55	5.6	0.3	378.89	371.97	7.536	22.2	0.423	34.148	121.26	43.41
EC-02-634	27.08.2009	10:00	634	9.72	53.56	5.6	0.3	378.89	374.38	7.615	22.2	0.339	23.820	143.76	51.47
EC-02-639	27.08.2009	09:30	639	9.65	53.57	5.6	0.6	378.89	376.78	7.659	22.1	0.434	22.088	149.07	53.30
EC-02-644	27.08.2009	09:00	644	9.69	53.57	5.6	0.6	378.89	379.19	7.640	22.7	0.478	19.660	152.20	
EC-03-609	08.09.2009	08:00	609	10.07	53.46	4.2	0.7	380.89	284.39	8.584	18.9	0.499	28.384	270.95	92.47
EC-03-614	08.09.2009	08:30	614	10.05	53.50	4.2	0.7	380.89	286.28	8.388	18.6	0.480	21.672	246.58	83.72
EC-03-624	08.09.2009	09:00	624	9.95	53.54	4.7	1.2	380.89	290.06	7.624	19.8	0.469	20.648	184.70	63.96
EC-03-634	08.09.2009	09:30	634	9.80	53.55	4.7	1.2	380.89	293.84	7.527	20.0	0.467	23.240	176.26	61.24
EC-03-649	09.09.2009	09:29	649	9.59	53.60	3.2	1.7	380.89	308.39	7.668	20.0	0.480	131.952	199.39	69.28
EC-03-659	09.09.2009	09:59	659	9.51	53.67	3.2	1.7	380.89	312.28	7.637	19.6	0.550	73.288	220.01	76.00
EC-03-669	09.09.2009	12:08	669	9.42	53.74	6.3	2.3	380.89	316.17	7.824	20.3	0.656	40.800	252.83	88.38
EC-03-679	10.09.2009	09:32	679	9.36	53.83	5.8	2.0	380.89	315.46	7.798	18.5	1.218	181.609	261.27	89.00
EC-03-689	10.09.2009	10:00	689	9.25	53.88	6.2	2.1	380.89	319.29	7.821	18.3	2.499	158.996	264.39	90.24
EC-03-694	11.09.2009	09:55	694	9.16	53.88	4.1	1.2	380.89	328.24	7.878	18.4	2.727	59.908	258.77	89.96
EC-03-699	11.09.2009	10:11	699	9.08	53.88	4.2	0.9	380.89	330.20	7.898	17.9	4.726	71.474	250.33	87.26
EC-03-704	11.09.2009	11:29	704	9.02	53.86	5.3	1.8	380.89	332.16	7.946	18.2	6.293	163.293	252.52	88.74
EC-03-709	11.09.2009	11:45	709	8.95	53.85	5.3	1.8	380.89	334.12	7.961	17.9	6.371	64.550	256.58	90.49
EC-03-714	12.09.2009	08:59	714	8.86	53.84	3.8	0.7	380.89	328.88	8.094	17.3	6.745	30.228	249.08	90.85
EC-03-719	12.09.2009	09:16	719	8.77	53.85	3.8	1.2	380.89	330.80	8.130	17.0	8.030	45.028	244.08	90.48
EC-03-729	12.09.2009	11:15	729	8.69	53.92	4.5	0.8	380.89	334.64	8.133	17.4	15.213	42.700	248.77	93.29
EC-04-609	15.10.2009	16:50	609	10.07	53.46	5.5	3.0	386.65	352.86	8.289	10.5	0.537	21.168	340.02	97.74
EC-04-619	15.10.2009	16:06	619	10.02	53.53	5.5	3.0	386.65	357.55	8.105	11.5	0.523	45.612	290.96	85.64
EC-04-629	15.10.2009	13:32	629	9.88	53.54	8.3	2.8	386.65	362.24	7.898	12.7	0.547	42.388	246.27	74.51
EC-04-639	15.10.2009	12:47	639	9.72	53.56	8.3	1.4	386.65	366.93	7.851	12.8	0.581	21.216	246.58	74.78
EC-04-649	15.10.2009	12:26	649	9.60	53.59	8.3	1.4	386.65	371.62	7.890	12.9	0.689	46.704	261.58	79.57
EC-04-659	15.10.2009	11:50	659	9.51	53.67	8.3	1.1	386.65	376.31	7.980	12.8	0.813	106.536	279.39	84.88
EC-04-669	15.10.2009	11:21	669	9.42	53.74	8.3	1.1	386.65	381.00	8.033	12.4	1.477	71.167	284.39	86.03
EC-04-674	15.10.2009	11:03	674	9.39	53.78	8.3	1.1	386.65	383.34	8.015	12.9	2.377	77.317	282.83	86.72
EC-04-679	15.10.2009	10:46	679	9.36	53.82	8.1	1.7	386.65	385.69	8.018	13.4	2.763	60.695	289.39	89.98
EC-04-684	15.10.2009	10:30	684	9.31	53.85	8.1	1.7	386.65	388.03	8.001	12.8	4.832	48.837	283.46	88.33
EC-04-689	15.10.2009	10:17	689	9.25	53.87	8.1	1.7	386.65	390.38	7.947	12.6	7.282	45.607	273.14	86.16
EC-04-694	15.10.2009	10:00	694	9.17	53.88	8.1	1.7	386.65	392.72	7.955	12.4	8.830	58.886	275.33	87.36
EC-04-699	15.10.2009	09:46	699	9.10	53.87	8.2	2.3	386.65	395.07	7.995	12.0	10.691	63.178	289.71	92.15
EC-04-709	15.10.2009	09:16	709	8.95	53.84	8.2	2.3	386.65	399.76	8.012	11.6	14.543	35.519	277.83	89.74
EC-04-719	15.10.2009	08:48	719	8.79	53.84	8.4	2.4	386.65	404.45	8.028	11.1	19.600	27.299	278.14	91.40
EC-04-724	15.10.2009	08:29	724	8.73	53.86	8.4	2.4	386.65	406.79	8.039	11.3	20.311	18.37	273.14	90.56
EC-05-570	25.03.2010	11:35	570	10.54	53.37	4.4	0.5	393.54	1153.00	8.250	9.7	0.411	16.136	393.15	110.42
EC-05-579	25.03.2010	10:48	579	10.42	53.40	3.8	0.5	393.54	1153.00	8.240	9.7	0.413	16.876	386.59	108.57
EC-05-589	25.03.2010	09:08	589	10.30	53.43	3.9	0.7	393.54	1182.17	8.270	9.4	0.415	18.204	393.77	109.76
EC-05-599	25.03.2010	08:27	599	10.18	53.40	3.7	0.6	393.54	1198.31	8.210	8.9	0.414	17.628	393.77	108.37
EC-05-609	24.03.2010	16:54	609	10.08	53.46	5.2	1.1	393.54	1189.18	8.300	8.7	0.417	16.960	403.78	110.55
EC-05-619	24.03.2010	16:10	619	10.03	53.53	5.2	1.1	393.54	1204.98	8.230	8.7	0.419	18.308	392.84	107.55
EC-05-624	24.03.2010	15:32	624	9.88	53.54	5.8	1.3	393.54	1212.88	8.100	8.4	0.422	23.080	383.77	104.25
EC-05-629	24.03.2010	15:46	629	9.94	53.54	5.8	1.3	393.54	1220.79	8.200	8.5	0.430	21.832	390.02	106.23
EC-05-639	24.03.2010	14:51	639	9.73	53.56	6.3	1.4	393.54	1236.59	8.070	8.5	0.429	24.620	390.02	106.23
EC-05-649	24.03.2010	14:12	649	9.60	53.59	6.3	1.4	393.54	1252.40	8.000	8.1	0.420	35.924	378.77	102.08
EC-05-659	24.03.2010	13:32	659	9.51	53.66	6.4	1.6	393.54	1268.21	7.930	7.6	0.451	75.212	370.96	98.65
EC-05-669	24.03.2010	12:55	669	9.43	53.74	6.3	1.5	393.54	1284.01	7.900	7.0	0.528	87.336	368.46	96.39
EC-05-679	24.03.2010	12:08	679	9.36	53.82	6.3	1.5	393.54	1299.82	7.900	6.6	0.472	98.484	372.21	96.29
EC-05-689	24.03.2010	11:25	689	9.25	53.87	6.5	1.5	393.54	1315.62	7.920	6.8	0.460	149.256	368.77	95.94
EC-05-699	24.03.2010	10:35	699	9.09	53.87	6.8	1.1	393.54	1331.43	7.910	6.7	0.666	116.284	363.77	94.37
EC-05-709	24.03.2010	09:49	709	8.95	53.84	6.3	1.2	393.54	1347.24	7.920	6.2	1.986	52.408	369.40	94.49
EC-05-719	24.03.2010	08:53	719	8.79	53.84	5.0	1.4	393.54	1363.04	7.930	6.4	7.171	32.303	367.52	94.55
EC-05-724	24.03.2010	08:21	724	8.71	53.87	5.0	1.4	393.54	1370.94	8.020	6.6	14.616	25.491	358.77	92.82
EC-06-609	07.04.2010	03:12	609	10.08	53.46	5.0	1.3	394.17	1757.96	8.135	10.2	0.313	11.716	356.90	101.48
EC-06-619	07.04.2010	03:42	619	10.03	53.53	5.0	1.3	394.17	1781.32	8.108	9.8	0.311	13.068	362.84	102.16
EC-06-624	07.04.2010	08:26	624	9.95	53.54	6.4	1.7	394.17	1793.01	8.112	10.2	0.309	11.912	357.83	101.75
EC-06-629	07.04.2010	08:41	629	9.88	53.54	6.4	1.7	394.17	1804.69	8.091	9.8	0.311	10.416	359.08	101.10
EC-06-639	07.04.2010	09:15	639	9.73	53.56	7.5	1.5	394.17	1828.06	8.036	10.1	0.310	11.820	350.33	99.37
EC-06-649	07.04.2010	09:45	649	9.60	53.60	7.5	1.5	394.17	1851.42	7.943	10.1	0.321	12.640	334.08	94.76
EC-06-659	07.04.2010	10:12	659	9.51	53.67	7.9	1.2	394.17	1874.79	7.915	10.1	0.354	13.880	326.90	92.72
EC-06-669	07.04.2010	10:40	669	9.43	53.74	7.9	1.2	394.17	1898.15	7.874	10.0	0.367	44.812	315.02	89.14
EC-06-679	07.04.2010	11:06	679	9.37	53.82	7.9	1.4	394.17	1921.52	7.752	9.9	0.374	149.240	306.58	86.53
EC-06-689	07.04.2010	11:34	689	9.25	53.88	7.9	1.4	394.17	1944.89	7.769	10.2	0.368	140.780	302.83	86.11
EC-06-699	07.04.2010	12:03	699	9.09	53.88	7.6	1.8	394.17	1968.25	7.833	9.9	0.395	209.380	298.14	84.15
EC-06-709	07.04.2010	12:31	709	8.95	53.85	7.6	1.8	394.17	1991.62	7.774	9.9	0.528	178.508	293.14	82.74
EC-06-719	07.04.2010	12:59	719	8.80	53.84	7.6	1.8	394.17	2014.98	7.816	9.5	1.454	65.243	300.96	84.10
EC-06-729	07.04.2010	13:32	729	8.69	53.91	7.1	1.6	394.17	2038.35	7.937	9.9	6.391	45.061	316.89	89.45
EC-07-570	06.05.2010	10:22	570	10.54	53.37	8.6	2.1	393.42	600.00	9.020	13.5	0.463	35.204	384.09	117.84
EC-07-579	06.05.2010	09:29	579	10.43	53.40	8.4	2.1	393.42	600.00	9.000	13.4	0.448	35.496	396.27	121.31

Overview over sampled stations and general water chemistry parameters, part 2 of 3.

ID	DATE	UTC TIME	River km	long	lat	wind speed	$\sigma_{wind\ speed}$	ambient pCO$_2$	Discharge (fac.corr.)	pH	temp-erature	Salinity	SPM	DO	DO saturation
	[dd.mm.yyyy]	[hh:mm]	[km]	[°]		[m s^{-1}]		[µatm]	[m^3 s^{-1}]	[ ]	[°C]	[ ]	[mg L^{-1}]	[µmol L^{-1}]	[%]
EC-07-589	06.05.2010	07:28	589	10.30	53.43	7.3	1.4	393.42	615.18	8.979	13.0	0.454	35.984	373.77	113.43
EC-07-599	06.05.2010	06:50	599	10.18	53.40	7.3	1.5	393.42	623.58	8.728	13.2	0.423	34.416	356.58	108.69
EC-07-609	06.05.2010	04:56	609	10.07	53.46	6.6	1.9	393.42	631.98	9.040	13.2	0.443	33.704	351.58	107.17
EC-07-619	06.05.2010	04:18	619	10.03	53.53	6.6	1.9	393.42	640.38	8.690	13.5	0.443	28.696	347.21	106.52
EC-07-624	05.05.2010	18:54	624	9.94	53.54	6.0	2.9	393.42	654.25	7.966	13.9	0.414	25.108	224.08	69.34
EC-07-629	05.05.2010	18:39	629	9.88	53.54	6.0	2.9	393.42	658.51	8.140	14.3	0.420	42.364	210.95	65.82
EC-07-639	05.05.2010	18:07	639	9.73	53.56	6.0	2.9	393.42	667.04	8.000	13.6	0.388	38.600	311.27	95.70
EC-07-644	05.05.2010	17:50	644	9.66	53.57	6.3	1.5	393.42	671.30	8.021	13.4	0.369	24.776	205.01	62.76
EC-07-649	05.05.2010	17:30	649	9.59	53.60	6.3	1.5	393.42	675.56	7.995	13.5	0.440	31.724	220.01	67.50
EC-07-659	05.05.2010	17:02	659	9.51	53.66	6.3	1.5	393.42	684.09	8.020	14.0	0.501	37.000	183.14	56.79
EC-07-669	05.05.2010	16:28	669	9.43	53.73	5.9	0.6	393.42	692.62	7.937	13.1	0.540	159.360	207.51	63.11
EC-07-679	05.05.2010	16:01	679	9.36	53.81	5.9	0.6	393.42	701.14	7.966	13.3	0.513	84.428	218.45	66.73
EC-07-689	05.05.2010	15:28	689	9.25	53.87	5.9	1.8	393.42	709.67	7.892	13.1	0.851	63.880	208.45	63.40
EC-07-699	05.05.2010	15:00	699	9.09	53.87	5.9	1.8	393.42	718.19	8.028	13.4	1.875	53.711	199.07	60.94
EC-07-709	05.05.2010	14:32	709	8.95	53.84	4.8	2.1	393.42	726.72	8.010	12.8	4.217	55.751	211.26	63.83
EC-07-719	05.05.2010	14:01	719	8.81	53.84	4.8	2.1	393.42	735.25	8.124	12.6	7.021	44.212	210.01	63.17
EC-07-724	05.05.2010	13:44	724	8.73	53.86	4.9	1.5	393.42	739.51	7.803	12.6	10.753	57.661	285.33	85.83
EC-08-644	16.07.2010	08:15	644	9.66	53.57	7.1	0.8	383.18	373.68	7.556	25.1	0.458	18.400	131.57	48.91
EC-08-649	16.07.2010	08:45	649	9.59	53.60	7.1	0.8	383.18	376.05	7.605	24.7	0.484	56.840	135.63	50.18
EC-08-659	16.07.2010	09:24	659	9.51	53.67	7.3	0.8	383.18	380.80	7.677	24.7	0.578	30.120	160.01	59.20
EC-08-669	16.07.2010	10:10	669	9.43	53.74	7.0	0.5	383.18	385.54	7.758	24.8	0.587	113.484	162.51	60.19
EC-08-679	16.07.2010	10:55	679	9.36	53.82	7.0	0.5	383.18	390.29	7.855	24.3	0.621	78.040	163.76	60.29
EC-08-689	16.07.2010	11:37	689	9.24	53.87	6.7	0.4	383.18	395.04	7.885	24.4	1.012	53.071	203.45	74.99
EC-08-699	16.07.2010	12:47	699	9.09	53.87	6.4	0.8	383.18	399.78	7.882	24.3	3.271	28.851	186.26	68.57
EC-08-709	16.07.2010	14:56	709	8.95	53.85	5.6	0.4	383.18	404.53	7.970	23.3	12.732	31.334	208.45	75.76
EC-08-719	16.07.2010	16:21	719	8.79	53.84	4.4	0.5	383.18	409.27	8.209	22.2	23.418	30.000	155.63	55.73
EC-09-609	10.08.2010	14:06	609	10.07	53.46	5.7	0.9	378.89	591.95	8.951	21.8	0.455	50.080	328.77	117.04
EC-09-619	10.08.2010	13:20	619	10.02	53.53	5.6	0.8	378.89	599.82	8.505	22.0	0.426	38.640	224.08	80.00
EC-09-624	10.08.2010	13:06	624	9.96	53.54	5.6	0.8	378.89	603.76	8.247	22.0	0.418	45.360	194.39	69.40
EC-09-629	10.08.2010	12:47	629	9.88	53.54	5.5	1.0	378.89	607.69	7.989	22.1	0.419	67.680	175.32	62.68
EC-09-634	10.08.2010	12:32	634	9.81	53.55	5.5	1.0	378.89	611.62	7.867	22.0	0.415	93.120	165.64	59.13
EC-09-639	10.08.2010	12:18	639	9.73	53.56	5.5	1.0	378.89	615.56	7.770	22.2	0.414	119.720	150.01	53.71
EC-09-644	10.08.2010	12:04	644	9.66	53.57	5.5	1.0	378.89	619.49	7.767	21.9	0.425	58.720	159.70	56.93
EC-09-649	10.08.2010	11:50	649	9.60	53.59	5.3	1.0	378.89	623.43	7.755	21.9	0.455	36.360	170.32	60.72
EC-09-659	10.08.2010	11:22	659	9.51	53.67	5.3	1.0	378.89	631.29	7.696	21.9	0.578	73.200	167.20	59.61
EC-09-669	10.08.2010	10:54	669	9.42	53.74	5.2	0.7	378.89	639.16	7.694	21.8	0.726	99.000	174.39	62.08
EC-09-679	10.08.2010	10:27	679	9.36	53.82	5.2	0.7	378.89	647.03	7.760	21.7	0.772	152.040	186.89	66.43
EC-09-689	10.08.2010	10:00	689	9.24	53.87	5.2	0.7	378.89	654.90	7.797	21.9	1.512	58.893	204.39	72.86
EC-09-699	10.08.2010	09:34	699	9.09	53.87	5.0	0.5	378.89	662.77	7.786	21.9	3.211	26.359	198.14	70.64
EC-09-709	10.08.2010	09:04	709	8.94	53.84	5.0	0.5	378.89	670.63	7.804	21.3	7.266	33.432	199.39	70.46
EC-09-719	10.08.2010	08:31	719	8.78	53.84	4.8	0.7	378.89	678.50	7.877	20.6	10.745	35.689	202.51	70.81
EC-09-724	10.08.2010	08:03	724	8.72	53.87	4.8	0.7	378.89	682.44	7.956	20.8	13.406	38.484	210.01	73.66
EC-10-609	16.09.2010	06:20	609	10.07	53.46	7.5	0.9	380.89	910.05	7.982	16.2	0.327	16.080	280.33	90.86
EC-10-619	16.09.2010	07:07	619	10.02	53.53	7.0	0.5	380.89	922.15	7.996	16.2	0.343	14.480	259.08	83.97
EC-10-624	16.09.2010	07:28	624	9.95	53.54	7.0	0.5	380.89	928.20	7.991	16.1	0.343	21.080	260.95	84.41
EC-10-629	16.09.2010	07:50	629	9.88	53.54	7.0	0.5	380.89	934.24	7.960	16.2	0.337	30.720	255.95	82.95
EC-10-634	16.09.2010	08:12	634	9.80	53.56	7.8	0.9	380.89	940.29	7.949	16.1	0.334	34.400	256.58	83.00
EC-10-639	16.09.2010	08:30	639	9.73	53.56	7.8	0.9	380.89	946.34	7.977	15.8	0.334	27.160	259.70	83.52
EC-10-644	16.09.2010	08:47	644	9.66	53.57	7.8	0.9	380.89	952.39	8.010	15.5	0.334	25.280	262.83	84.03
EC-10-649	16.09.2010	08:04	649	9.60	53.60	7.8	0.9	380.89	958.44	8.044	15.8	0.353	23.120	215.95	69.45
EC-10-659	16.09.2010	09:33	659	9.51	53.67	8.5	0.4	380.89	970.53	8.040	16.0	0.373	23.992	260.95	84.25
EC-10-669	16.09.2010	10:00	669	9.43	53.74	8.7	0.3	380.89	982.63	8.072	15.9	0.383	38.120	260.95	84.09
EC-10-679	16.09.2010	10:26	679	9.37	53.82	8.7	0.3	380.89	994.72	8.048	16.4	0.432	127.680	250.64	81.54
EC-10-689	16.09.2010	10:55	689	9.24	53.88	8.7	0.3	380.89	1006.82	8.043	16.6	0.873	192.000	255.02	83.28
EC-10-699	16.09.2010	11:26	699	9.09	53.88	7.2	2.0	380.89	1018.92	7.996	16.3	2.232	343.680	249.70	81.08
EC-10-709	16.09.2010	11:56	709	8.95	53.85	7.2	2.0	380.89	1031.01	7.993	16.1	4.731	140.234	249.39	80.67
EC-10-719	16.09.2010	12:32	719	8.79	53.85	6.8	2.9	380.89	1043.11	8.033	15.8	7.529	71.456	251.89	81.01
EC-10-724	16.09.2010	12:48	724	8.73	53.87	6.8	2.9	380.89	1049.16	8.045	15.7	8.710	49.870	250.95	80.55
EC-11-609	06.10.2010	08:19	609	10.07	53.46	5.7	0.4	386.65	1981.26	7.736	13.1	0.275	13.480	292.52	88.97
EC-11-619	06.10.2010	09:01	619	10.02	53.53	6.2	1.3	386.65	2007.59	7.719	13.1	0.279	13.320	291.89	88.78
EC-11-624	06.10.2010	09:29	624	9.95	53.54	6.2	1.3	386.65	2020.76	7.733	13.2	0.287	12.920	293.46	89.45
EC-11-629	06.10.2010	09:52	629	9.88	53.54	6.2	1.3	386.65	2033.93	7.738	13.2	0.293	22.120	296.27	90.31
EC-11-639	06.10.2010	10:45	639	9.73	53.56	6.1	1.1	386.65	2060.26	7.762	13.4	0.315	65.200	300.64	92.04
EC-11-649	06.10.2010	11:30	649	9.60	53.60	6.0	0.9	386.65	2086.59	7.882	13.7	0.382	50.880	315.64	97.25
EC-11-659	06.10.2010	12:11	659	9.52	53.67	5.5	0.5	386.65	2112.93	7.958	14.1	0.434	55.968	321.27	99.83
EC-11-669	06.10.2010	13:01	669	9.43	53.74	5.0	0.6	386.65	2139.26	8.012	14.6	0.435	36.000	325.33	102.15
EC-11-679	06.10.2010	13:37	679	9.36	53.83	5.0	0.6	386.65	2165.60	7.980	15.1	0.532	30.880	314.71	99.82
EC-11-689	06.10.2010	14:13	689	9.25	53.88	4.7	0.3	386.65	2191.93	7.910	14.9	1.232	35.539	307.83	97.25
EC-11-699	06.10.2010	14:39	699	9.10	53.88	4.7	0.3	386.65	2218.26	7.911	14.8	2.734	34.474	301.58	95.08
EC-11-709	06.10.2010	15:15	709	8.95	53.85	4.3	0.4	386.65	2244.60	7.901	14.6	6.119	74.202	296.27	93.02
EC-11-719	06.10.2010	15:40	719	8.80	53.85	4.3	0.4	386.65	2270.93	7.959	14.6	10.946	51.393	300.64	94.40
EC-11-724	06.10.2010	16:01	724	8.73	53.87	4.1	0.6	386.65	2284.10	7.971	14.6	12.867	34.860	300.33	94.30
EC-12-609	26.11.2010	17:54	609	10.07	53.46	3.8	0.9	391.24	1570.47	7.850	4.7	0.330	9.407		
EC-12-619	26.11.2010	16:54	619	10.02	53.53	3.7	0.6	391.24	1591.34	7.963	5.6	0.326	10.040	336.27	84.55
EC-12-624	26.11.2010	16:35	624	9.95	53.54	3.7	0.6	391.24	1601.78	7.952	5.5	0.323	15.200	340.96	85.48
EC-12-629	26.11.2010	16:15	629	9.88	53.54	3.7	0.6	391.24	1612.22	7.926	5.8	0.323	19.960	340.65	86.15
EC-12-639	26.11.2010	15:38	639	9.74	53.56	3.2	0.5	391.24	1633.09	7.925	6.0	0.322	23.200	337.52	85.85
EC-12-649	26.11.2010	15:10	649	9.60	53.59	3.2	0.5	391.24	1653.97	7.942	6.3	0.333	28.387	331.90	85.14
EC-12-659	26.11.2010	14:35	659	9.51	53.66	3.1	0.7	391.24	1674.84	7.930	6.8	0.387	111.400	328.77	85.53
EC-12-669	26.11.2010	14:07	669	9.42	53.74	3.1	0.7	391.24	1695.71	7.956	7.0	0.451	87.080	320.33	83.80
EC-12-679	26.11.2010	13:37	679	9.36	53.82	2.6	0.5	391.24	1716.59	7.970	7.1	0.456	90.920	321.90	84.44
EC-12-689	26.11.2010	13:11	689	9.25	53.87	2.6	0.5	391.24	1737.46	7.965	7.3	0.450	79.200	317.83	83.83
EC-12-699	26.11.2010	12:38	699	9.09	53.87	2.8	0.7	391.24	1758.34	8.003	7.1	0.489	73.800	307.52	80.67
EC-12-709	26.11.2010	12:06	709	8.94	53.84	2.8	0.7	391.24	1779.21	7.949	7.4	0.883	77.331	311.58	82.41
EC-12-719	26.11.2010	11:24	719	8.78	53.84	3.3	1.0	391.24	1800.08	7.924	7.3	3.036	81.829	310.96	82.02
EC-12-724	26.11.2010	10:50	724	8.72	53.87	3.7	1.6	391.24	1810.52	7.946	6.9	4.115	80.773	317.52	82.83
EC-13-609	21.02.2011	10:23	609	10.07	53.46	6.9	1.7	392.73	1731.63	8.024	1.1	0.354	7.760	424.09	92.65

Overview over sampled stations and general water chemistry parameters, part 3 of 3.

ID	DATE	UTC TIME	River km	long	lat	wind speed	$\sigma_{\text{wind speed}}$	ambient *p*CO$_2$	Discharge (fac.corr.)	pH	temperature	Salinity	SPM	DO	DO saturation
	[dd.mm.yyyy]	[hh:mm]	[km]	[°]		[m s^{-1}]	[µatm]		[m^3 s^{-1}]	[ ]	[°C]	[ ]	[mg L^{-1}]	[µmol L^{-1}]	[%]
EC-13-619	21.02.2011	12:12	619	10.02	53.53	6.2	1.8	392.73	1754.64	8.036	1.4	0.355	7.680	419.40	92.55
EC-13-624	22.02.2011	08:02	624	9.95	53.54	6.1	1.6	392.73	1701.69	8.064	1.3	0.353	8.320	361.59	79.53
EC-13-629	22.02.2011	08:28	629	9.87	53.55	6.1	1.6	392.73	1712.78	7.987	0.9	0.354	10.760	420.03	91.15
EC-13-639	22.02.2011	09:01	639	9.72	53.57	6.7	0.9	392.73	1734.96		1.1	0.354	19.200	412.21	90.06
EC-13-649	22.02.2011	09:31	649	9.60	53.60	6.7	0.9	392.73	1757.13	8.019	1.2	0.359	21.129	410.65	90.02
EC-13-659	22.02.2011	10:01	659	9.51	53.67	6.0	1.1	392.73	1779.31	8.000	1.3	0.365	32.240	400.34	88.05
EC-13-669	22.02.2011	10:35	669	9.42	53.75	6.0	1.1	392.73	1801.48	8.021	1.1	0.383	41.920	409.40	89.44
EC-13-679	22.02.2011	11:07	679	9.36	53.83	5.6	1.3	392.73	1823.66	8.044	1.1	0.371	62.640	405.96	88.69
EC-13-689	22.02.2011	11:40	689	9.23	53.88	5.6	1.3	392.73	1845.84	8.024	1.3	0.385	63.600	405.03	89.08
EC-13-699	22.02.2011	12:17	699	9.08	53.88	5.2	1.7	392.73	1868.01	8.011	1.5	0.393	54.800	397.21	87.94
EC-13-709	22.02.2011	13:03	709	8.95	53.85	5.2	1.7	392.73	1890.19	8.024	2.0	1.589	100.903	395.34	88.98
EC-13-719	22.02.2011	13:56	719	8.79	53.85	5.2	1.7	392.73	1912.36	8.040	1.4	11.321	99.620	370.34	81.72
EC-13-724	22.02.2011	14:22	724	8.73	53.87	5.0	1.8	392.73	1923.45	8.008	1.6	19.118	78.085	363.46	80.75
EC-14-609	26.04.2011	07:09	609	10.07	53.46	4.3	1.6	394.17	700.44	8.869	15.9	0.468	45.141	413.15	133.13
EC-14-619	26.04.2011	08:31	619	10.02	53.53	4.9	1.0	394.17	709.75	8.511	16.0	0.449	22.065	278.77	90.00
EC-14-624	26.04.2011	08:51	624	9.95	53.54	4.9	1.0	394.17	714.41	8.424	15.8	0.436	25.120	268.14	86.24
EC-14-629	26.04.2011	09:19	629	9.88	53.54	5.1	0.7	394.17	719.06	8.341	15.6	0.448	24.040	241.58	77.39
EC-14-634	26.04.2011	09:40	634	9.80	53.55	5.1	0.7	394.17	723.72	8.196	15.3	0.448	18.000	229.39	73.05
EC-14-639	26.04.2011	10:08	639	9.73	53.56	5.4	1.0	394.17	728.37	8.142	15.6	0.449	17.520	227.83	72.98
EC-14-644	26.04.2011	10:29	644	9.66	53.57	5.4	1.0	394.17	733.03	8.001	15.0	0.452	14.600	219.39	69.45
EC-14-649	26.04.2011	10:52	649	9.59	53.60	5.4	1.0	394.17	737.68	7.916	15.0	0.463	16.040	205.64	65.09
EC-14-659	26.04.2011	11:20	659	9.51	53.67	5.8	1.3	394.17	746.99	7.784	14.6	0.507	130.640	205.95	64.66
EC-14-669	26.04.2011	12:00	669	9.43	53.74	6.8	1.6	394.17	756.30	7.760	14.4	0.521	114.240	216.26	67.62
EC-14-679	26.04.2011	12:37	679	9.36	53.83	6.8	1.6	394.17	765.61	7.771	14.5	0.533	265.000	228.45	71.58
EC-14-689	26.04.2011	13:10	689	9.25	53.88	7.2	1.9	394.17	774.92	7.775	14.7	0.564	356.040	234.08	73.65
EC-14-699	26.04.2011	13:45	699	9.09	53.88	7.2	1.9	394.17	784.23	7.762	14.6	1.409	277.109	236.89	74.38
EC-14-709	26.04.2011	14:21	709	8.95	53.85	7.3	2.2	394.17	793.54	7.740	14.4	2.999	60.519	237.20	74.17
EC-14-719	26.04.2011	14:57	719	8.79	53.85	7.3	2.2	394.17	802.85	7.787	13.7	6.875	60.157	253.45	78.09
EC-14-724	26.04.2011	15:25	724	8.74	53.87	7.2	2.3	394.17	807.51	7.866	13.7	9.188	40.096	258.45	79.64
EC-15-609	13.07.2011	13:40	609	10.08	53.46	6.3	2.9	383.18	521.38	8.55	22.4	0.406	60.800	387.52	139.47
EC-15-619	13.07.2011	12:41	619	10.02	53.53	6.1	3.0	383.18	528.31	7.767	22.1	0.466	37.440	233.45	83.69
EC-15-624	13.07.2011	12:23	624	9.95	53.54	6.1	3.0	383.18	531.78	7.573	21.6	0.483	92.360	187.82	66.86
EC-15-629	13.07.2011	12:07	629	9.88	53.54	6.1	3.0	383.18	535.24	7.509	21.3	0.489	25.440	177.51	62.91
EC-15-634	13.07.2011	11:51	634	9.81	53.55	6.2	3.3	383.18	538.71	7.461	21	0.489	35.840	154.70	54.58
EC-15-639	13.07.2011	11:34	639	9.73	53.56	6.2	3.3	383.18	542.17	7.498	20.8	0.485	43.000	171.26	60.24
EC-15-644	13.07.2011	11:18	644	9.66	53.57	6.2	3.3	383.18	545.64	7.513	20.6	0.486	44.400	173.76	60.93
EC-15-649	13.07.2011	11:00	649	9.60	53.59	6.2	3.3	383.18	549.10	7.573	20.5	0.563	36.160	188.14	65.97
EC-15-659	13.07.2011	10:30	659	9.51	53.67	6.7	3.6	383.18	556.03	7.586	20.5	0.589	59.120	175.01	61.32
EC-15-669	13.07.2011	09:59	669	9.42	53.74	7.7	3.3	383.18	562.96	7.677	20.4	0.680	144.720	220.95	77.34
EC-15-679	13.07.2011	09:26	679	9.36	53.82	7.7	3.3	383.18	569.89	7.757	19.9	0.770	243.000	248.77	86.45
EC-15-689	13.07.2011	08:59	689	9.25	53.87	7.7	2.9	383.18	576.82	7.845	19.5	1.744	138.722	265.64	92.32
EC-15-699	13.07.2011	08:30	699	9.10	53.87	7.7	2.9	383.18	583.75	7.826	19.2	3.272	31.650	258.14	90.20
EC-15-709	13.07.2011	07:54	709	8.95	53.85	8.1	4.2	383.18	590.68	7.841	18.9	5.882	42.550	264.70	93.77
EC-16-609	08.09.2011	06:09	609	10.07	53.46	5.9	0.9	380.89	623.55	8.442	17.6	0.467	34.720	281.58	93.89
EC-16-619	08.09.2011	06:47	619	10.02	53.53	5.9	0.9	380.89	631.84	8.283	17.8	0.419	31.400	257.52	86.16
EC-16-624	08.09.2011	07:09	624	9.95	53.54	5.8	1.0	380.89	635.99	8.290	17.8	0.394	26.320	256.27	85.73
EC-16-629	08.09.2011	07:31	629	9.88	53.54	5.8	1.0	380.89	640.13	8.182	18.1	0.431	26.089	241.89	81.36
EC-16-639	08.09.2011	08:15	639	9.73	53.56	6.8	1.3	380.89	648.42	7.960	18.1	0.415	37.400	216.89	72.95
EC-16-649	08.09.2011	08:58	649	9.60	53.60	6.8	1.3	380.89	656.71	8.017	17.8	0.429	153.880	238.45	79.78
EC-16-659	08.09.2011	09:40	659	9.52	53.67	7.9	1.0	380.89	664.99	8.033	18.2	0.504	82.840	241.27	81.34
EC-16-669	08.09.2011	10:22	669	9.43	53.74	7.7	0.5	380.89	673.28	8.014	17.8	0.494	76.680	244.08	81.70
EC-16-679	08.09.2011	10:59	679	9.37	53.82	7.7	0.5	380.89	681.57	8.007	18	0.895	60.880	255.95	86.21
EC-16-689	08.09.2011	11:33	689	9.25	53.88	7.4	0.9	380.89	689.86	7.892	17.4	2.492	60.804	243.14	81.89
EC-16-699	08.09.2011	12:06	699	9.09	53.88	7.2	0.9	380.89	698.15	7.948	16.8	5.097	35.507	250.02	84.74
EC-16-709	08.09.2011	12:36	709	8.95	53.85	7.2	0.9	380.89	706.43	8.011	16.4	9.015	37.571	257.83	89.03
EC-16-719	08.09.2011	13:04	719	8.79	53.84	6.2	0.6	380.89	714.72	8.009	16.4	13.287	25.572	252.52	89.79
EC-16-724	08.09.2011	13:18	724	8.73	53.87	6.2	0.6	380.89	718.87	8.020	16.4	17.014	58.248	245.64	89.53
EC-17-609	25.10.2011	06:24	609	10.08	53.46	8.9	2.9	386.65	638.30	8.176	8.8	0.415	17.000	338.46	93.11
EC-17-619	25.10.2011	07:09	619	10.02	53.53	9.0	3.1	386.65	646.78	8.105	8.8	0.408	21.120	328.46	90.36
EC-17-624	25.10.2011	07:36	624	9.95	53.54	9.0	3.1	386.65	651.03	8.091	9.0	0.414	17.040	320.33	88.58
EC-17-629	25.10.2011	07:57	629	9.88	53.54	9.0	3.1	386.65	655.27	8.103	9.2	0.423	21.480	317.21	88.17
EC-17-639	25.10.2011	08:32	639	9.73	53.56	8.9	2.3	386.65	663.75	8.110	9.5	0.435	28.880	311.58	87.27
EC-17-649	25.10.2011	09:19	649	9.60	53.60	8.9	1.7	386.65	672.24	8.038	9.7	0.459	74.080	299.08	84.21
EC-17-659	25.10.2011	10:06	659	9.52	53.66	9.4	1.9	386.65	680.72	8.090	10.1	0.504	230.560	288.14	81.96
EC-17-669	25.10.2011	11:00	669	9.43	53.74	9.6	2.8	386.65	689.20	8.060	10.6	0.551	136.320	290.64	83.72
EC-17-679	25.10.2011	11:46	679	9.36	53.83	9.6	2.8	386.65	697.69	8.042	11.3	0.586	205.640	285.96	83.78
EC-17-689	25.10.2011	12:28	689	9.25	53.88	9.6	2.8	386.65	706.17	8.032	11.4	1.152	141.000	284.08	83.74
EC-17-699	25.10.2011	13:08	699	9.09	53.88	8.5	2.1	386.65	714.66	8.053	11.3	2.487	76.125	286.89	85.14
EC-17-709	25.10.2011	13:44	709	8.93	53.85	8.5	2.1	386.65	723.14	8.088	10.8	8.610	54.723	296.89	90.52
EC-17-719	25.10.2011	14:13	719	8.79	53.85	8.1	3.1	386.65	731.62	8.108	10.6	10.908	51.393	292.21	89.92
EC-17-724	25.10.2011	14:30	724	8.73	53.87	8.1	3.1	386.65	735.87	8.116	10.5	17.757	75.398	284.39	90.43
EC-18-609	20.12.2011	17:00	609	10.07	53.46	3.6	1.9	393.19	674.11	8.137	3.2	0.421	12.400	389.09	91.00
EC-18-619	20.12.2011	16:13	619	10.02	53.53	3.1	0.6	393.19	683.07	8.113	3.1	0.410	14.320	382.21	89.11
EC-18-624	20.12.2011	15:56	624	9.95	53.54	3.9	0.9	393.19	687.55	8.09	3.4	0.404	15.800	378.15	89.00
EC-18-629	20.12.2011	15:24	629	9.88	53.54	3.9	0.9	393.19	692.03	8.033	3.5	0.417	20.720	376.90	88.98
EC-18-639	20.12.2011	14:39	639	9.73	53.56	4.5	1.5	393.19	700.99	8.034	3.6	0.430	72.720	373.77	88.51
EC-18-649	20.12.2011	14:00	649	9.60	53.60	4.5	1.5	393.19	709.95	8.008	3.7	0.447	56.840	365.02	86.71
EC-18-659	20.12.2011	13:17	659	9.51	53.66	5.2	1.3	393.19	718.91	8.007	3.8	0.535	237.600	356.27	84.89
EC-18-669	20.12.2011	12:35	669	9.43	53.74	5.5	1.6	393.19	727.87	8.04	3.9	0.595	364.450	349.71	83.59
EC-18-679	20.12.2011	11:41	679	9.36	53.82	6.0	1.4	393.19	736.83	8.12	4	0.631	197.000	361.90	86.76
EC-18-689	20.12.2011	11:00	689	9.25	53.87	6.0	1.4	393.19	745.79	8.12	4	1.397	121.254	360.96	86.54
EC-18-699	20.12.2011	10:14	699	9.09	53.87	6.4	0.8	393.19	754.75	8.101	4.1	3.670	183.172	348.46	83.80
EC-18-709	20.12.2011	09:33	709	8.95	53.84	6.5	1.4	393.19	763.71	8.056	3.9	10.161	44.306	338.77	80.97
EC-18-719	20.12.2011	08:49	719	8.79	53.84	6.5	1.2	393.19	772.67	8.024	4.1	19.443	37.631	318.46	76.59
EC-18-724	20.12.2011	08:20	724	8.72	53.87	6.5	1.2	393.19	777.15	7.913	4.2	13.401	21.772	326.58	78.78

2. Overview over nutrient parameters, part 1 of 3.

ID	DATE	NO_3	σ_{NO3}	NO_2	σ_{NO2}	NH_4	σ_{NH4}	PO_4	σ_{PO4}	DSi	σ_{DSi}	BSi	BSi	σ_{BSi}
	[dd.mm.yyyy]					[µmol L^{-1}]							[SiO2%SPM]	
EC-01-589	29.07.2009							0.11	0.01	61.94	1.89	76.45	16.02	
EC-01-592	29.07.2009													
EC-01-594	29.07.2009							0.08	0.00	63.04	2.19	75.21	16.07	
EC-01-597	29.07.2009													
EC-01-599	29.07.2009							0.76	0.01	63.70	1.26	75.72	16.03	
EC-01-604	29.07.2009							0.07	0.00	63.76	2.28			
EC-01-609	29.07.2009							0.38	0.00	68.89	2.07	76.16	17.99	
EC-01-614	29.07.2009							0.86	0.01	71.68	2.58	73.32	18.23	
EC-01-619	29.07.2009							0.85	0.01	80.58	0.65	81.80	15.95	
EC-01-624	29.07.2009							0.07	0.00	85.82	1.26			
EC-01-629	29.07.2009							1.02	0.01	82.56	2.40	57.43	27.61	
EC-01-634	29.07.2009							0.95	0.01	58.12	2.09	102.76	36.68	
EC-01-639	29.07.2009							0.48	0.00	36.99	1.00	78.95	32.22	
EC-01-644	29.07.2009							1.44	0.01	34.14	3.36	67.61	25.22	
EC-02-619	27.08.2009							0.19	0.00	19.19	1.10	70.92	16.75	
EC-02-621	27.08.2009													
EC-02-624	27.08.2009							0.20	0.00	8.15	0.46	62.98	15.08	
EC-02-629	27.08.2009							0.22	0.01	3.98	0.52	41.84	13.70	
EC-02-634	27.08.2009							0.23	0.01	1.95	0.33	35.53	17.02	
EC-02-639	27.08.2009							0.31	0.01	2.70	0.29	31.13	14.87	
EC-02-644	27.08.2009							0.22	0.01	15.41	0.97	30.25	13.01	
EC-03-609	08.09.2009							0.08	0.00	13.33	0.02	58.11	22.37	
EC-03-614	08.09.2009							0.09	0.00	13.69	0.49	90.43	16.17	
EC-03-624	08.09.2009							0.59	0.01	6.33	0.35	39.66	17.79	
EC-03-634	08.09.2009							1.20	0.00	2.55	0.72	41.65	15.80	
EC-03-649	09.09.2009							0.17	0.01	2.12	0.39	133.43	7.79	0.11
EC-03-659	09.09.2009							1.54	0.01	5.49	0.50	84.39	9.37	0.01
EC-03-669	09.09.2009							1.77	0.03	8.77	0.31	47.49	10.62	
EC-03-679	10.09.2009							2.36	0.01	23.95	1.15	163.51	5.65	0.04
EC-03-689	10.09.2009							5.96	0.04	29.86	1.99	145.03	5.80	0.66
EC-03-694	11.09.2009							2.18	0.01	34.40	1.87	57.98	7.74	
EC-03-699	11.09.2009							2.08	0.02	35.61	2.02	73.13	8.04	
EC-03-704	11.09.2009							2.23	0.01	36.42	1.61	198.00	4.75	0.54
EC-03-709	11.09.2009							2.19	0.00	35.72	1.86	37.32	4.87	
EC-03-714	12.09.2009							1.28	0.01	25.65	0.54	54.62	15.44	
EC-03-719	12.09.2009							1.51	0.02	19.15	1.56	23.83	3.65	
EC-03-729	12.09.2009							1.15	0.00	18.19	0.03	37.05	6.72	
EC-04-609	15.10.2009							0.83	0.01	90.82	0.25	33.12	17.89	
EC-04-619	15.10.2009							0.04	0.00	75.51	3.92	66.34	11.44	
EC-04-629	15.10.2009							0.03	0.00	50.88	1.20	59.60	12.55	
EC-04-639	15.10.2009							0.32	0.01	25.45	0.11	56.92	10.65	
EC-04-649	15.10.2009							0.04	0.00	16.04	0.46	61.49	8.81	
EC-04-659	15.10.2009							0.04	0.01	19.49	0.97	64.26	7.82	
EC-04-669	15.10.2009							1.23	0.02	24.20	1.46	69.79	8.39	
EC-04-674	15.10.2009							1.24	0.04	26.86	1.79	50.39	8.99	
EC-04-679	15.10.2009							0.28	0.08	28.48	2.00	46.27	9.61	
EC-04-684	15.10.2009							0.14	0.01	30.06	1.34	25.61	10.89	
EC-04-689	15.10.2009							0.05	0.01	28.63	1.50	28.59	9.57	
EC-04-694	15.10.2009							1.90	0.03	31.77	1.89	36.11	6.81	
EC-04-699	15.10.2009							2.30	0.13	29.36	1.59	25.21	10.10	
EC-04-709	15.10.2009							1.29	0.28	25.78	1.82	22.99	8.73	
EC-04-719	15.10.2009							1.78	0.19	20.43	1.78	41.97	7.28	
EC-04-724	15.10.2009							0.11	0.01	18.77	2.17	17.92	7.43	
EC-05-570	25.03.2010							0.54	0.01	157.57	0.26	27.63	11.15	0.55
EC-05-579	25.03.2010							0.33	0.03	158.31	0.11	23.32	9.05	0.47
EC-05-589	25.03.2010							0.09	0.00	158.87	0.60	23.35	8.08	0.78
EC-05-599	25.03.2010							0.29	0.01	158.45	0.52	36.35	10.11	0.35
EC-05-609	24.03.2010							0.50	0.00	163.02	0.19	38.13	9.56	0.22
EC-05-619	24.03.2010							0.09	0.01	163.68	0.30	31.83	7.98	0.39
EC-05-624	24.03.2010							0.67	0.01	172.32	0.04	31.23	7.83	1.02
EC-05-629	24.03.2010							0.69	0.01	167.24	0.19	34.99	8.77	0.53
EC-05-639	24.03.2010							0.15	0.01	173.38	0.34	22.07	5.53	0.19
EC-05-649	24.03.2010							0.13	0.00	179.40	0.19	32.51	8.15	0.16
EC-05-659	24.03.2010							0.86	0.02	177.08	3.05	25.14	6.30	0.54
EC-05-669	24.03.2010							1.02	0.10	182.94	0.04	23.18	5.81	0.27
EC-05-679	24.03.2010							1.12	0.01	183.17	4.49	23.16	5.81	0.21
EC-05-689	24.03.2010							0.87	0.03	182.29	1.44	28.36	4.93	0.13
EC-05-699	24.03.2010							1.32	0.01	183.47	0.04	62.25	6.96	0.06
EC-05-709	24.03.2010							1.46	0.03	119.58	0.04	105.35	9.24	0.14
EC-05-719	24.03.2010							0.76	0.04	142.33	0.15	107.26	8.63	0.14
EC-05-724	24.03.2010							0.39	0.04	96.69	0.04	91.20	7.34	0.34
EC-06-609	07.04.2010							0.96	0.01	128.72	0.04	15.39	10.40	3.04
EC-06-619	07.04.2010							0.36	0.01	131.23	0.22	15.51	12.41	1.39
EC-06-624	07.04.2010							0.06	0.01	131.44	0.22	16.48	10.82	0.66
EC-06-629	07.04.2010							0.08	0.01	132.92	0.00	18.90	10.61	0.23
EC-06-639	07.04.2010							0.61	0.01	135.35	0.07	15.76	9.62	0.32
EC-06-649	07.04.2010							1.10	0.03	138.52	0.07	16.31	9.33	0.68
EC-06-659	07.04.2010							0.41	0.03	141.77	0.11	15.29	7.05	1.65
EC-06-669	07.04.2010							1.66	0.01	143.12	0.00	40.36	7.82	0.38
EC-06-679	07.04.2010							1.15	0.06	145.13	0.00	95.25	4.64	0.12
EC-06-689	07.04.2010							1.32	0.07	146.55	0.22	105.21	5.06	0.21
EC-06-699	07.04.2010							1.60	0.05	149.25	0.00	125.21	4.69	0.38
EC-06-709	07.04.2010							1.17	0.11	154.88	0.04	131.88	4.92	0.25
EC-06-719	07.04.2010							1.29	0.03	156.54	0.52	76.26	8.19	0.43
EC-06-729	07.04.2010							0.78	0.00	133.84	0.04	52.48	8.49	0.10
EC-07-570	06.05.2010							0.21	0.01	6.43	0.04	105.37	30.59	2.09
EC-07-579	06.05.2010							0.36	0.01	6.84	0.04	80.83	19.79	1.21

Overview over nutrient parameters, part 2 of 3.

ID	DATE	NO$_3$	σ_{NO3}	NO$_2$	σ_{NO2}	NH$_4$	σ_{NH4}	PO$_4$	σ_{PO4}	DSi	σ_{DSi}	BSi	BSi	σ_{BSi}
	[dd.mm.yyyy]					[µmol L^{-1}]							[SiO2%SPM]	
EC-07-589	06.05.2010							0.20	0.01	4.72	0.00	102.83	27.01	0.49
EC-07-599	06.05.2010							0.92	0.04	22.52	0.00	71.59	21.25	3.11
EC-07-609	06.05.2010							0.49	0.03	8.31	0.04	83.88	19.28	0.37
EC-07-619	06.05.2010							0.42	0.01	4.25	0.00	63.13	19.89	1.20
EC-07-624	05.05.2010							1.51	0.01	16.53	0.04	89.24	23.11	0.41
EC-07-629	05.05.2010							1.64	0.05	21.31	0.00	62.08	16.29	0.66
EC-07-639	05.05.2010							1.78	0.03	28.88	0.11	66.49	11.67	0.71
EC-07-644	05.05.2010							2.13	0.01	28.90	0.15	84.98	10.88	1.05
EC-07-649	05.05.2010							1.65	0.03	36.83	0.19	47.53	11.21	0.73
EC-07-659	05.05.2010							1.80	0.01	44.52	0.04	44.25	10.69	0.67
EC-07-669	05.05.2010							1.42	0.02	56.06	0.22	116.39	6.32	0.47
EC-07-679	05.05.2010							2.38	0.03	76.08	0.11	117.61	6.11	0.26
EC-07-689	05.05.2010							2.23	0.03	85.35	0.11	74.25	5.89	1.48
EC-07-699	05.05.2010							2.84	0.05	94.79	0.30	88.55	9.28	0.20
EC-07-709	05.05.2010							2.63	0.01	93.01	0.37	72.46	9.12	0.66
EC-07-719	05.05.2010									90.26	2.26	44.03	10.53	0.76
EC-07-724	05.05.2010							1.77	0.07	67.58	0.37	49.28	7.91	0.24
EC-08-644	16.07.2010	169.983	1.671	0.031	0.003	2.490	0.028	2.293	0.009	2.78	0.07	41.39	17.14	0.60
EC-08-649	16.07.2010	147.872	7.379	0.034	0.001	3.422	0.024	2.403	0.007	3.19	0.03	76.12	10.31	0.83
EC-08-659	16.07.2010	102.911	2.567	0.034	0.000	2.568	0.028	2.261	0.006	4.51	0.10	41.87	11.10	0.59
EC-08-669	16.07.2010	30.014	1.274	0.031	0.000	1.775	0.044	2.066	0.005	7.48	0.03	114.08	7.88	0.48
EC-08-679	16.07.2010	135.338	3.070	0.034	0.001	1.533	0.053	2.381	0.012	15.95	0.03	75.57	7.58	0.08
EC-08-689	16.07.2010	140.342	2.547	0.035	0.001	2.044	0.047	2.751	0.002	28.89	0.07	58.85	8.24	0.17
EC-08-699	16.07.2010	151.369	1.485	0.033	0.000	1.857	0.057	3.162	0.073	49.37	0.17	38.40	10.10	0.99
EC-08-709	16.07.2010	138.558	0.938	0.026	0.002	4.977	0.010	2.990	0.003	46.57	0.00	37.12	7.25	0.42
EC-08-719	16.07.2010	159.120	2.963	0.012	0.001	3.200	0.044	1.274	0.001	14.52	0.07	10.83	6.06	0.20
EC-09-609	10.08.2010	85.164	2.373	0.037	0.002	1.934	0.040	5.970	0.045	84.28	0.17	89.08	13.03	0.12
EC-09-619	10.08.2010	80.123	4.214	0.049	0.001	15.341	0.016	13.362	0.064	78.42	0.24	70.67	13.13	1.03
EC-09-624	10.08.2010	68.699	15.991	0.044	0.002	15.988	0.102	14.331	0.041	82.34	1.22	79.50	11.07	0.28
EC-09-629	10.08.2010	56.245	1.813	0.039	0.004	12.045	0.006	1.714	0.051	66.68	0.07	105.03	10.03	0.55
EC-09-634	10.08.2010	104.299	0.661	0.047	0.003	12.500	0.044	2.218	0.005	61.00	0.17	123.73	9.38	0.29
EC-09-639	10.08.2010	111.202	5.269	0.032	0.001	6.183	0.079	2.090	0.049	46.62	0.07	177.39	9.47	0.64
EC-09-644	10.08.2010	87.121	0.384	0.035	0.004	2.555	0.039	1.406	0.016	18.58	0.20	114.29	14.70	0.02
EC-09-649	10.08.2010	105.767	3.043	0.029	0.002	3.277	0.306	1.896	0.114	6.15	0.34	81.37	15.68	0.04
EC-09-659	10.08.2010	74.580	0.578	0.021	0.000	1.571	0.018	1.360	0.001	3.10	0.03	70.00	7.86	0.40
EC-09-669	10.08.2010	69.089	2.720	0.021	0.001	1.727	0.002	1.865	0.055	5.06	0.03	92.26	7.52	0.47
EC-09-679	10.08.2010	103.194	2.683	0.026	0.000	1.319	0.021	2.563	0.030	14.59	0.41	140.41	7.06	0.32
EC-09-689	10.08.2010	101.135	0.724	0.025	0.001	1.092	0.036	2.412	0.002	25.61	0.31	56.84	8.12	0.14
EC-09-699	10.08.2010	132.509	0.975	0.029	0.001	1.661	0.065	3.602	0.007	38.22	0.07	34.53	10.42	0.46
EC-09-709	10.08.2010	118.988	4.860	0.025	0.000	2.472	0.018	3.634	0.007	45.15	0.03	31.67	7.97	0.05
EC-09-719	10.08.2010	81.872	1.294	0.021	0.000	3.329	0.036	2.769	0.015	43.21	0.07	28.61	6.99	0.33
EC-09-724	10.08.2010	61.722	1.845	0.022	0.002	4.307	0.073	2.572	0.050	36.94	0.10	31.38	6.83	0.21
EC-10-609	16.09.2010	187.284	0.181	0.009	0.003	1.326	0.011	2.798	0.067	146.91	0.55	24.63	12.61	0.82
EC-10-619	16.09.2010	190.198	0.239	0.034	0.006	4.525	0.002	2.736	0.002	140.63	1.03	24.48	13.43	0.94
EC-10-624	16.09.2010	160.960	0.296	0.035	0.008	5.517	0.007	2.435	0.005	141.51	0.34	28.21	11.11	0.66
EC-10-629	16.09.2010	191.571	0.732	1.149	0.011	6.163	0.015	1.781	0.009	140.92	0.76	38.53	10.19	0.08
EC-10-634	16.09.2010	136.857	1.645	0.045	0.001	6.258	0.397	2.502	0.168	137.22	1.03	69.46	16.28	1.43
EC-10-639	16.09.2010	175.873	1.217	0.047	0.002	5.978	0.246	2.694	0.119	131.86	0.34	78.62	24.11	0.26
EC-10-644	16.09.2010	136.602	0.625	0.043	0.001	4.912	0.241	2.404	0.152	129.28	0.69	64.05	20.54	0.29
EC-10-649	16.09.2010	207.106	0.970	0.051	0.005	2.911	0.037	2.840	0.014	122.41	0.21	68.24	23.33	0.66
EC-10-659	16.09.2010	203.512	4.261	0.056	0.001	2.826	0.144	2.779	0.055	121.90	0.86	51.36	16.41	0.57
EC-10-669	16.09.2010	192.467	1.094	0.060	0.000	2.323	0.012	2.747	0.011	120.66	0.21	55.33	11.45	0.46
EC-10-679	16.09.2010	128.069	1.933	0.047	0.001	1.236	0.285	2.292	0.291	119.78	0.90	102.34	6.22	0.38
EC-10-689	16.09.2010	181.300	0.156	0.080	0.005	2.095	0.053	3.047	0.009	110.92	0.48	135.05	5.34	0.15
EC-10-699	16.09.2010	96.672	2.213	0.105	0.001	1.248	0.119	2.504	0.013	101.32	0.00	201.81	4.44	0.08
EC-10-709	16.09.2010	113.034	4.377	0.119	0.002	1.862	0.032	2.695	0.112	90.36	0.48	101.96	5.65	0.05
EC-10-719	16.09.2010	125.940	2.558	0.128	0.005	3.867	0.048	3.322	0.026	79.45	0.48	56.87	6.08	0.09
EC-10-724	16.09.2010	128.133	2.517	0.130		4.866	0.039	3.403	0.007	74.58	0.07	45.42	6.42	0.53
EC-11-609	06.10.2010	262.823	5.093	0.023	0.001	3.073	0.015	3.203	0.012	168.54	0.34	12.22	6.31	0.14
EC-11-619	06.10.2010	193.567	1.190	0.025	0.006	3.834	0.721	3.274	0.657	166.35	1.38	10.60	5.21	0.24
EC-11-624	06.10.2010	214.089	0.676	0.031	0.001	4.979	0.028	2.998	0.119	164.16	1.38	13.65	7.61	0.27
EC-11-629	06.10.2010	252.508	3.686	0.044	0.004	5.503	0.196	3.226	0.055	164.40	1.03	17.85	6.14	0.03
EC-11-639	06.10.2010	249.074	2.467	0.050	0.003	6.512	0.021	3.273	0.002	166.59	0.69	36.17	4.47	0.32
EC-11-649	06.10.2010	227.926	0.362	0.058	0.002	4.746	0.006	3.021	0.001	153.56	1.21	93.56	14.30	1.13
EC-11-659	06.10.2010	197.096	1.724	0.055	0.001	1.874	0.042	2.475	0.003	131.40	0.86	115.54	16.99	1.39
EC-11-669	06.10.2010	185.777	2.285	0.048	0.000	1.145	0.010	2.002	0.017	112.89	0.17	83.54	17.49	0.03
EC-11-679	06.10.2010	194.564	0.657	0.047	0.002	1.142	0.012	2.979	0.001	118.98	0.86	52.51	13.92	0.05
EC-11-689	06.10.2010	127.630	1.371	0.039	0.002	0.808	0.056	2.156	0.137	116.79	0.17	48.50	11.27	0.40
EC-11-699	06.10.2010	165.383	2.199	0.051	0.002	1.110	0.023	2.538	0.008	108.50	0.86	46.46	10.51	0.10
EC-11-709	06.10.2010	130.567	0.152	0.047	0.000	2.163	0.038	2.255	0.022	94.26	0.69	66.97	7.12	0.21
EC-11-719	06.10.2010	116.575	2.722	0.046	0.002	5.032	0.196	2.564	0.121	80.86	0.34	48.64	7.46	0.01
EC-11-724	06.10.2010	94.296	4.904	0.050	0.003	5.560	0.074			72.70	0.17	39.17	7.49	0.17
EC-12-609	26.11.2010	305.009	4.305	1.107	0.003	2.507	0.013	2.478	0.001	194.24	1.21	6.71	4.95	0.70
EC-12-619	26.11.2010	300.679	8.086	1.158	0.001	4.127	0.035	2.920	0.002	190.95	0.69	7.53	6.12	0.65
EC-12-624	26.11.2010	307.225	1.225	1.163	0.005	3.969	0.000	2.507	0.001	191.56	0.17	6.73	3.17	0.73
EC-12-629	26.11.2010	316.816	3.358	1.195	0.001	4.954	0.025	2.460	0.002	190.46	0.69	13.42	3.89	0.22
EC-12-639	26.11.2010	311.424	3.661	1.208	0.002	5.241	0.008	2.479	0.003	189.49	1.38	18.86	4.90	0.42
EC-12-649	26.11.2010	288.174	3.911	1.278	0.001	5.631	0.005	2.526	0.001	189.73	1.03	35.03	7.14	0.02
EC-12-659	26.11.2010	263.699	7.025	1.324	0.067	5.590	0.178	2.512	0.046	189.37	0.52	63.91	3.67	0.18
EC-12-669	26.11.2010	264.524	0.330	1.662	0.002	4.899	0.014	2.431	0.001	192.53	0.17	69.83	5.34	0.23
EC-12-679	26.11.2010	267.019	0.014	1.657	0.002	2.799	0.048	2.364	0.002	195.82	0.34	66.80	4.89	0.16
EC-12-689	26.11.2010	260.557	0.592	1.475	0.000	2.981	0.013	2.774	0.001	198.86	0.17	92.26	7.73	0.28
EC-12-699	26.11.2010									200.69	1.38	64.70	5.39	0.56
EC-12-709	26.11.2010	256.637	5.558	0.855	0.002	2.362	0.010	2.417	0.003	196.55	1.72	99.05	9.25	0.63
EC-12-719	26.11.2010	226.850	1.936	0.427	0.000	3.936	0.111	2.612	0.000	179.26	0.34	87.50	8.11	0.05
EC-12-724	26.11.2010	218.089	7.348	0.448	0.001	4.881	0.016	3.147	0.003	174.39	0.34	96.74	9.21	0.16
EC-13-609	21.02.2011	291.387	1.782	1.373	0.005	2.541	0.230	1.683	0.007	188.15	0.86	4.67	4.44	0.45

Overview over nutrient parameters, part 3 of 3.

ID	DATE	NO_3	σ_{NO3}	NO_2	σ_{NO2}	NH_4	σ_{NH4}	PO_4	σ_{PO4}	DSi	σ_{DSi}	BSi	BSi	σ_{BSi}
	[dd.mm.yyyy]					[μmol L^{-1}]							[SiO2%SPM]	
EC-13-619	21.02.2011	295.679	1.117	1.482	0.010	2.927	0.058	1.707	0.007	190.46	0.00	7.88	5.92	0.57
EC-13-624	22.02.2011	282.522	4.481	1.439	0.014	2.989	0.102	1.434	0.002	188.76	0.69	6.52	4.56	0.39
EC-13-629	22.02.2011	278.691	0.805	1.430	0.003	3.008	0.379	1.355	0.005	187.54	0.69	9.01	5.18	0.25
EC-13-639	22.02.2011	287.220	1.516	1.510	0.003	8.379	4.471	1.480	0.006	188.64	0.52	7.70	4.11	0.67
EC-13-649	22.02.2011	298.119	1.223	1.563	0.011	10.274	5.527	1.722	0.005	191.92	0.00	17.61	5.85	0.73
EC-13-659	22.02.2011	276.133	36.301	1.564	0.014	4.242	0.344	1.342	0.006	189.12	0.52	41.99	7.19	0.79
EC-13-669	22.02.2011	316.466	5.047	1.583	0.011	4.758	0.697	1.719	0.000	190.22	0.00	61.69	7.16	0.14
EC-13-679	22.02.2011	330.136	5.674	1.605	0.002	4.931	1.012	1.822	0.000	190.95	0.00	53.08	6.23	0.46
EC-13-689	22.02.2011	312.618	0.911	1.545	0.014	4.326	0.032	1.599	0.003	191.68	1.72	82.19	8.53	0.59
EC-13-699	22.02.2011	327.681	0.257	1.681	0.014	5.976	1.051	1.724	0.006	195.58	0.34	72.47	8.90	1.08
EC-13-709	22.02.2011	285.062	4.237	1.884	0.000	5.897	0.054	2.309	0.000	188.88	1.55	77.57	5.33	0.33
EC-13-719	22.02.2011	208.077	11.341	1.942	0.000	7.909	0.881	1.686	0.005	134.81	0.52	66.88	5.33	0.29
EC-13-724	22.02.2011	136.209	3.371	1.741	0.008	8.180	1.898	1.560	0.007	86.58	0.86	52.60	4.89	0.06
EC-14-609	26.04.2011	162.919	1.505	0.815	0.001	0.633	0.127	1.381	0.002	0.94	0.00	94.37	18.15	0.73
EC-14-619	26.04.2011	165.570	0.446	1.427	0.010	3.478	0.092	1.696	0.002	14.53	0.20	68.06	23.34	0.40
EC-14-624	26.04.2011	166.247	1.675	1.771	0.006	7.928	0.038	1.711	0.001	21.06	0.07	57.42	21.95	0.01
EC-14-629	26.04.2011	191.222	0.006	0.092	0.006	0.295	0.031	0.690	0.001	33.54	0.10	46.38	19.42	2.94
EC-14-634	26.04.2011	178.147	1.569	4.037	0.003	8.945	0.065	2.625	0.001	41.32	0.00	42.92	23.62	0.84
EC-14-639	26.04.2011	179.375	0.586	5.989	0.011	8.071	0.042	2.664	0.007	43.02	0.20	45.22	25.81	1.53
EC-14-644	26.04.2011	176.923	10.812	8.948	0.021	6.359	0.222	2.721	0.002	48.31	0.17	38.49	24.57	1.66
EC-14-649	26.04.2011	189.239	1.001	10.655	0.004	3.907	0.018	2.930	0.001	52.21	0.10	43.66	24.49	0.04
EC-14-659	26.04.2011	205.042	1.902	6.562	0.026	1.228	0.186	3.117	0.004	61.61	0.03	105.76	8.94	0.79
EC-14-669	26.04.2011	210.403	0.667	1.865	0.001	0.728	0.014	3.134	0.002	66.17	0.30	109.75	9.85	0.69
EC-14-679	26.04.2011	224.555	5.115	0.254	0.011	0.584	0.098	3.188	0.005	73.90	0.07	185.04	5.87	0.47
EC-14-689	26.04.2011	220.997	3.338	0.149	0.000	0.584	0.030	3.248	0.002	77.12	0.17	219.01	5.23	0.45
EC-14-699	26.04.2011	232.832	0.842	0.271	0.003	0.723	0.075	3.374	0.002	89.56	0.13	191.93	5.58	0.05
EC-14-709	26.04.2011	225.679	2.962	0.540	0.005	1.011	0.013	3.504	0.002	93.13	0.27	61.69	8.55	0.42
EC-14-719	26.04.2011	204.243	2.151	1.495	0.005	1.478	0.037	3.451	0.001	87.40	0.73	74.03	9.41	0.31
EC-14-724	26.04.2011	182.414	10.239	1.915	0.010	1.754	0.037	3.330	0.003	78.37	0.33	47.71	9.30	0.71
EC-15-609	13.07.2011	73.049	0.183	1.225	0.001	2.317	0.064	0.093	0.005	12.84	0.03	102.33	14.46	0.70
EC-15-619	13.07.2011	71.202	0.024	4.031	0.002	10.167	0.242	0.381	0.002	4.82	0.03	70.41	14.92	0.66
EC-15-624	13.07.2011	81.125	0.406	8.777	0.011	9.505	0.046	0.560	0.002	4.91	0.22	116.93	9.06	0.33
EC-15-629	13.07.2011	75.278	0.005	6.970	0.010	7.787	0.491	0.868	0.003	5.66	0.00	49.25	16.43	0.94
EC-15-634	13.07.2011	86.592	0.089	8.581	0.001	4.037	0.090	1.014	0.001	4.21	0.00	60.28	13.44	0.54
EC-15-639	13.07.2011	94.133	0.430	4.022	0.003	1.795	0.003	1.106	0.001	2.22	0.06	59.72	11.28	0.03
EC-15-644	13.07.2011	100.335	0.491	0.574	0.007	1.230	0.119	1.497	0.003	1.47	0.03	64.97	11.97	0.05
EC-15-649	13.07.2011	102.859	0.293	0.312	0.003	2.772	1.781	1.710	0.000	1.68	0.06	49.81	12.06	0.41
EC-15-659	13.07.2011	113.502	0.349	0.126	0.005	1.237	0.238	1.867	0.001	2.51	0.10	56.45	9.08	0.13
EC-15-669	13.07.2011	111.058	9.150	0.171	0.005	1.153	0.225	2.031	0.005	5.44	0.19	91.00	4.83	0.12
EC-15-679	13.07.2011	121.976	0.627	0.160	0.005	1.079	0.219	2.314	0.004	15.49	0.13	189.21	5.96	0.03
EC-15-689	13.07.2011	125.410	0.922	0.300	0.002	1.210	0.200	2.565	0.001	23.74	0.26	119.46	6.88	0.15
EC-15-699	13.07.2011	123.416	0.190	0.345	0.001	11.089	6.967	3.048	0.004	29.06	0.10	39.48	10.64	0.09
EC-15-709	13.07.2011	115.870	1.685	0.489	0.008	3.762	1.817	2.911	0.000	32.07	0.06	29.05	6.28	0.15
EC-16-609	08.09.2011	81.807	1.418	0.524	0.003	1.389	0.039	1.326	0.003	103.48	0.85	68.93	17.63	0.12
EC-16-619	08.09.2011	76.954	0.346	0.973	0.002	3.196	0.048	1.303	0.002	109.77	0.85	68.68	17.93	0.03
EC-16-624	08.09.2011	73.307	0.947	1.056	0.001	2.623	0.010	1.300	0.006	94.85	0.14	63.56	20.64	0.18
EC-16-629	08.09.2011	78.867	0.623	2.079	0.004	3.992	0.096	1.533	0.004	97.12	0.25	62.39	19.29	0.32
EC-16-639	08.09.2011	86.872	0.439	0.942	0.005	2.602	0.397	2.300	0.004	78.67	0.21	96.07	20.71	0.25
EC-16-649	08.09.2011	85.105	3.239	0.400	0.001	0.526	0.003	1.761	0.000	25.81	0.00	222.59	10.89	0.09
EC-16-659	08.09.2011	82.526	1.255	0.173	0.007	0.325	0.096	1.824	0.017	12.16	0.04	129.01	11.62	0.16
EC-16-669	08.09.2011	84.899	4.549	0.251	0.003	0.266	0.008	2.096	0.001	28.95	0.07	103.64	10.78	0.49
EC-16-679	08.09.2011	94.992	2.127	0.234	0.008	0.338	0.016	2.487	0.000	38.74	0.07	82.87	11.26	0.02
EC-16-689	08.09.2011	96.516	0.248	0.344	0.005	1.763	0.095	3.068	0.001	53.76	0.14	89.36	11.82	0.28
EC-16-699	08.09.2011	88.601	0.249	0.735	0.015	0.690	0.028	3.150	0.014	57.01	0.14	49.69	10.85	0.14
EC-16-709	08.09.2011	73.545	2.169	1.428	0.009	1.530	0.065	3.072	0.000	53.16	0.07	44.22	8.71	0.01
EC-16-719	08.09.2011	61.343	0.329	1.890	0.002	3.995	0.367	2.849	0.001	46.28	0.14	28.21	7.37	0.01
EC-16-724	08.09.2011	50.108	0.682	2.107	0.004	4.717	0.601	2.603	0.003	39.11	0.04	45.26	5.77	0.26
EC-17-609	25.10.2011	131.785	4.449	0.459	0.004	1.638		2.253	0.002	157.57	0.84	27.68	9.51	0.87
EC-17-619	25.10.2011	124.946	1.158	0.639	0.001	2.535	0.028	2.274	0.002	157.57	0.84	30.97	9.66	0.23
EC-17-624	25.10.2011	128.705	0.862	0.683	0.002	3.066	0.046	2.297	0.000	157.69	0.00	26.00	10.79	0.59
EC-17-629	25.10.2011	129.945	0.770	0.749	0.001	2.291	0.001	2.295	0.001	155.54	0.67	28.90	10.07	0.05
EC-17-639	25.10.2011	130.358	3.371	5.125	0.003	2.413	0.049	1.802	0.003	154.71	0.51	42.57	10.49	
EC-17-649	25.10.2011	133.958	4.210	1.365	0.006	2.114	0.002	2.215	0.001	148.86	0.67	115.14	12.64	0.30
EC-17-659	25.10.2011	132.555	1.832	0.568	0.006	0.442	0.032	1.860	0.003	129.18	0.84	266.99	9.07	0.10
EC-17-669	25.10.2011	122.421	1.095	0.132	0.002	0.909		2.186	0.002	110.45	1.01	147.84	8.14	0.13
EC-17-679	25.10.2011	119.671	2.006	0.120	0.003	0.353	0.027	1.899	0.000	110.98	1.55	183.72	6.83	0.22
EC-17-689	25.10.2011	117.832	3.137	0.203	0.008	0.784	0.165	2.551	0.034	93.75	0.00	176.80	9.38	0.07
EC-17-699	25.10.2011	110.352	1.773	0.233	0.010	0.481	0.067	2.765	0.013	87.31	0.00	99.86	10.39	0.16
EC-17-709	25.10.2011	83.982	0.125	0.646	0.007	2.009		2.696	0.006	70.29	0.28	71.74	9.98	0.29
EC-17-719	25.10.2011	76.652	1.965	0.748	0.004	2.520	0.176	2.596	0.003	64.65	0.34	59.68	9.95	0.23
EC-17-724	25.10.2011	55.986	2.110	0.936	0.007	2.296		2.259	0.003	48.75	0.73	80.19	7.45	0.08
EC-18-609	20.12.2011	154.036	5.486	0.861	0.004	3.233	0.001	2.322	0.089	182.02	2.70	11.62	7.14	0.18
EC-18-619	20.12.2011	152.765	1.249	0.872	0.002	3.463		2.404	0.021	182.14	1.18	12.19	7.27	0.52
EC-18-624	20.12.2011	152.378	0.024	0.951	0.001	3.999	0.133	2.314	0.003	185.93	0.17	14.49	7.38	0.84
EC-18-629	20.12.2011	150.377	0.041	1.124	0.001	4.821	0.017	2.139	0.001	192.06	3.45	20.59	6.94	0.58
EC-18-639	20.12.2011	155.479	0.479	1.329	0.000	5.387	0.039	2.324	0.010	184.76	1.18	52.73	5.58	0.04
EC-18-649	20.12.2011	158.915	0.336	1.591	0.001	4.687	0.021	2.295	0.011	187.15	1.18	60.15	9.07	0.25
EC-18-659	20.12.2011	160.582	2.743	1.806	0.002	3.104	0.036	2.224	0.011	197.88	2.87	191.51	6.16	0.01
EC-18-669	20.12.2011	163.186	1.791	1.576	0.002	2.440	0.017	2.291	0.020	202.42	3.54	250.60	5.27	0.11
EC-18-679	20.12.2011	164.375	0.321	0.708	0.022	2.175		2.184	0.009	198.12	0.84	160.07	6.47	0.11
EC-18-689	20.12.2011	152.252	7.564	0.484	0.000	1.887	0.007	2.162	0.106	191.20	2.87	133.30	8.58	0.16
EC-18-699	20.12.2011	141.598	3.023	0.630	0.007	2.897	0.088	2.427	0.040	179.52	0.17	93.78	9.80	0.32
EC-18-709	20.12.2011	105.573	1.503	1.073	0.001	4.245	0.012	2.213	0.048	141.47	2.02	52.53	9.08	0.09
EC-18-719	20.12.2011	59.175	1.212	1.642	0.022	5.863		2.138	0.034	87.91	1.52	41.12	7.26	0.56
EC-18-724	20.12.2011	83.682	2.296	1.326	0.005	5.276	0.023	2.219	0.080	128.96	2.14	31.08	8.58	0.01

3. Overview over parameters of the inorganic carbon system, part 1 of 3.

ID	DATE	TA	σ_{TA}	DIC	σ_{DIC}	CO_2	HCO_3^-	CO_3^{2-}	pCO_2	CO_2 flux (A09)	CO_2 flux (J08)	sat. index $CaCO_3$	$\delta^{13}C_{DIC}$	σ_{D13C}
	[dd.mm.yyyy]				[µmol kg^{-1}]				[µatm]	[mol m^{-2} d^{-1}]			[‰]	
EC-01-589	29.07.2009													
EC-01-592	29.07.2009													
EC-01-594	29.07.2009													
EC-01-597	29.07.2009													
EC-01-599	29.07.2009			1604.88		3.4	1409.6	73.9	91.88	-0.04	-0.02	1.16		
EC-01-604	29.07.2009													
EC-01-609	29.07.2009			1592.64		3.9	1417.8	65.2	107.03	-0.05	-0.03	1.10		
EC-01-614	29.07.2009													
EC-01-619	29.07.2009			1687.99		12.1	1592.9	26.1	330.07	-0.01	0.00	0.69		
EC-01-624	29.07.2009													
EC-01-629	29.07.2009													
EC-01-634	29.07.2009													
EC-01-639	29.07.2009													
EC-01-644	29.07.2009													
EC-02-619	27.08.2009	1478.82		1488.76	0.62	21.8	1415.7	11.5	594.43	0.05	0.02	0.37		
EC-02-621	27.08.2009													
EC-02-624	27.08.2009	1497.48	0.43	1453.77	0.95	66.6	1355.5	3.5	1815.52	0.30	0.16	-0.16		
EC-02-629	27.08.2009	1500.94	0.24	1416.76	113.98	80.2	1307.3	2.7	2184.24	0.37	0.19	-0.26		
EC-02-634	27.08.2009	1518.91	1.54	1591.76	0.45	76.4	1483.8	3.6	2081.13	0.35	0.18	-0.17		
EC-02-639	27.08.2009	1563.37	0.67	1546.97	113.20	66.7	1444.5	3.9	1812.17	0.30	0.15	-0.08		
EC-02-644	27.08.2009	1608.81	0.26	1663.56	4.66	73.9	1550.5	4.2	2041.74	0.35	0.18	-0.06		
EC-03-609	08.09.2009			1529.89	2.06	8.1	1421.5	30.8	201.74	-0.03	-0.01	0.82		
EC-03-614	08.09.2009													
EC-03-624	08.09.2009	1484.62												
EC-03-634	08.09.2009													
EC-03-649	09.09.2009	1608.38	4.35	1550.29	4.05	67.3	1447.7	3.9	1721.87	0.16	0.07	-0.11		
EC-03-659	09.09.2009	1616.62	1.75	1655.49	0.98	77.1	1542.0	3.9	1949.40	0.19	0.09	-0.14		
EC-03-669	09.09.2009	1630.84		1629.59	4.62	49.0	1537.6	6.2	1266.78	0.21	0.12	0.05		
EC-03-679	10.09.2009	1735.98	0.00	1760.71		55.6	1647.0	6.5	1364.58	0.20	0.11	-0.01		
EC-03-689	10.09.2009	1784.09		1826.31	1.49	51.6	1685.4	8.0	1267.07	0.19	0.11	-0.01		
EC-03-694	11.09.2009			1838.62	1.70	43.8	1664.0	9.4	1082.68	0.11	0.05	0.12		
EC-03-699	11.09.2009	1862.61		1857.22	0.56	41.2	1679.3	10.7	1008.79	0.10	0.04	0.07		
EC-03-704	11.09.2009	1871.85		1873.49	0.02	35.5	1669.8	12.7	883.89	0.09	0.05	0.13		
EC-03-709	11.09.2009			1889.56	1.87	34.7	1681.3	13.2	856.25	0.09	0.05	0.23		
EC-03-714	12.09.2009	2007.80		1960.81	5.08	26.5	1739.0	18.4	644.32	0.04	0.02	0.28		
EC-03-719	12.09.2009	2073.74		2006.64	0.65	24.4	1757.9	20.9	589.93	0.03	0.01	0.33		
EC-03-729	12.09.2009	2148.71	0.00	2022.60	0.51	21.2	1668.3	23.4	533.95	0.03	0.01	0.52		
EC-04-609	15.10.2009	2297.06	0.25											
EC-04-619	15.10.2009	2211.46	0.19	2142.98		40.1	2034.1	12.2	787.23	0.08	0.04	0.45		
EC-04-629	15.10.2009	2102.15	0.01	2157.36		62.9	2034.5	7.9	1284.69	0.28	0.23	0.27		
EC-04-639	15.10.2009	1990.59	0.00	2052.97		66.3	1931.1	6.8	1358.00	0.30	0.25	0.19		
EC-04-649	15.10.2009	1913.18	0.18	1965.99		57.7	1854.2	7.3	1186.31	0.25	0.21	0.18		
EC-04-659	15.10.2009	1871.31	16.56	1897.56		45.2	1796.7	8.8	927.47	0.16	0.14	0.21		
EC-04-669	15.10.2009	1829.71	0.52	1812.10		37.0	1703.9	10.2	752.14	0.11	0.09	0.17		
EC-04-674	15.10.2009	1834.04	2.54	1844.41		37.3	1715.3	10.9	772.50	0.12	0.10	0.14		
EC-04-679	15.10.2009	1839.09	3.30	1843.59		36.0	1706.3	11.4	760.50	0.11	0.09	0.14		
EC-04-684	15.10.2009	1688.14	3.85	1863.65		35.9	1690.4	11.9	750.07	0.11	0.09	0.11		
EC-04-689	15.10.2009	1886.88	0.00	1892.57		39.1	1681.8	11.4	819.97	0.13	0.10	0.07		
EC-04-694	15.10.2009	1922.63	0.17	1927.26		38.1	1694.9	12.1	798.73	0.12	0.10	0.06		
EC-04-699	15.10.2009	1961.00	6.44	1939.84		34.1	1682.9	13.6	710.07	0.09	0.08	0.14		
EC-04-709	15.10.2009	2012.53	1.79	1992.86		31.9	1685.2	15.0	666.04	0.08	0.07	0.18		
EC-04-719	15.10.2009	2109.44	4.85	2041.37		29.7	1677.3	16.4	622.44	0.07	0.06	0.24		
EC-04-724	15.10.2009	2103.62	4.88											
EC-05-570	25.03.2010	2270.73	2.23	2265.76		31.9	2154.3	16.8	588.57	0.04	0.02	0.59		
EC-05-579	25.03.2010	2281.46	0.32	2284.12		32.9	2171.6	16.6	607.02	0.03	0.02	0.59		
EC-05-589	25.03.2010	2280.47	0.42	2273.03	3.80	30.8	2160.9	17.5	561.69	0.03	0.02	0.61		
EC-05-599	25.03.2010	2288.75	0.64	2289.86	0.84	36.0	2178.5	15.2	646.55	0.04	0.02	0.55		
EC-05-609	24.03.2010	2322.59	2.77	2321.98	2.49	29.8	2207.4	18.8	531.01	0.03	0.02	0.64		
EC-05-619	24.03.2010	2328.18	1.20	2325.34	2.07	35.1	2211.6	16.1	624.88	0.05	0.03	0.58		
EC-05-624	24.03.2010	2336.57	1.57	2347.38	3.12	48.0	2230.8	11.9	847.23	0.10	0.07	0.44		
EC-05-629	24.03.2010	2323.77	3.48	2340.80	1.36	38.0	2226.8	15.0	672.20	0.06	0.05	0.54		
EC-05-639	24.03.2010	2341.03	0.19	2368.23	2.14	51.7	2249.0	11.2	915.80	0.13	0.10	0.42		
EC-05-649	24.03.2010	2335.26	5.02	2368.81	8.75	61.3	2245.1	9.4	1069.79	0.16	0.13	0.34		
EC-05-659	24.03.2010	2360.10	0.83	2411.59	1.39	73.8	2278.3	8.1	1265.61	0.21	0.17	0.27		
EC-05-669	24.03.2010	2361.39	0.73	2411.11	2.82	79.7	2274.4	7.5	1338.14	0.23	0.18	0.20		
EC-05-679	24.03.2010	2292.55	4.04	2362.10	2.12	79.2	2229.0	7.2	1310.99	0.22	0.18	0.18		
EC-05-689	24.03.2010	2232.74	0.99	2306.84	0.80	73.8	2180.9	7.4	1229.42	0.20	0.18	0.18		
EC-05-699	24.03.2010	2165.04	0.14	2204.73	1.65	71.0	2077.2	7.1	1180.32	0.20	0.18	0.13		
EC-05-709	24.03.2010	2144.08	0.31	2185.81		64.7	2030.3	8.2	1063.16	0.16	0.13	0.05		
EC-05-719	24.03.2010	2185.11	0.96	2191.65		54.4	1947.6	10.5	920.03	0.10	0.07	0.03		
EC-05-724	24.03.2010			2213.63		38.9	1869.4	14.7	684.38	0.05	0.04	0.18		
EC-06-609	07.04.2010	1714.63	0.52	1710.73	0.39	31.6	1636.0	9.6	593.47	0.04	0.03	0.25		
EC-06-619	07.04.2010	1729.52	2.19	1725.78		34.3	1649.7	9.0	633.87	0.05	0.03	0.22		
EC-06-624	07.04.2010	1712.25	0.02	1712.50		33.4	1637.0	9.1	626.18	0.06	0.04	0.23		
EC-06-629	07.04.2010	1700.82	0.23	1698.80	0.41	35.1	1623.3	8.5	648.63	0.06	0.05	0.19		
EC-06-639	07.04.2010	1706.47	0.79	1693.24		39.3	1615.3	7.5	735.19	0.10	0.08	0.15		
EC-06-649	07.04.2010	1718.45	1.41	1719.09	6.52	49.2	1634.1	6.1	920.45	0.15	0.12	0.05		
EC-06-659	07.04.2010	1745.00	0.44	1730.25	21.82	52.6	1642.2	5.8	983.56	0.18	0.15	0.02		
EC-06-669	07.04.2010	1771.31	0.10	1811.62		60.4	1714.9	5.6	1125.90	0.22	0.19	0.00		
EC-06-679	07.04.2010	1824.38	0.70	1877.20		82.2	1760.1	4.3	1527.21	0.32	0.29	-0.10		
EC-06-689	07.04.2010	1883.28	0.40	1932.42	11.13	81.0	1814.6	4.7	1519.50	0.32	0.29	-0.06		
EC-06-699	07.04.2010	1966.80	0.20	2036.08		74.2	1919.5	5.7	1378.16	0.26	0.24	0.05		
EC-06-709	07.04.2010	2070.44	0.81	2060.06		84.5	1929.3	5.2	1570.00	0.32	0.29	0.00		
EC-06-719	07.04.2010	2182.56	0.28	2144.25		76.0	1993.1	6.7	1400.23	0.28	0.25	0.01		
EC-06-729	07.04.2010	2258.23	2.06	2162.03	8.06	49.3	1930.9	11.5	940.59	0.14	0.12	0.10		
EC-07-570	06.05.2010	2250.44	4.60	1938.45	3.17	3.9	1692.6	87.2	82.05	-0.10	-0.08	1.29		
EC-07-579	06.05.2010	2216.28	18.51	1968.15		4.2	1730.0	84.6	87.82	-0.09	-0.08	1.28		

Overview over parameters of the inorganic carbon system, part 2 of 3.

ID	DATE	TA	σ_{TA}	DIC	σ_{DIC}	CO_2	HCO_3^-	CO_3^{2-}	pCO_2	CO_2 flux (A09)	CO_2 flux (J08)	sat. index $CaCO_3$	$\delta^{13}C_{DIC}$	σ_{D13C}
	[dd.mm.yyyy]			[µmol kg^{-1}]					[µatm]	[mol m^{-2} d^{-1}]			[‰]	
EC-07-589	06.05.2010	2221.52	10.83	1954.38		4.4	1727.5	79.7	91.54	-0.08	-0.06	1.25		
EC-07-599	06.05.2010	2211.29	1.89	2048.24	6.94	8.7	1890.8	48.9	179.43	-0.06	-0.04	1.03		
EC-07-609	06.05.2010	2218.25	1.74	2033.13	1.64	3.9	1773.0	94.4	81.90	-0.07	-0.05	1.32		
EC-07-619	06.05.2010	2180.73	21.18	2091.90	87.24	9.6	1935.2	46.5	200.82	-0.05	-0.03	1.02		
EC-07-624	05.05.2010	2099.58	7.76	2115.29		52.4	2006.2	9.1	1111.22	0.16	0.10	0.30		
EC-07-629	05.05.2010	2079.44	1.74	2125.48	3.97	35.0	2021.0	13.9	753.18	0.08	0.05	0.49		
EC-07-639	05.05.2010	2074.48	0.68	2122.22		49.1	2016.8	9.8	1031.57	0.15	0.09	0.31		
EC-07-644	05.05.2010	2041.28	2.92	2121.57					1010.12	0.15	0.10			
EC-07-649	05.05.2010	2075.03	9.56	2129.00		49.6	2020.9	9.8	1010.12	0.15	0.10	0.32		
EC-07-659	05.05.2010	2044.11	1.48	2120.11	0.92	46.1	2014.8	10.6	1010.12	0.15	0.10	0.32		
EC-07-669	05.05.2010	2030.93	12.59	2109.77		56.2	1999.2	8.5	1010.12	0.13	0.09	0.22		
EC-07-679	05.05.2010	2016.63	0.39	2093.02	3.75	52.1	1985.3	9.1	1083.68	0.15	0.10	0.25		
EC-07-689	05.05.2010	2047.00	0.84	2089.95	1.81	60.1	1967.5	8.0	1244.51	0.19	0.12	0.15		
EC-07-699	05.05.2010	2040.48	6.65	2080.53		41.2	1942.7	12.4	865.96	0.10	0.07	0.23		
EC-07-709	05.05.2010	2039.32	24.19	2068.58		39.6	1884.0	13.2	825.85	0.08	0.05	0.18		
EC-07-719	05.05.2010	2070.38	5.37	2062.50		28.4	1830.7	18.5	594.98	0.04	0.02	0.29		
EC-07-724	05.05.2010	2108.24	3.49	2051.68	6.82	55.0	1771.5	9.4	1170.04	0.14	0.08	-0.02		
EC-08-644	16.07.2010	1685.48	1.76	1772.71	1.86	91.8	1638.4	3.8	2712.06	0.60	0.32	-0.07	-11.61	0.011
EC-08-649	16.07.2010	1732.95	3.52	1812.39	1.75	84.6	1684.1	4.4	2471.72	0.53	0.29	-0.03	-11.58	0.011
EC-08-659	16.07.2010	1812.66	1.41	1882.75	1.09	74.6	1762.3	5.5	2179.21	0.47	0.26	0.01	-11.54	0.070
EC-08-669	16.07.2010	1882.29	1.52	1952.92	9.55	64.3	1835.9	6.9	1883.65	0.36	0.20	0.13	-11.59	0.016
EC-08-679	16.07.2010	2025.40	0.52	2078.88	0.86	55.3	1965.7	9.2	1598.45	0.30	0.16	0.20	-11.68	0.007
EC-08-689	16.07.2010	2093.82	2.93	2124.39	1.14	51.1	1998.5	10.8	1484.91	0.26	0.14	0.22	-11.35	0.038
EC-08-699	16.07.2010	2147.87	6.76	2181.09	1.99	47.4	1991.7	13.1	1388.35	0.23	0.12	0.24	-10.50	0.007
EC-08-709	16.07.2010	2255.79	0.48	2191.29	1.59	35.0	1927.7	18.4	1018.36	0.13	0.06	0.42	-6.78	0.003
EC-08-719	16.07.2010	2315.74	12.50	2105.59	0.86	17.3	1741.2	32.3	500.15	0.02	0.01	0.68	-2.46	0.048
EC-09-609	10.08.2010	1942.47	2.07	1776.40	9.15	3.6	1539.7	82.6	97.88	-0.06	-0.03	1.27	-9.11	0.009
EC-09-619	10.08.2010	1777.79	0.39	1882.01	1.88	11.6	1754.6	33.7	312.97	-0.01	-0.01	0.87	-10.32	0.025
EC-09-624	10.08.2010	1896.48	1.05	1895.88	1.91	21.4	1794.4	19.0	580.23	0.04	0.02	0.62	-10.86	0.011
EC-09-629	10.08.2010	1823.96	0.31	1903.68	0.72	38.9	1804.6	10.6	1058.28	0.14	0.07	0.36	-11.20	0.038
EC-09-634	10.08.2010	1845.84	0.76	1920.31	0.58	52.0	1815.1	8.0	1408.32	0.20	0.10	0.24	-11.40	0.012
EC-09-639	10.08.2010	1862.03	1.18	1939.37	12.16	65.1	1824.6	6.4	1775.42	0.27	0.14	0.14	-11.39	0.014
EC-09-644	10.08.2010	1827.96	0.26	1911.55	5.34	64.8	1797.3	6.3	1751.86	0.28	0.14	0.13	-11.34	0.111
EC-09-649	10.08.2010	1832.28	0.68	1900.73	2.05	66.0	1785.3	6.1	1784.84	0.28	0.13	0.12	-11.29	0.031
EC-09-659	10.08.2010	1837.41	0.67	1925.86	3.97	75.5	1799.1	5.5	2042.21	0.32	0.16	0.08	-11.33	0.014
EC-09-669	10.08.2010	1806.54	0.47	1897.81	12.03	74.0	1770.1	5.5	1997.10	0.30	0.15	0.07	-11.27	0.009
EC-09-679	10.08.2010	1767.75	4.64	1853.06	0.31	62.3	1735.7	6.4	1676.10	0.24	0.12	0.11	-11.26	0.012
EC-09-689	10.08.2010	1856.90	2.20	1925.62	4.53	56.7	1791.7	8.0	1540.64	0.22	0.11	0.11	-11.03	0.025
EC-09-699	10.08.2010	1959.54	3.51	1995.00	0.83	55.9	1819.0	9.1	1530.38	0.21	0.10	0.10	-10.34	0.005
EC-09-709	10.08.2010			2104.97		51.4	1855.5	11.3	1407.02	0.19	0.09	0.12	-8.86	
EC-09-719	10.08.2010	2157.78	0.23	2137.31	0.89	41.6	1836.4	14.2	1133.97	0.13	0.06	0.20	-7.62	0.007
EC-09-724	10.08.2010	2194.66	8.75	2147.61	2.57	33.1	1806.4	17.8	917.91	0.09	0.04	0.30	-6.65	0.003
EC-10-609	16.09.2010	2090.55	1.12	2085.04	3.27				1130.65	0.21	0.15		-11.91	0.050
EC-10-619	16.09.2010	2043.88	0.72	2070.99	3.90	46.3	1969.6	10.0	1055.12	0.18	0.12	0.31	-11.93	0.023
EC-10-624	16.09.2010	2030.04	1.00	2056.07	2.28	46.6	1956.0	9.8	1059.01	0.18	0.12	0.28	-11.96	
EC-10-629	16.09.2010	1975.96	0.08	2025.65	2.46	49.2	1925.7	9.0	1121.76	0.20	0.13	0.25	-12.01	0.031
EC-10-634	16.09.2010	1967.63	0.58	2012.69	1.35	50.2	1913.0	8.7	1142.09	0.22	0.16	0.23	-12.04	0.037
EC-10-639	16.09.2010	1959.70	0.80	2005.10	2.65	47.2	1907.2	9.1	1063.16	0.20	0.14	0.26	-11.90	0.006
EC-10-644	16.09.2010	1950.82	0.31	1995.48	2.75	43.8	1899.9	9.7	977.91	0.17	0.13	0.28	-11.91	0.034
EC-10-649	16.09.2010	1945.89	0.55	1982.33	2.08	40.0	1888.7	10.6	900.95	0.15	0.11	0.31	-11.96	0.030
EC-10-659	16.09.2010	1951.87	0.16	1982.91	3.25	40.2	1889.5	10.6	910.54	0.17	0.13	0.30	-12.00	0.013
EC-10-669	16.09.2010	1964.26	0.21	1985.88	2.73	37.4	1893.3	11.5	845.86	0.15	0.12	0.33	-11.96	0.020
EC-10-679	16.09.2010	1969.40	0.54	2002.60	2.03	39.3	1907.6	11.2	903.23	0.16	0.13	0.30	-12.13	0.000
EC-10-689	16.09.2010	1959.80	0.78	2002.04	7.22	37.9	1884.9	12.1	877.00	0.15	0.13	0.36	-11.85	0.006
EC-10-699	16.09.2010	1982.73	0.59	2011.83	4.64	40.0	1871.0	12.3	922.78	0.13	0.10	0.17	-11.31	0.001
EC-10-709	16.09.2010	1961.32	0.47	1969.71	1.46	36.6	1794.7	13.4	848.79	0.12	0.09	-0.03	-10.27	0.032
EC-10-719	16.09.2010	1972.72	0.00	1960.19	1.44	31.1	1736.7	15.7	721.94	0.08	0.06	0.19	-9.00	0.050
EC-10-724	16.09.2010	1997.45	1.35	1965.50	0.29	29.1	1707.4	16.5	679.83	0.07	0.05	0.31	-8.09	0.045
EC-11-609	06.10.2010	1818.82	1.66	1895.01	1.02	81.3	1779.9	4.5	1680.35	0.28	0.17	-0.10	-12.98	0.019
EC-11-619	06.10.2010	1833.26	0.71	1920.11	4.64	85.5	1800.5	4.4	1767.26	0.33	0.22	-0.10	-13.01	0.010
EC-11-624	06.10.2010	1880.30	9.53	1932.35	6.34	83.2	1814.0	4.6	1724.65	0.32	0.21	-0.08	-12.95	0.027
EC-11-629	06.10.2010	1865.40	1.75	1940.01	3.44	82.5	1821.6	4.6	1710.41	0.31	0.21	-0.07	-12.88	0.015
EC-11-639	06.10.2010	1908.81	0.50	1973.53	1.52	79.0	1855.6	5.1	1648.54	0.29	0.19	-0.01	-12.75	0.003
EC-11-649	06.10.2010	2054.94	1.63	2115.12	2.13	63.8	2000.4	7.4	1344.00	0.22	0.14	0.19	-12.40	0.029
EC-11-659	06.10.2010	2195.06	0.11	2229.17	2.98	55.8	2112.7	9.5	1192.34	0.17	0.10	0.32	-12.00	0.019
EC-11-669	06.10.2010	2169.27	0.44	2209.96	0.07	48.6	2099.6	10.9	1053.42	0.13	0.07	0.36	-11.76	0.038
EC-11-679	06.10.2010	2137.18	0.43	2165.82	14.31	50.3	2054.5	10.2	1109.43	0.14	0.08	0.30	-11.74	0.003
EC-11-689	06.10.2010	2121.69	0.18	2152.86	1.31	56.0	2019.6	9.5	1231.69	0.15	0.08	0.16	-11.52	0.017
EC-11-699	06.10.2010	2112.53	4.01	2134.27	0.64	51.8	1969.2	10.6	1143.67	0.14	0.07	0.11	-10.88	0.001
EC-11-709	06.10.2010	2106.16	1.78	2127.14	2.58	48.1	1903.1	11.8	1070.04	0.11	0.06	0.09	-9.56	0.021
EC-11-719	06.10.2010	2140.53	0.53	2123.37	3.33	38.2	1833.9	14.8	866.36	0.08	0.04	0.17	-7.80	0.001
EC-11-724	06.10.2010	2152.13	4.80	2124.18	7.50	39.4	1883.2	14.6	883.28	0.08	0.04	0.27	-7.09	0.020
EC-12-609	26.11.2010	2158.80	7.08	2208.48	2.01	88.2	2078.9	5.4	1359.88	0.16	0.11	0.04		
EC-12-619	26.11.2010	2121.82	6.22	2193.55	6.46	66.5	2081.5	7.2	1060.47	0.10	0.07	0.16		
EC-12-624	26.11.2010	2094.82	12.51	2164.28	16.29	67.5	2052.7	6.9	1071.77	0.11	0.07	0.14		
EC-12-629	26.11.2010	2100.35	4.77	2165.11	13.21	71.0	2050.7	6.6	1140.51	0.12	0.08	0.11		
EC-12-639	26.11.2010	2097.24	0.45	2136.22	6.79	69.9	2023.9	6.5	1131.10	0.10	0.06	0.10		
EC-12-649	26.11.2010	2132.67	3.40	2203.54	0.36	68.8	2089.5	7.1	1125.38	0.10	0.06	0.14		
EC-12-659	26.11.2010	2203.64	0.87	2291.60	2.60	72.2	2170.3	7.4	1202.54	0.10	0.07	0.17		
EC-12-669	26.11.2010	2345.44	0.11	2375.59	4.05	69.8	2251.3	8.3	1171.39	0.10	0.06	0.22		
EC-12-679	26.11.2010	2341.80	0.45	2427.62	2.00	68.9	2301.4	8.8	1159.85	0.09	0.06	0.26		
EC-12-689	26.11.2010			2468.80	5.81	70.5	2339.7	8.9	1195.64	0.09	0.06	0.27		
EC-12-699	26.11.2010	2454.48	1.60	2490.34	7.77	65.4	2362.8	9.8	1101.29	0.08	0.05	0.30		
EC-12-709	26.11.2010	2409.39	1.13	2449.22	3.92	69.9	2306.5	9.2	1192.34	0.09	0.06	0.20		
EC-12-719	26.11.2010	2351.96	0.05	2379.39	3.87	65.2	2187.1	10.1	1118.92	0.10	0.06	0.09		
EC-12-724	26.11.2010	2338.50	2.09	2366.99	1.24	60.2	2155.4	10.9	1024.24	0.09	0.06	0.11		

Overview over parameters of the inorganic carbon system, part 3 of 3.

ID	**DATE**	**TA**	**σ_{TA}**	**DIC**	**σ_{DIC}**	**CO_2**	**HCO_3^-**	**CO_3^{2-}**	**pCO_2**	**CO_2 flux (A09)**	**CO_2 flux (J08)**	**sat. index $CaCO_3$**	**$\delta^{13}C_{DIC}$**	**σ_{D13C}**
	[dd.mm.yyyy]			**[µmol kg^{-1}]**					**[µatm]**	**[mol m^{-2} d^{-1}]**			**[‰]**	
EC-13-609	21.02.2011			2274.76	23.96	67.0	2148.6	7.6	900.12	0.14	0.14	0.39		
EC-13-619	21.02.2011			2248.02	10.19	63.8	2124.6	7.8	868.36	0.12	0.11	0.40		
EC-13-624	22.02.2011			2296.18	9.50	61.6	2175.3	8.4	834.07	0.11	0.10	0.41		
EC-13-629	22.02.2011			2261.74	32.66	73.0	2134.5	6.9	973.42	0.14	0.14	0.32		
EC-13-639	22.02.2011			2245.97	27.57									
EC-13-649	22.02.2011			2268.11	4.10	67.3	2142.3	7.5	908.66	0.14	0.14	0.38		
EC-13-659	22.02.2011			2313.75	37.86	71.6	2185.7	7.3	970.29	0.14	0.13	0.34		
EC-13-669	22.02.2011	2203.29	0.46	2297.82	3.63	68.0	2170.3	7.7	913.90	0.13	0.12	0.38		
EC-13-679	22.02.2011	2272.26	0.17	2318.56	0.22	65.2	2193.0	8.1	876.60	0.11	0.10	0.40		
EC-13-689	22.02.2011	2267.40	1.83	2323.38	1.48	68.0	2197.8	7.8	921.93	0.12	0.11	0.36		
EC-13-699	22.02.2011	2245.76	1.07	2308.97	2.77	64.7	2159.7	8.8	887.77	0.10	0.09	0.30		
EC-13-709	22.02.2011	2255.84	0.71	2300.93	0.83	49.0	2016.3	12.7	713.84	0.07	0.06	0.31		
EC-13-719	22.02.2011	2271.71	0.31	2266.95	1.74	42.6	1910.1	13.8	625.03	0.05	0.04	0.34		
EC-13-724	22.02.2011	2309.81	0.31	2254.61	0.15				606.29	0.04	0.03			
EC-14-609	26.04.2011	1827.11	0.52	1831.18	0.58	5.0	1608.2	63.3	113.27	-0.05	-0.02	1.30		
EC-14-619	26.04.2011	2022.37		2077.56	4.51	13.6	1919.7	33.2	308.67	-0.02	-0.01	1.04		
EC-14-624	26.04.2011	2124.31	0.88	2163.18	8.49	17.5	2013.0	28.3	394.46	0.00	0.00	0.98		
EC-14-629	26.04.2011	2192.63	0.45	2269.30	0.51	22.4	2121.9	24.6	501.53	0.02	0.01	0.92		
EC-14-634	26.04.2011			2336.84	5.17	32.5	2194.9	18.1	721.11	0.06	0.04	0.79		
EC-14-639	26.04.2011			2357.18	9.79	36.9	2215.2	16.3	827.18	0.09	0.05	0.75		
EC-14-644	26.04.2011			2408.92	4.69	52.7	2262.9	11.9	1159.58	0.16	0.09	0.61		
EC-14-649	26.04.2011	2312.74	3.62	2431.22	18.82	64.6	2279.9	9.8	1420.37	0.21	0.12	0.52		
EC-14-659	26.04.2011			2480.52	5.72	89.1	2311.2	7.4	1935.53	0.32	0.21	0.39		
EC-14-669	26.04.2011	2358.70	3.77	2508.16	31.51	95.5	2335.2	7.0	2061.58	0.41	0.29	0.35		
EC-14-679	26.04.2011	2341.60	3.14	2481.77	4.58	91.9	2311.0	7.1	1988.84	0.36	0.27	0.37		
EC-14-689	26.04.2011	2325.88	3.36	2483.00	6.87	90.6	2313.8	7.3	1975.15	0.37	0.30	0.36		
EC-14-699	26.04.2011	2357.10	1.21	2487.04	2.95	89.2	2299.9	7.9	1945.81	0.37	0.29	0.30		
EC-14-709	26.04.2011	2377.67	0.56	2483.02	25.47	88.3	2265.0	8.3	1927.52	0.41	0.30	0.24		
EC-14-719	26.04.2011	2391.45	0.60	2454.53	3.43	72.4	2186.0	10.4	1569.28	0.31	0.23	0.27		
EC-14-724	26.04.2011	2397.34	3.11	2447.16	0.40	57.7	2152.1	13.1	1262.41	0.22	0.16	0.35		
EC-15-609	13.07.2011	1687.29	0.44	1641.68	6.76				258.78	-0.03	-0.01			
EC-15-619	13.07.2011	1878.34	0.61	1869.14	1.95				1752.19	0.31	0.16			
EC-15-624	13.07.2011	1900.47	0.27	1946.83	1.97				2777.37	0.52	0.28			
EC-15-629	13.07.2011	1822.32	1.98	1906.86	3.23				3111.33	0.61	0.32			
EC-15-634	13.07.2011	1797.16	2.09	1892.11	2.87				3409.47	0.69	0.37			
EC-15-639	13.07.2011	1755.26	0.96	1869.09	2.93				3101.68	0.62	0.34			
EC-15-644	13.07.2011	1725.49	0.61	1806.68	10.18				2893.78	0.57	0.31			
EC-15-649	13.07.2011	1705.35	0.30	1771.70	3.58				2467.83	0.48	0.26			
EC-15-659	13.07.2011	1709.43	0.30	1758.94	2.35				2375.51	0.48	0.28			
EC-15-669	13.07.2011	1740.31	1.49	1765.36	0.18				1932.62	0.41	0.28			
EC-15-679	13.07.2011	1807.48	8.64	1833.50	2.63				1655.73	0.32	0.23			
EC-15-689	13.07.2011	1910.91	3.13	1943.81	1.51				1345.59	0.26	0.18			
EC-15-699	13.07.2011	1978.70	0.00	2008.68	2.32				1353.79	0.27	0.18			
EC-15-709	13.07.2011	2069.18	0.69	2077.79	1.03				1248.58	0.25	0.17			
EC-16-609	08.09.2011	2468.92	0.53	2421.43	0.50	18.2	2250.4	34.7	432.81	0.01	0.01	1.01		
EC-16-619	08.09.2011	2422.65	2.75	2436.13	4.96	26.6	2286.7	24.3	637.82	0.06	0.03	0.86		
EC-16-624	08.09.2011	2397.12	0.59	2441.46	5.42	26.2	2290.1	24.7	629.07	0.06	0.03	0.87		
EC-16-629	08.09.2011	2407.02	0.67	2458.64	6.23	33.8	2313.0	19.7	816.58	0.10	0.05	0.76		
EC-16-639	08.09.2011	2384.76	0.60	2422.11	0.53	55.5	2279.6	11.6	1343.38	0.24	0.15	0.53		
EC-16-649	08.09.2011	2352.20	0.08	2396.75	1.73	48.4	2258.0	13.0	1161.18	0.19	0.12	0.58		
EC-16-659	08.09.2011	2318.56	0.03	2360.76	0.62	45.4	2222.3	13.7	1101.54	0.21	0.15	0.59		
EC-16-669	08.09.2011	2302.34	1.92	2342.35	6.34	47.5	2209.5	12.8	1139.99	0.21	0.15	0.54		
EC-16-679	08.09.2011	2258.93	3.75	2291.40	2.55	45.7	2149.6	13.2	1104.33	0.20	0.14	0.48		
EC-16-689	08.09.2011	2236.88	0.97	2266.52	1.53	50.1	2027.5	13.0	1213.11	0.22	0.15	0.23		
EC-16-699	08.09.2011	2198.24	0.37	2210.36	1.88	39.7	1913.3	15.6	960.28	0.15	0.10	0.27		
EC-16-709	08.09.2011	2192.52	0.48	2167.68	3.21	30.9	1806.4	18.6	756.31	0.10	0.07	0.35		
EC-16-719	08.09.2011	2211.10	2.55	2167.15	2.12	29.6	1770.1	19.0	734.68	0.08	0.05	0.36		
EC-16-724	08.09.2011	2238.28	0.56	2175.66	3.15				698.48	0.07	0.04			
EC-17-609	25.10.2011	2361.17	0.62	2403.00	4.01	40.7	2279.6	14.8	728.45	0.12	0.12	0.59		
EC-17-619	25.10.2011	2422.93	0.01	2482.16	8.73	49.5	2353.4	12.9	885.93	0.17	0.17	0.53		
EC-17-624	25.10.2011	2438.35	0.23	2478.04	9.43	50.8	2348.5	12.6	914.74	0.18	0.18	0.52		
EC-17-629	25.10.2011	2421.17	2.01	2487.31	0.43	49.3	2357.0	13.1	894.54	0.17	0.17	0.54		
EC-17-639	25.10.2011	2434.16	0.35	2489.91	2.43	48.1	2357.6	13.5	882.27	0.17	0.16	0.56		
EC-17-649	25.10.2011	2450.72	0.26	2503.57	1.38	56.7	2366.3	11.6	1045.92	0.22	0.22	0.50		
EC-17-659	25.10.2011	2483.05	0.18	2558.86	0.70	50.8	2419.2	13.6	950.17	0.18	0.20	0.57		
EC-17-669	25.10.2011	2530.75	0.30	2601.72	7.63	54.5	2460.1	13.2	1038.72	0.22	0.24	0.54		
EC-17-679	25.10.2011	2490.60	0.05	2590.05	2.01	55.6	2448.2	13.0	1084.43	0.23	0.25	0.51		
EC-17-689	25.10.2011	2488.23	0.44	2515.50	3.14	53.1	2361.2	13.4	1041.84	0.22	0.23	0.44		
EC-17-699	25.10.2011	2470.62	0.20	2482.50	0.85	46.9	2292.4	15.4	922.78	0.17	0.15	0.40		
EC-17-709	25.10.2011	2443.86	1.02	2412.18	3.14	36.2	2111.8	19.5	719.28	0.10	0.09	0.37		
EC-17-719	25.10.2011	2428.18	3.61	2374.96	0.90	32.7	2041.6	20.8	651.48	0.08	0.07	0.39		
EC-17-724	25.10.2011	2392.42	0.33	2327.75	5.54	28.9	1929.1	21.8	586.95	0.06	0.05	0.40		
EC-18-609	20.12.2011	2548.18	0.15	2553.47	27.27	54.7	2425.3	12.0	797.63	0.06	0.04	0.49		
EC-18-619	20.12.2011	2499.99	0.99	2520.67	5.84	57.2	2392.3	11.2	831.19	0.06	0.04	0.47		
EC-18-624	20.12.2011	2509.43	0.00	2516.99	0.86	59.8	2388.9	10.7	878.62	0.08	0.06	0.43		
EC-18-629	20.12.2011	2500.58	0.00	2516.84	0.13	67.7	2383.1	9.4	999.08	0.10	0.07	0.39		
EC-18-639	20.12.2011	2497.60	0.61	2541.07	0.58	67.9	2405.2	9.6	1006.00	0.11	0.08	0.40		
EC-18-649	20.12.2011	2525.58	2.56	2565.97	7.59	72.4	2425.8	9.2	1076.96	0.12	0.09	0.38		
EC-18-659	20.12.2011	2521.51	0.44	2600.65	12.19	72.9	2457.1	9.4	1088.43	0.13	0.11	0.38		
EC-18-669	20.12.2011	2500.10	1.05	2567.41	1.45	66.3	2426.8	10.2	993.34	0.11	0.11	0.42		
EC-18-679	20.12.2011	2488.13	0.61	2511.68	0.32	53.8	2379.8	12.1	809.84	0.09	0.09	0.47		
EC-18-689	20.12.2011	2481.41	1.56	2473.11	0.56	50.5	2321.8	13.2	763.13	0.09	0.08	0.39		
EC-18-699	20.12.2011	2418.66	0.07	2391.26	1.24	46.4	2188.1	14.2	710.72	0.07	0.07	0.29		
EC-18-709	20.12.2011	2343.23	6.30	2296.59	0.60	43.0	1997.0	14.3	671.43	0.07	0.06	0.20		
EC-18-719	20.12.2011	2354.73	1.47	2246.95	2.73	39.0	1841.3	14.3	638.41	0.06	0.05	0.21		
EC-18-724	20.12.2011	2343.52	5.33	2289.54	1.15	55.7	1943.2	10.8	893.10	0.12	0.11	0.08		

4. Overview over particulate matter parameters, part 1 of 3.

ID	DATE	PC	σ_{PC}	POC	σ_{POC}	PN	σ_{PN}	PIC	POC	σ_{POC}	PIC
	[dd.mm.yyyy]				[µmol L^{-1}]					[%SPM]	
EC-01-589	29.07.2009	584.42	10.80	546.20	13.17	73.24	1.22	38.22	16.20	0.39	1.13
EC-01-592	29.07.2009										
EC-01-594	29.07.2009	574.54		526.53		70.86		48.01	16.11		1.47
EC-01-597	29.07.2009										
EC-01-599	29.07.2009	612.29		545.67		72.93		66.62	14.95		1.82
EC-01-604	29.07.2009	591.47		544.09		70.88		47.38	15.37		1.34
EC-01-609	29.07.2009	522.87		468.47		62.84		54.40	15.78		1.83
EC-01-614	29.07.2009	520.79		481.12		60.73		39.67	16.29		1.34
EC-01-619	29.07.2009	529.34	22.29	480.76	4.94	57.37	0.68	48.58	12.66	0.13	1.28
EC-01-624	29.07.2009	301.91		285.90		32.36		16.01	15.34		0.86
EC-01-629	29.07.2009	280.75		264.55		27.36		16.20	15.52		0.95
EC-01-634	29.07.2009	328.83		311.06		38.05		17.77	14.96		0.85
EC-01-639	29.07.2009	277.48		266.52		27.80		10.97	13.75		0.57
EC-01-644	29.07.2009	256.55		238.52		23.71		18.03	11.76		0.89
EC-02-619	27.08.2009	480.41		482.72		36.20			13.15		
EC-02-621	27.08.2009										
EC-02-624	27.08.2009	356.41		320.04		14.42		36.38	9.36		1.06
EC-02-629	27.08.2009	328.88		318.32		6.36		10.55	11.20		0.37
EC-02-634	27.08.2009	240.50		230.53		8.93		9.97	11.62		0.50
EC-02-639	27.08.2009	198.80		180.82				17.99	9.83		0.98
EC-02-644	27.08.2009	153.81		145.15				8.66	8.87		0.53
EC-03-609	08.09.2009	457.01		398.60		38.26		58.41	16.87		2.47
EC-03-614	08.09.2009	342.12	1.43	315.19	10.83	32.04	1.51	26.93	17.47	0.60	1.49
EC-03-624	08.09.2009	214.21		201.27		7.93		12.94	11.71		0.75
EC-03-634	08.09.2009	218.10		197.65		5.04		20.45	10.21		1.06
EC-03-649	09.09.2009	587.29		503.96				83.33	4.59		0.76
EC-03-659	09.09.2009	308.11		260.39				47.72	4.27		0.78
EC-03-669	09.09.2009	200.07		172.26				27.82	5.07		0.82
EC-03-679	10.09.2009	844.30		629.88				214.42	4.07		1.42
EC-03-689	10.09.2009	733.21	6.32	551.93	2.36			181.29	4.00	0.02	1.37
EC-03-694	11.09.2009	357.06		307.97				49.08	4.99		0.98
EC-03-699	11.09.2009	438.88		319.75				119.13	4.23		2.00
EC-03-704	11.09.2009	880.01		656.70				223.32	4.29		1.64
EC-03-709	11.09.2009	406.12		307.07				99.04	4.13		1.84
EC-03-714	12.09.2009	359.89		306.49				53.40	4.89		2.12
EC-03-719	12.09.2009	462.18		380.53				81.65	4.57		2.18
EC-03-729	12.09.2009	519.49		400.96				118.53	4.84		3.33
EC-04-609	15.10.2009	271.91		229.78		29.24		42.13	13.04		2.39
EC-04-619	15.10.2009	345.66		298.97		34.71		46.69	7.87		1.23
EC-04-629	15.10.2009	258.64		218.88		26.19		39.76	6.20		1.13
EC-04-639	15.10.2009	108.90		88.05		9.04		20.85	4.98		1.18
EC-04-649	15.10.2009	231.39		181.43		17.75		49.96	4.67		1.28
EC-04-659	15.10.2009	433.91		358.60		30.46		75.32	4.04		0.85
EC-04-669	15.10.2009	358.36		290.94		26.21		67.42	4.59		1.14
EC-04-674	15.10.2009	404.41	5.63	323.44	3.72	29.01	0.73	80.97	4.66	0.05	1.26
EC-04-679	15.10.2009	328.65		262.54		22.27		66.11	4.63		1.31
EC-04-684	15.10.2009	316.13		248.05		20.00		68.09	4.71		1.67
EC-04-689	15.10.2009	364.60		267.74		24.06		96.86	4.75		2.55
EC-04-694	15.10.2009	422.90		327.65		28.54		95.25	4.59		1.94
EC-04-699	15.10.2009	465.51		342.73		29.15		122.77	4.32		2.33
EC-04-709	15.10.2009	456.21		361.28		28.52		94.93	5.51		3.21
EC-04-719	15.10.2009			384.69					5.52		
EC-04-724	15.10.2009	256.14		197.54		18.66		58.60	4.23		3.83
EC-05-570	25.03.2010	208.89		190.48		27.35		18.41	14.18		1.37
EC-05-579	25.03.2010	207.04		209.85		27.15			14.93		
EC-05-589	25.03.2010	215.31		199.44		30.73		15.87	13.16		1.05
EC-05-599	25.03.2010	225.57		198.67		26.79		26.91	13.54		1.83
EC-05-609	24.03.2010	226.19		210.56		27.50		15.63	14.91		1.11
EC-05-619	24.03.2010	228.59		220.77		30.61		7.83	14.48		0.51
EC-05-624	24.03.2010	214.46		193.31		25.71		21.15	10.06		1.10
EC-05-629	24.03.2010	207.87		193.52		24.38		14.35	10.65		0.79
EC-05-639	24.03.2010	193.70		178.39		22.27		15.31	8.70		0.75
EC-05-649	24.03.2010	270.14	13.16	227.04	19.79	24.64	0.24	43.10	7.59	0.66	1.44
EC-05-659	24.03.2010	471.96		384.08		38.85		87.88	6.13		1.40
EC-05-669	24.03.2010	484.39		445.74		40.26		38.65	6.13		0.53
EC-05-679	24.03.2010	539.61		447.47		41.44		92.14	5.46		1.12
EC-05-689	24.03.2010	788.75		662.08		57.65		126.67	5.33		1.02
EC-05-699	24.03.2010	537.84		445.33		42.05		92.51	4.60		0.96
EC-05-709	24.03.2010	295.53		248.80		26.73		46.72	5.09		1.07
EC-05-719	24.03.2010	273.30		226.94		30.94		46.36	5.03		1.72
EC-05-724	24.03.2010	408.56		327.26		47.85		81.30	5.68		3.83
EC-06-609	07.04.2010	179.60		161.17		21.77		18.43	16.52		1.89
EC-06-619	07.04.2010	177.23		148.99		23.16		28.25	13.69		2.60
EC-06-624	07.04.2010	140.96		137.25		18.71		3.71	13.84		0.37
EC-06-629	07.04.2010	131.73		115.25		17.79		16.48	13.29		1.90
EC-06-639	07.04.2010	125.57		109.35		16.63		16.22	11.11		1.65
EC-06-649	07.04.2010	130.05		110.78		15.38		19.26	10.53		1.83
EC-06-659	07.04.2010	137.77		123.39		14.58		14.38	10.68		1.24
EC-06-669	07.04.2010	284.43	6.75	230.17	7.95	24.72	0.77	54.26	6.17	0.21	1.45
EC-06-679	07.04.2010	697.79		556.54		50.49		141.25	4.48		1.14
EC-06-689	07.04.2010	738.61		606.72		53.38		131.89	5.18		1.13
EC-06-699	07.04.2010	928.22		771.66		68.56		156.56	4.43		0.90
EC-06-709	07.04.2010	887.37		626.49		61.54		260.89	4.22		1.76
EC-06-719	07.04.2010	317.73		241.98		29.60		75.75	4.15		1.39
EC-06-729	07.04.2010	334.78		254.51		32.37		80.27	4.74		2.14
EC-07-570	06.05.2010	560.26		932.80	31.80	73.81			31.82	1.09	
EC-07-579	06.05.2010	558.69		1093.45	9.37	79.78			37.00	0.32	

Overview over particulate matter parameters, part 2 of 3.

ID	DATE	PC	σ_{PC}	POC	σ_{POC}	PN	σ_{PN}	PIC	POC	σ_{POC}	PIC
	[dd.mm.yyyy]					[µmol L^{-1}]				[%SPM]	
EC-07-599	06.05.2010	519.83		962.01	17.31	68.19			33.57	0.60	
EC-07-609	06.05.2010	497.27		813.30	9.45	71.70			28.98	0.34	
EC-07-619	06.05.2010	453.29	21.62	571.61	16.32	66.21	1.36		23.92	0.68	
EC-07-624	05.05.2010	248.26		302.43	1.99	28.84			14.47	0.10	
EC-07-629	05.05.2010	335.70		263.77	1.63	33.40		71.93	7.48	0.05	2.04
EC-07-639	05.05.2010	239.07		240.92	0.79	30.53			7.50	0.02	
EC-07-644	05.05.2010	195.03		152.41	2.75	19.87		42.62	7.39	0.13	2.07
EC-07-649	05.05.2010	199.68		107.59	1.38	13.71		92.09	4.07	0.05	3.49
EC-07-659	05.05.2010	216.66	0.53	149.28	1.64	18.21	4.22	67.37	4.85	0.05	2.19
EC-07-669	05.05.2010	703.82		437.41	4.03	39.29		266.41	3.30	0.03	2.01
EC-07-679	05.05.2010	440.14		178.09	3.96	26.16		262.05	2.53	0.06	3.73
EC-07-689	05.05.2010	263.64		434.55	26.25	15.78			8.17	0.49	
EC-07-699	05.05.2010	273.05		236.89	1.72	20.97		36.16	4.78	0.03	0.81
EC-07-709	05.05.2010	278.81		242.06	4.19	16.39		36.75	4.31	0.07	0.79
EC-07-719	05.05.2010	258.24		208.06	6.60	13.49		50.19	3.87	0.12	1.36
EC-07-724	05.05.2010	430.94		653.47	23.52	42.19			8.75	0.32	
EC-08-644	16.07.2010	210.83		173.86		24.62		36.97	11.35		2.41
EC-08-649	16.07.2010	368.96		313.35		41.71		55.61	6.62		1.18
EC-08-659	16.07.2010	214.13		169.70		29.54		44.43	6.77		1.77
EC-08-669	16.07.2010	614.37		493.13		80.94		121.24	5.22		1.28
EC-08-679	16.07.2010	421.12	9.85	338.70	14.51	58.11	8.11	82.42	5.21	0.22	1.27
EC-08-689	16.07.2010	326.15		254.17		22.64		71.97	5.40		1.63
EC-08-699	16.07.2010	208.25		157.40				50.85	4.95		2.12
EC-08-709	16.07.2010	444.42		335.25		49.29		109.17	5.76		4.18
EC-08-719	16.07.2010	526.47	0.69	454.55	6.81	40.15	56.78	71.92	10.35	0.15	2.88
EC-09-609	10.08.2010	687.71		566.09		74.99		121.62	13.58		2.92
EC-09-619	10.08.2010	477.49		381.60		56.49		95.88	11.86		2.98
EC-09-624	10.08.2010	447.47	7.40	359.70	24.48	44.91	0.60	87.77	9.52	0.65	2.32
EC-09-629	10.08.2010	617.77		429.48		44.29		188.29	7.62		3.34
EC-09-634	10.08.2010	645.43		544.88		45.08		100.56	7.03		1.30
EC-09-639	10.08.2010	860.97	12.26	697.11	19.00	67.31	2.41	163.86	6.99	0.19	1.64
EC-09-644	10.08.2010	504.05		411.30		45.02		92.75	8.41		1.90
EC-09-649	10.08.2010	289.14	0.60	278.18	17.94	18.84	0.31	10.95	9.19	0.59	0.36
EC-09-659	10.08.2010	429.25		346.47		40.44		82.78	5.68		1.36
EC-09-669	10.08.2010	517.07		385.83		16.59		131.23	4.68		1.59
EC-09-679	10.08.2010	702.34	11.17	511.67	59.94	30.19	2.28	190.68	4.04	0.47	1.51
EC-09-689	10.08.2010	320.23		215.83		12.80		104.40	4.07		2.13
EC-09-699	10.08.2010	183.20	3.96	158.91		9.59	0.24	24.29	5.41		1.11
EC-09-709	10.08.2010	247.68		193.97		11.37		53.71	4.19		1.93
EC-09-719	10.08.2010	321.93		235.35				86.59	4.12		2.91
EC-09-724	10.08.2010	394.30	9.48	310.12	1.16	23.86	0.62	84.18	4.70	0.02	2.63
EC-10-609	16.09.2010										
EC-10-619	16.09.2010	177.78		149.48		19.85		28.30	12.40		2.35
EC-10-624	16.09.2010	188.88		160.23		19.44		28.64	9.13		1.63
EC-10-629	16.09.2010	234.47	1.12	199.75	2.13	23.92	0.27	34.73	7.81	0.08	1.36
EC-10-634	16.09.2010	312.58		253.76		35.30		58.83	8.86		2.05
EC-10-639	16.09.2010	252.89	6.38	200.88	2.08	31.24	1.09	52.02	8.88	0.09	2.30
EC-10-644	16.09.2010	214.21		208.36		26.63		5.85	9.90		0.28
EC-10-649	16.09.2010	204.37		173.07		24.84		31.31	8.99		1.63
EC-10-659	16.09.2010	195.61		145.48		21.30		50.14	7.28		2.51
EC-10-669	16.09.2010	230.63	2.89	188.29	9.73	22.13	0.39	42.33	5.93	0.31	1.33
EC-10-679	16.09.2010	633.29	45.26	457.42	19.13	51.83	4.10	175.86	4.30	0.18	1.65
EC-10-689	16.09.2010	877.29		654.50		70.23		222.79	4.09		1.39
EC-10-699	16.09.2010	1487.82		1082.32		112.75		405.50	3.72		1.42
EC-10-709	16.09.2010	578.07		433.99		42.18		144.07	3.39		1.23
EC-10-719	16.09.2010	374.48		287.12		28.40		87.36	3.66		1.47
EC-10-724	16.09.2010	405.92	7.94	299.22	1.33	32.06	2.45	106.70	4.54	0.02	2.57
EC-11-609	06.10.2010										
EC-11-619	06.10.2010	123.66		119.01		11.25		4.66	10.73		0.42
EC-11-624	06.10.2010	124.75		109.57		12.17		15.18	10.19		1.41
EC-11-629	06.10.2010	161.83		152.11		12.31		9.73	8.26		0.53
EC-11-639	06.10.2010	331.08	7.12	281.00	0.18	30.32	0.28	50.08	5.18	0.00	0.92
EC-11-649	06.10.2010	328.65		296.94		33.27		31.70	7.01		0.75
EC-11-659	06.10.2010	404.08		353.57		36.00		50.51	7.59		1.08
EC-11-669	06.10.2010	259.07		229.96		27.09		29.11	7.67		0.97
EC-11-679	06.10.2010	169.80		148.56		16.11		21.24	5.78		0.83
EC-11-689	06.10.2010	190.43	3.92	167.52	5.90	21.71	12.92	22.91	5.07	0.18	0.77
EC-11-699	06.10.2010	190.61		159.63		16.43		30.97	4.56		1.08
EC-11-709	06.10.2010	384.55		237.16		33.12		147.39	3.06		2.39
EC-11-719	06.10.2010	354.58		203.96		20.76		150.63	2.90		3.52
EC-11-724	06.10.2010	367.88		183.57		16.63		184.32	2.99		6.35
EC-12-609	26.11.2010	98.78	2.49			11.85	0.03				
EC-12-619	26.11.2010	84.31	1.73	75.78		10.83	0.08	8.53	9.07		1.02
EC-12-624	26.11.2010	121.81	3.30	98.49	2.73	14.34	0.57	23.32	7.78	0.22	1.84
EC-12-629	26.11.2010	157.28	12.50	132.38	1.76	17.22	0.43	24.90	7.97	0.11	1.50
EC-12-639	26.11.2010	157.98	9.30	126.85	3.77	16.29	0.11	31.12	6.57	0.20	1.61
EC-12-649	26.11.2010	197.51	2.49			23.57	3.87				
EC-12-659	26.11.2010	504.21	58.68	352.72	36.25	44.41	0.48	151.49	3.80	0.39	1.63
EC-12-669	26.11.2010	447.48	64.09	302.83	16.56	40.48	0.09	144.66	4.18	0.23	2.00
EC-12-679	26.11.2010	440.25	11.76	345.95	12.08	43.32	0.51	94.30	4.57	0.16	1.25
EC-12-689	26.11.2010	474.65	48.23	365.12	32.13	39.50	10.88	109.53	5.54	0.49	1.66
EC-12-699	26.11.2010	331.31	39.18			38.27	1.51				
EC-12-709	26.11.2010	424.09	6.84	341.36	0.85	44.87	0.02	82.73	5.08	0.01	1.28
EC-12-719	26.11.2010	453.04	22.71	344.38	3.17	46.71	1.00	108.65	4.54	0.04	1.59
EC-12-724	26.11.2010	467.73	5.55	373.17	15.04	48.86	1.95	94.56	4.78	0.19	1.41
EC-13-609	21.02.2011	87.66		80.64		8.32		7.03	12.48		1.09

Overview over particulate matter parameters, part 3 of 3.

ID	DATE	PC	σ_{PC}	POC	σ_{POC}	PN	σ_{PN}	PIC	POC	σ_{POC}	PIC
	[dd.mm.yyyy]				[µmol L^{-1}]					[%SPM]	
EC-13-619	21.02.2011	79.60		75.64		8.35		3.96	11.83		0.62
EC-13-624	22.02.2011	86.45		73.35		9.65		13.10	10.59		1.89
EC-13-629	22.02.2011	102.71		89.61		10.56		13.11	10.00		1.46
EC-13-639	22.02.2011	147.63	0.15	134.22	7.38	14.87	1.14	13.40	8.40	0.46	0.84
EC-13-649	22.02.2011	168.93	2.70	147.35	9.09	17.30	0.41	21.58	8.38	0.52	1.23
EC-13-659	22.02.2011	232.77	5.32	212.21	5.30	23.89	0.23	20.56	7.91	0.20	0.77
EC-13-669	22.02.2011	290.02	10.40	255.16	12.01	27.70	2.12	34.86	7.31	0.34	1.00
EC-13-679	22.02.2011	364.31	10.81	333.22	47.02	32.03	1.09	31.09	6.39	0.90	0.60
EC-13-689	22.02.2011	367.18	9.04	338.69	1.45	31.41	1.24	28.49	6.40	0.03	0.54
EC-13-699	22.02.2011	292.80	2.13	276.19	3.60	26.63	0.67	16.61	6.05	0.08	0.36
EC-13-709	22.02.2011	569.01	13.07	512.82	42.65	45.87	3.73	56.19	5.82	0.48	0.67
EC-13-719	22.02.2011	668.07	1.18	543.40	26.47	52.47	1.63	124.67	4.89	0.24	1.50
EC-13-724	22.02.2011	703.74	8.20	583.05	24.74	53.10	2.59	120.69	5.20	0.22	1.86
EC-14-609	26.04.2011	721.58	29.19	630.73	36.53	78.02	1.63	90.85	16.78	0.97	2.42
EC-14-619	26.04.2011	228.46	13.02	207.75	2.82	28.37	0.68	20.72	11.31	0.15	1.13
EC-14-624	26.04.2011	278.00	1.10	261.72	0.45	36.45	0.66	16.29	12.51	0.02	0.78
EC-14-629	26.04.2011	231.66	0.88	218.31	1.16	28.75	0.01	13.35	10.91	0.06	0.67
EC-14-634	26.04.2011	176.73	0.94	156.87	4.41	21.78	0.50	19.87	10.47	0.29	1.33
EC-14-639	26.04.2011	158.19	11.43	142.66	0.98	19.44	1.18	15.53	9.78	0.07	1.06
EC-14-644	26.04.2011	139.19	0.22	125.28	1.57	17.24	0.06	13.92	10.31	0.13	1.14
EC-14-649	26.04.2011	143.18	3.31	125.55	2.74	17.08	0.68	17.64	9.40	0.20	1.32
EC-14-659	26.04.2011	620.07	21.86	478.90	0.32	54.55	1.77	141.17	4.40	0.00	1.30
EC-14-669	26.04.2011	495.21	10.26	412.20	23.33	43.19	0.41	83.01	4.33	0.25	0.87
EC-14-679	26.04.2011	1168.30	21.75	1016.08	21.01	91.71	0.16	152.22	4.61	0.10	0.69
EC-14-689	26.04.2011	1516.80	8.17	1228.27	256.58	118.91	0.56	288.53	4.14	0.87	0.97
EC-14-699	26.04.2011	1227.39	1.09	1054.47	13.83	97.35	2.20	172.92	4.50	0.06	0.75
EC-14-709	26.04.2011	325.90	4.99	229.08	9.08	34.93	1.50	96.81	4.03	0.16	1.92
EC-14-719	26.04.2011	403.81	18.26	292.49	2.86	31.90	2.18	111.32	4.39	0.04	2.22
EC-14-724	26.04.2011	355.15	5.79	237.04	0.05	38.59	2.39	118.11	4.27	0.00	3.54
EC-15-609	13.07.2011	920.66	19.46	762.62	13.25	101.95	0.60	158.04	15.07	0.26	3.12
EC-15-619	13.07.2011	508.95	13.61	454.54	21.78	68.93	2.38	54.41	14.58	0.70	1.75
EC-15-624	13.07.2011	727.58	1.77	612.83	4.97	83.81	3.46	114.75	7.97	0.06	1.49
EC-15-629	13.07.2011	336.73	7.57	311.79	16.34	45.42	0.78	24.93	14.72	0.77	1.18
EC-15-634	13.07.2011	356.08	16.00	322.85	6.43	45.52	4.69	33.24	10.82	0.22	1.11
EC-15-639	13.07.2011	404.70	45.55	355.92	16.03	45.46	1.60	48.78	9.94	0.45	1.36
EC-15-644	13.07.2011	367.64	7.07	322.51	14.31	40.93	1.07	45.13	8.72	0.39	1.22
EC-15-649	13.07.2011	274.77	4.15	250.76	3.04	30.95	0.58	24.01	8.33	0.10	0.80
EC-15-659	13.07.2011	314.23	0.50	270.05	12.83	28.88	2.18	44.18	5.49	0.26	0.90
EC-15-669	13.07.2011	593.23	8.68	493.95	35.69	43.92	0.05	99.28	4.10	0.30	0.82
EC-15-679	13.07.2011	1126.42	11.73	874.61	5.11	79.52	4.56	251.81	4.32	0.03	1.24
EC-15-689	13.07.2011	666.23	1.70	474.19	12.65	45.40	1.69	192.04	3.95	0.11	1.66
EC-15-699	13.07.2011	197.53	3.53	134.05	2.26	15.55	0.67	63.48	3.99	0.07	2.41
EC-15-709	13.07.2011	256.64	5.62	184.38	7.56	19.30	3.98	72.26	3.71	0.15	2.04
EC-16-609	08.09.2011	489.08	34.74	398.92		61.34	9.54	90.16	13.80		3.12
EC-16-619	08.09.2011	398.21	0.93	367.77	4.35	48.19	0.45	30.43	14.07	0.17	1.16
EC-16-624	08.09.2011	342.70	32.52	332.20	21.37	42.41	3.15	10.50	15.16	0.98	0.48
EC-16-629	08.09.2011	303.59	9.42	280.05	0.20	36.65	2.45	23.55	12.89	0.01	1.08
EC-16-639	08.09.2011	335.12	12.75	302.16	9.81	39.32	0.98	32.95	9.70	0.32	1.06
EC-16-649	08.09.2011	820.49	22.99	713.31	45.67	73.22	6.07	107.18	5.57	0.36	0.84
EC-16-659	08.09.2011	458.85	0.94	394.07	17.00	44.67	2.64	64.77	5.71	0.25	0.94
EC-16-669	08.09.2011	392.37	7.07	326.43	0.59	33.75	0.47	65.94	5.11	0.01	1.03
EC-16-679	08.09.2011	281.12	7.36	222.58	1.17	23.21	0.15	58.54	4.39	0.02	1.15
EC-16-689	08.09.2011	285.54	1.59	226.07	0.49	24.54	0.49	59.46	4.06	0.01	1.17
EC-16-699	08.09.2011	228.20	5.66	172.99	1.20	20.15	1.49	55.21	4.14	0.03	1.87
EC-16-709	08.09.2011	298.29	5.71	214.48	1.16	24.93	2.66	83.80	3.99	0.02	2.68
EC-16-719	08.09.2011	325.31	0.88	233.83	2.38	30.49	0.45	91.48	4.30	0.04	4.30
EC-16-724	08.09.2011	444.80	0.42	334.94	7.39	37.72	0.88	109.85	3.69	0.08	2.27
EC-17-609	25.10.2011	188.67	1.87	153.83	7.09	19.21	0.07	34.84	10.87	0.50	2.46
EC-17-619	25.10.2011	204.40	5.77	157.71	3.85	19.90	0.80	46.69	8.97	0.22	2.66
EC-17-624	25.10.2011	158.21	3.74	123.77	0.30	16.41	0.64	34.43	8.72	0.02	2.43
EC-17-629	25.10.2011	191.37	14.67	146.88	9.01	18.80	1.57	44.48	8.21	0.50	2.49
EC-17-639	25.10.2011	184.96	4.98	143.44	0.07	17.95	0.57	41.53	5.97	0.00	1.73
EC-17-649	25.10.2011	484.24	23.78	363.20	12.70	44.48	1.14	121.04	5.89	0.21	1.96
EC-17-659	25.10.2011	1231.42	6.82	920.01	20.43	109.14	0.31	311.41	4.79	0.11	1.62
EC-17-669	25.10.2011	687.03	14.28	531.55	25.62	57.78	0.01	155.48	4.68	0.23	1.37
EC-17-679	25.10.2011	1040.07	26.93	762.20	27.41	81.68	1.36	277.87	4.45	0.16	1.62
EC-17-689	25.10.2011	652.36	13.25	497.34	13.43	50.61	0.61	155.03	4.13	0.11	1.32
EC-17-699	25.10.2011	375.35	2.99	267.04	4.84	28.65	0.02	108.31	3.90	0.07	1.71
EC-17-709	25.10.2011	345.70	3.29	238.71	0.83	24.61	1.59	106.99	3.60	0.01	2.35
EC-17-719	25.10.2011	350.84	0.82	240.56	10.69	25.26	0.34	110.29	3.49	0.16	2.58
EC-17-724	25.10.2011	611.95	11.07	430.37	14.93	43.02	3.28	181.59	4.03	0.14	2.89
EC-18-609	20.12.2011	120.21	1.40	101.77	3.32	10.91	0.05	18.43	9.86	0.32	1.79
EC-18-619	20.12.2011	130.83	2.04	102.52	3.02	11.63	0.33	28.31	8.60	0.25	2.37
EC-18-624	20.12.2011	128.98	1.88	100.49	2.55	11.45	0.50	28.49	7.64	0.19	2.17
EC-18-629	20.12.2011	146.60	6.45	112.67	6.98	12.46	1.04	33.93	6.53	0.40	1.97
EC-18-639	20.12.2011	406.36	9.86	346.21		29.98	0.10	60.15	5.72		0.99
EC-18-649	20.12.2011	324.84	7.61	249.06	3.46	27.40	0.99	75.78	5.26	0.07	1.60
EC-18-659	20.12.2011	1243.90	1.71	909.78	15.66	101.01	3.69	334.11	4.60	0.08	1.69
EC-18-669	20.12.2011	1854.18	29.09	1352.32	0.56	142.73	2.60	501.86	4.46	0.00	1.65
EC-18-679	20.12.2011	966.88	7.57	714.07	10.65	75.67	0.61	252.81	4.35	0.06	1.54
EC-18-689	20.12.2011	585.46	10.11	391.73	35.07	44.93	0.80	193.73	3.74	0.33	1.92
EC-18-699	20.12.2011	335.47	16.18	231.44	3.74	23.53	0.82	104.03	1.43	0.02	0.68
EC-18-709	20.12.2011	365.95	1.08	239.84	4.98	25.60	0.12	126.11	3.85	0.08	3.42
EC-18-719	20.12.2011	525.30	4.53	363.39	14.60	37.81	0.12	161.91	4.59	0.18	5.17
EC-18-724	20.12.2011	425.81	2.96	280.51	15.10	30.45	0.47	145.29	5.47	0.29	8.02

5. Overview over major ion composition, part 1 of 3.

ID	DATE	F^-	σ_F	Cl^-	σ_{Cl}	Br^-	σ_{Br}	SO_4^{2-}	σ_{SO4}	K^+	σ_K	Ca^{2+}	σ_{Ca}	Mg^{2+}	σ_{Mg}	Na^+	σ_{Na}
	[dd.mm.yyyy]									[µmol L^{-1}]							
EC-01-589	29.07.2009	46.07	10.04	3295.13	55.89	1.86	0.12	887.05	9.70	239.55	10.77	1379.73	21.30	470.52	6.87	2597.21	74.20
EC-01-592	29.07.2009																
EC-01-594	29.07.2009	48.06	9.82	3206.82	70.67	1.81	0.13	881.27	7.60	235.14	4.37	1624.13	27.86	469.45	4.68	2542.41	69.07
EC-01-597	29.07.2009																
EC-01-599	29.07.2009	47.82	9.94	3192.10	56.33	1.84	0.05	888.80	11.89	233.78	1.23	1636.55	5.88	466.33	9.88	2537.54	69.85
EC-01-604	29.07.2009	48.36	9.83	3075.69	66.43	2.17	0.05	872.61	9.92	227.02	3.04	1603.42	22.89	453.71	3.19	2470.76	76.02
EC-01-609	29.07.2009	48.02	9.80	2958.93	65.12	1.69	0.07	868.47	10.30	221.37	5.38	1583.07	12.90	450.36	11.54	2406.98	70.66
EC-01-614	29.07.2009	49.11	9.91	3346.40	58.91	1.67	0.07	865.29	9.28	212.91	8.62	1503.16	29.35	444.34	13.38	2372.62	79.51
EC-01-619	29.07.2009	58.19	0.11	2679.84	6.24	1.60	0.03	853.30	2.38	185.44	1.03	1487.70	10.87	421.85	7.27	2355.87	14.64
EC-01-624	29.07.2009	57.87	0.04	2905.38	7.84	1.73	0.02	857.28	0.49	182.66	5.23	1521.55	1.89	448.63	1.63	2528.28	10.00
EC-01-629	29.07.2009	56.82	0.04	2916.72	4.89	1.68	0.08	841.35	0.83	183.24	0.52	1509.86	18.38	443.24	11.40	2515.86	2.71
EC-01-634	29.07.2009	56.43	0.07	2920.27	5.52	1.63	0.03	817.93	1.41	180.34	2.82	1462.12	1.76	429.34	5.93	2518.79	8.70
EC-01-639	29.07.2009	56.90		2846.23	3.65	1.61	0.02	785.02	0.63	180.67	3.47	1428.88	4.75	418.80	1.40	2468.82	4.71
EC-01-644	29.07.2009																
EC-02-619	27.08.2009	51.21	0.07	3984.74	11.85	2.35		1008.02	2.94	219.15	5.26	1671.02	6.88	482.35	5.50	3046.14	13.10
EC-02-621	27.08.2009	50.77	0.63	4107.62	3.61	2.28	0.01	1002.37	0.56	220.87	2.26	1664.17	69.29	501.79	7.91	3126.22	9.66
EC-02-624	27.08.2009	50.45	0.19	4114.19	4.89	2.37	0.03	1020.48	0.98	228.49	7.11	1650.43	26.89	504.30	1.69	3199.99	11.56
EC-02-629	27.08.2009	50.66	0.04	4078.23	4.93	2.27	0.02	1018.55	0.70	235.93	18.54	1688.26	20.29	482.14	4.33	3192.51	6.15
EC-02-634	27.08.2009	50.29	0.04	3018.02	6.90	1.85	0.01	826.85	1.84	197.45	23.87	1483.08	9.49	428.88	27.99	2455.81	6.12
EC-02-639	27.08.2009	51.11	0.22	4209.77	7.90	2.35	0.03	1046.14	1.89	234.13	4.49	1759.78	22.60	519.54	11.84	3320.78	9.78
EC-02-644	27.08.2009	51.06		4994.63	2.09	2.70	0.03	1061.99	0.32	229.26	12.79	1790.25	41.09	537.30	9.08	4176.92	13.01
EC-03-609	08.09.2009	34.77	0.04	4930.44	4.11	2.28	0.01	1237.07	1.24	258.60	1.19	1982.67	8.80	587.94	1.51	3726.44	14.58
EC-03-614	08.09.2009																
EC-03-624	08.09.2009																
EC-03-634	08.09.2009																
EC-03-649	09.09.2009	34.58	0.22	4918.53	4.93	2.74		1109.55	1.16	244.75	3.71	1782.96	9.09	543.02	3.20	3957.80	15.50
EC-03-659	09.09.2009	50.58	0.30	6331.48	16.59	3.20		1068.50	2.64	240.68	1.45	1731.57	38.14	515.31	2.65	5549.62	9.81
EC-03-669	09.09.2009	50.77	0.04	8276.65	3.47	3.89	0.02	1089.06	0.34	237.16	3.38	1757.30	7.23	550.85	12.31	7643.07	16.89
EC-03-679	10.09.2009	71.53	0.45	17584.83	22.26	19.00	0.08	1551.33	0.25	418.55	1.54	1881.16	35.99	1471.10	13.79	15914.40	13.81
EC-03-689	10.09.2009	73.66	0.04	38689.10	45.45	52.41	0.14	2655.51	2.97	813.67	22.97	2156.53	16.85	3521.95	3.61	34530.18	53.39
EC-03-694	11.09.2009	298.68	0.63	42692.82	312.74	64.06	0.56	2759.79	16.78	1460.45	9.08	2743.40	13.21	7004.65	29.70	40409.63	335.72
EC-03-699	11.09.2009	76.40	0.04	74291.19	49.04	108.49	0.05	4492.51	9.10	1453.13	10.16	2752.45	37.46	6976.79	30.43	66564.78	109.80
EC-03-704	11.09.2009	78.24	0.11	98534.57	57.16	146.73	0.04	5739.71	5.84	1940.52	30.96	3139.00	23.25	9396.26	33.34	88866.31	59.73
EC-03-709	11.09.2009	25.29	0.04	103020.48	79.46	188.99	0.28	4597.04	3.71	2385.83	6.37	3805.52	49.95	9105.51	2.12	85987.38	63.11
EC-03-714	12.09.2009	119.43	0.07	105599.02	323.15	157.08	0.54	6077.24	20.10	2017.35	2.75	3224.56	5.12	10031.33	43.96	94385.76	152.37
EC-03-719	12.09.2009	120.90	0.07	125435.62	148.27	188.58	0.22	7114.55	9.59	2386.17	9.84	3540.08	9.05	11928.80	24.64	112535.88	3.08
EC-03-729	12.09.2009	41.90	0.15	242815.49	57.94	448.23	0.03	10529.09	6.20	5404.30	0.11	6886.93	47.65	21740.44	15.97	204598.41	106.33
EC-04-609	15.10.2009	41.14	0.11	5113.20	59.99	2.82	0.04	1429.22	15.36	279.65	4.97	2495.50	25.67	618.36	15.20	3937.29	53.55
EC-04-619	15.10.2009	42.83	0.21	5037.35	75.34	3.68	0.06	1361.06	19.95	293.52	6.75	2364.18	38.09	611.86	8.84	3956.06	62.88
EC-04-629	15.10.2009	41.39	0.24	5554.77	82.87	3.58	0.07	1335.82	19.40	294.83	17.86	2384.51	28.30	626.54	5.25	4307.09	152.41
EC-04-639	15.10.2009	42.37	0.14	6144.29	87.73	3.75	0.08	1357.52	18.36	292.71	6.19	2379.37	30.01	653.21	6.40	4786.98	69.71
EC-04-649	15.10.2009	63.72	0.04	8256.18	1.30	4.49	0.01	1326.69	0.58	287.20	7.99	2235.78	18.51	650.65	6.81	7115.73	7.38
EC-04-659	15.10.2009	64.06	0.07	10593.38	1.91	6.05	0.06	1321.10	1.02	288.06	0.63	2059.42	60.11	715.66	11.46	9607.27	20.18
EC-04-669	15.10.2009	64.11	0.37	21707.92	28.68	23.57	0.13	1828.83	2.78	485.00	5.37	2105.83	0.12	1785.21	1.31	19577.34	78.34
EC-04-674	15.10.2009	65.43		36625.29	67.99	46.75	0.12	2567.01	5.83	752.36	2.39	2273.62	22.09	3177.74	4.65	32610.18	80.43
EC-04-679	15.10.2009	93.29	0.08	43031.21	329.44	56.78	0.49	2883.10	20.18	863.58	7.74	2377.36	44.68	3818.51	26.80	38351.54	343.33
EC-04-684	15.10.2009	95.01	0.05	76170.33	520.77	107.99	0.72	4490.57	31.54	1435.31	3.73	2840.28	8.70	6889.91	38.72	66972.19	412.57
EC-04-689	15.10.2009	125.15	0.08	114285.78	638.88	166.88	1.07	6362.73	38.82	2100.27	6.12	3401.73	56.50	10397.57	38.64	99788.34	352.70
EC-04-694	15.10.2009	126.87	0.06	138492.40	588.53	203.69	0.89	7501.33	34.66	2503.41	17.63	3509.41	381.61	12574.66	54.96	119869.58	729.13
EC-04-699	15.10.2009	128.24	0.08	167697.85	764.47	247.58	0.97	8830.71	36.22	2999.17	33.75	4151.06	37.98	15157.21	66.04	143972.25	690.75
EC-04-709	15.10.2009	159.54	0.05	227856.85	758.07	338.73	1.09	11691.03	42.06	3999.26	12.04	4974.07	29.97	20699.87	258.79	194592.80	613.46
EC-04-719	15.10.2009	182.98	31.62	307352.04	9089.29	455.56	10.61	15253.12	242.71	5258.75	111.63	6085.33	110.21	27338.82	544.32	258625.81	
EC-04-724	15.10.2009	183.35	31.44	318635.19	4811.45	471.89	2.93	15717.09	106.05	5455.83	2.47	6260.74	28.61	28368.84	81.79	267391.06	
EC-05-570	25.03.2010	34.21	0.22	2842.30	17.15	1.56	0.01	1395.19	9.27	183.17	1.90	2296.26	13.50	622.92	11.11	2361.22	12.49
EC-05-579	25.03.2010	34.21	0.22	2853.93	2.17	1.59	0.02	1403.79	0.59	184.61	0.47	2319.13	5.61	619.85	3.23	2372.01	15.44
EC-05-589	25.03.2010	34.34	0.04	2890.97	5.80	1.60	0.03	1403.71	2.43	187.19	0.61	2307.51	0.55	625.98	0.26	2403.05	1.26
EC-05-599	25.03.2010	34.27		2876.98	0.66	1.46	0.01	1399.32	0.09	184.39	4.07	2302.00	5.24	619.11	2.59	2381.34	9.44
EC-05-609	24.03.2010	34.27		2890.19	2.23	1.70	0.04	1415.10	2.02	190.61	0.20	2325.68	20.87	622.28	4.10	2398.83	11.84
EC-05-619	24.03.2010	34.16		2921.60	5.41	1.70	0.01	1419.87	2.99	189.93	2.46	2346.06	25.11	626.06	2.01	2440.35	0.06
EC-05-624	24.03.2010	34.48	0.15	2963.16	0.64	1.82	0.03	1423.29	0.25	191.52	1.99	2331.43	2.01	631.04	4.80	2475.49	13.23
EC-05-629	24.03.2010	33.98	0.11	3109.58	7.06	2.05	0.05	1424.48	3.61	207.52	2.22	2316.51	6.10	642.13	0.93	2598.22	6.37
EC-05-639	24.03.2010	34.00		3132.99	3.31	2.16	0.01	1411.46	1.73	203.17	1.94	2321.90	24.74	643.14	2.88	2587.46	3.51
EC-05-649	24.03.2010	33.84		3003.91	1.26	1.99	0.02	1397.59	0.48	206.68	1.48	2331.12	30.79	616.46	5.00	2508.42	0.98
EC-05-659	24.03.2010	50.93	0.04	3575.59	7.24	2.12	0.04	1398.11	3.02	200.17	0.63	2327.60	25.85	618.95	2.59	3135.68	8.83
EC-05-669	24.03.2010	51.00		5079.77	11.49	2.56	0.01	1379.48	1.76	192.59	2.28	2258.35	64.05	602.82	3.23	4838.15	6.03
EC-05-679	24.03.2010	50.50	0.04	4152.75	3.13	2.20	0.01	1334.83	0.86	187.82	3.20	2178.31	16.11	602.69	8.70	3875.48	13.50
EC-05-689	24.03.2010	50.95		4073.22	0.48	2.17	0.04	1276.17	0.74	190.87	0.34	2100.45	2.12	563.34	1.51	3794.25	32.36
EC-05-699	24.03.2010	51.29	0.04	7646.01	0.64	8.29	0.01	1390.11	0.07	278.54	7.00	2127.49	19.11	947.85	15.68	6961.14	10.58
EC-05-709	24.03.2010	74.30	0.11	29564.31	52.91	42.15	0.05	2461.77	3.52	666.32	12.12	2363.83	46.28	3020.86	29.91	26417.05	53.70
EC-05-719	24.03.2010	101.69		111895.88	228.43	168.49	0.44	6526.61	21.11	2129.62	1.79	3467.49	9.28	10689.73	49.46	99350.58	220.04
EC-05-724	24.03.2010	131.43	0.07	227992.26	347.78	344.56	0.55	12118.07	15.91	4223.83	29.93	5294.34	36.89	21595.60	96.30	201965.92	399.35
EC-06-609	07.04.2010	44.23	9.68	2056.02	52.16	1.21	0.05	1001.71	16.32	137.52	0.93	1603.59	6.44	465.38	19.51	1756.39	49.01
EC-06-619	07.04.2010	44.28	9.72	2045.64	49.44	1.38	0.08	995.53	17.71	138.03	8.53	1623.42	25.98	450.24	7.35	1745.34	50.77
EC-06-624	07.04.2010	44.35	9.74	2035.56	42.98	1.38	0.09	980.82	13.74	135.84	3.30	1612.56	35.37	459.33	10.82	1745.01	39.46
EC-06-629	07.04.2010	45.53	8.46	2066.24	36.28	1.35	0.08	987.41	12.24	138.05	3.20	1606.13	23.69	463.80	24.35	1764.42	40.95
EC-06-639	07.04.2010	44.46	9.74	2071.79	41.54	1.35	0.06	976.82	12.19	139.67	7.85	1627.20	52.08	451.76	4.90	1776.17	45.17
EC-06-649	07.04.2010	44.42	9.67	2295.29	45.76	1.40	0.16	970.84	13.21	141.61	3.48	1608.44	44.69	453.24	9.70	2025.61	41.65
EC-06-659	07.04.2010	44.39	9.63	2902.74	48.74	1.70	0.13	976.82	13.84	147.79	11.82	1612.23	17.47	459.75	28.95	2636.14	41.59
EC-06-669	07.04.2010	44.67	9.79	3109.53	53.77	1.70	0.16	989.51	12.38	150.87	6.42	1630.05	14.21	474.58	14.04	2867.74	47.36
EC-06-679	07.04.2010	44.64	9.71	3179.04	46.05	1.69	0.15	1009.83	11.14	150.94	1.67	1691.72	32.92	467.48	7.82	2940.26	45.01
EC-06-689	07.04.2010	44.60	9.95	3049.88	48.84	1.79	0.10	1022.15	12.87	157.82	9.39	1715.55	23.07	476.03	15.81	2804.45	61.91
EC-06-699	07.04.2010	45.07	9.86	3324.65	47.06	2.03	0.09	1102.78	12.71	159.54	9.74	1825.75	21.47	521.99	12.01	3065.16	26.76
EC-06-709	07.04.2010	64.81	12.05	5370.42	63.77	5.21	0.11	1274.39	11.00	202.36	5.40	1963.83	28.09	743.99	13.83	4879.81	86.64
EC-06-719	07.04.2010	66.06	12.08	20567.00	83.12	28.43	0.13	2087.96	7.54	483.78	4.81	2271.95	16.96	2182.95	20.81	18349.55	110.82
EC-06-729	07.04.2010	100.35	30.11	99609.68	404.20	149.82	0.70	5984.06	49.73	1889.35	5.77	3447.84	19.46	9652.52	39.60	87881.31	245.51
EC-07-570	06.05.2010	37.93	4.45	3822.44	47.73	2.08	0.07	1393.19	18.62	185.22	11.32	2279.39	39.35	644.54	71.98	2980.46	31.08
EC-07-579	06.05.2010	37.65	4.38	3650.90	49.34	2.01	0.07	1351.00	19.25	181.74	11.23	2242.74	36.21	601.84	7.12	2870.36	46.38

Overview over major ion composition, part 2 of 3.

ID	DATE	F^-	σ_F	Cl^-	σ_{Cl}	Br^-	σ_{Br}	SO_4^{2-}	σ_{SO4}	K^+	σ_K	Ca^{2+}	σ_{Ca}	Mg^{2+}	σ_{Mg}	Na^+	σ_{Na}
	[dd.mm.yyyy]									[µmol L^{-1}]							
EC-07-589	06.05.2010	37.91	4.40	3729.33	57.91	2.07	0.07	1367.69	22.42	182.60	15.66	2251.53	44.84	614.62	12.22	2915.41	38.89
EC-07-599	06.05.2010	37.27	4.24	3416.36	54.70	1.88	0.07	1263.27	23.62	177.26	19.91	2125.14	39.47	559.60	9.53	2712.08	57.52
EC-07-609	06.05.2010	37.75	4.52	3596.68	53.51	2.07	0.07	1334.14	21.14	171.86	20.96	2224.60	43.39	593.93	22.82	2813.89	54.47
EC-07-619	06.05.2010	38.83	4.47	3600.89	57.40	2.26	0.07	1332.82	20.04	181.50	13.45	2208.18	48.26	594.66	12.12	2829.69	60.35
EC-07-624	05.05.2010	37.98	4.13	3395.62	180.09	2.11	0.10	1212.79	72.31	172.65	22.21	2019.06	124.79	554.90	32.40	2668.44	109.50
EC-07-629	05.05.2010	38.54	5.00	3445.63	55.98	2.14	0.06	1233.48	20.76	187.23	17.46	2080.69	39.22	556.70	4.77	2725.79	52.09
EC-07-639	05.05.2010	38.12	4.58	3106.04	255.30	1.94	0.12	1136.23	101.46	169.29	12.96	1918.20	183.38	524.22	41.52	2498.30	215.34
EC-07-644	05.05.2010																
EC-07-649	05.05.2010	38.38	4.55	3930.88	726.79	2.17	0.20	1191.72	17.99	178.92	13.17	2004.76	42.40	570.81	58.76	3343.11	786.05
EC-07-659	05.05.2010	38.07	4.79	5115.72	81.57	2.54	0.04	1176.29	19.06	175.74	16.89	1913.51	29.97	560.76	24.93	4684.37	83.57
EC-07-669	05.05.2010	38.32	6.10	5802.15	4.41	2.88	0.04	1196.60	2.66	179.18	1.43	1942.90	18.54	557.64	8.47	5428.24	6.52
EC-07-679	05.05.2010	38.16	6.10	5291.06	1.32	3.20	0.04	1197.94	6.36	171.66	19.30	1929.92	19.04	591.89	28.74	4840.35	20.64
EC-07-689	05.05.2010	34.42		10789.64	4.39	11.91	0.01	1516.79	0.44	277.67	17.56	2033.38	9.10	1139.81	4.77	9651.64	34.14
EC-07-699	05.05.2010	63.37	15.04	27832.69	32.13	38.69	0.17	2329.19	15.60	580.75	5.70	2217.81	2.45	2741.62	0.41	24654.97	10.40
EC-07-709	05.05.2010	88.17	15.33	65973.02	213.11	98.52	0.60	4253.81	18.98	1203.12	50.24	2808.34	7.18	6316.89	7.56	58048.21	104.33
EC-07-719	05.05.2010	102.11		109463.42	411.76	167.28	0.61	6447.06	16.99	1959.61	16.08	3446.30	40.54	10400.95	1.28	96417.17	489.20
EC-07-724	05.05.2010	106.38		167388.88	155.33	261.31	0.21	9348.40	5.45	2887.45	71.67	4256.23	20.36	15754.60	74.51	147062.35	939.79
EC-08-644	16.07.2010	39.92	9.04	4192.64	12.35	2.55	0.03	1221.33	2.16	213.37	9.35	1875.03	22.07	615.57	27.20	3367.89	133.36
EC-08-649	16.07.2010	39.77	9.12	4726.17	22.34	2.75	0.06	1203.50	0.99	212.82	11.25	1833.00	6.53	585.48	8.03	3918.85	40.82
EC-08-659	16.07.2010	39.21	9.23	6518.73	11.83	3.38	0.04	1197.36	1.52	194.54	8.54	1659.94	8.72	592.96	8.03	5826.81	11.20
EC-08-669	16.07.2010	39.24	8.82	6723.44	8.94	3.27	0.03	1185.60	3.30	207.84	5.97	1755.21	51.64	626.19	70.90	6087.51	41.80
EC-08-679	16.07.2010	38.95	8.93	7375.82	35.90	4.40	0.06	1179.20	1.58	228.67	29.79	1604.71	4.92	647.36	7.27	6709.96	56.44
EC-08-689	16.07.2010	87.67	22.22	13884.73	5.88	15.37	0.05	1489.94	6.35	352.09	37.69	1696.22	10.30	1354.41	12.28	12329.98	49.00
EC-08-699	16.07.2010	90.88	22.59	51624.47	253.44	74.62	0.66	3393.03	23.56	935.00	22.06	2580.43	33.82	4981.61	49.69	44481.83	218.81
EC-08-709	16.07.2010	100.82	22.52	198628.27	1287.40	304.16	0.84	10696.06	6.08	3149.48	6.46	4850.25	17.27	18951.45	84.89		
EC-08-719	16.07.2010	144.22	22.55	364883.48		560.51	1.66	18864.24	74.81	5680.69	3.06	7339.26	41.81	34720.80	57.20		
EC-09-609	10.08.2010	40.00	8.86	4230.14	21.90	2.02	0.06	1187.82	0.54	216.53	7.81	2051.09	4.25	597.28	7.80	3213.32	44.08
EC-09-619	10.08.2010	40.40	8.82	3899.59	17.51	1.94	0.04	1107.52	0.48	205.35	8.64	1941.03	5.28	558.34	5.15	2982.61	39.40
EC-09-624	10.08.2010	40.29	9.04	3814.84	12.31	2.06	0.04	1084.78	2.49	198.01	21.85	1891.50	27.75	547.44	0.73	2941.31	50.75
EC-09-629	10.08.2010	40.06	8.86	3843.91	23.57	2.28	0.05	1082.17	1.33	202.41	0.94	1869.64	28.99	566.69	22.49	2988.61	29.93
EC-09-634	10.08.2010	40.21	9.08	3793.95	7.74	2.29	0.04	1071.71	2.81	210.71	7.87	1837.16	15.51	545.85	11.75	2965.23	29.90
EC-09-639	10.08.2010	40.29	8.97	3781.53	7.36	2.38	0.03	1071.52	3.00	213.21	8.25	1814.74	10.87	550.44	3.87	2964.86	29.00
EC-09-644	10.08.2010	40.40	9.12	3883.62	10.89	2.52	0.05	1109.21	1.59	221.47	12.19	1847.04	12.69	583.07	20.51	3080.20	33.46
EC-09-649	10.08.2010	40.21	8.93	4283.84	6.98	2.72	0.04	1168.13	3.72	223.05	9.04	1887.03	10.29	594.45	10.07	3455.78	33.13
EC-09-659	10.08.2010	40.58	9.01	6156.52	12.25	3.32	0.05	1328.97	2.14	224.91	11.34	2044.30	3.48	653.43	17.83	5174.13	7.75
EC-09-669	10.08.2010	40.56	9.04	8590.26	21.00	4.28	0.04	1458.00	0.60	254.84	11.36	2162.78	4.69	753.73	50.88	7436.87	36.79
EC-09-679	10.08.2010	40.48	9.01	9391.21	3.69	6.33	0.03	1481.08	5.57	260.22	3.36	2099.03	22.58	842.30	23.74	8085.81	9.60
EC-09-689	10.08.2010	60.43	18.09	21809.68	44.90	25.72	0.10	2032.77	10.50	463.64	11.34	2203.96	8.80	2029.34	2.33	18978.48	4.98
EC-09-699	10.08.2010	90.90	22.63	50510.90	53.09	70.57	0.14	3416.00	6.28	917.81	23.00	2717.58	92.91	4888.79	7.62	43713.62	86.06
EC-09-709	10.08.2010	175.07	45.33	113601.09	27.42	168.25	0.65	6515.26	15.55	1945.74	50.17	3606.55	5.35	10969.84	82.04	98006.00	103.81
EC-09-719	10.08.2010	178.70	45.18	167616.17	563.76	252.77	1.89	9214.01	32.59	2764.40	22.34	4387.77	21.00	16261.53	1.89	144558.30	747.22
EC-09-724	10.08.2010	213.65	45.18	208931.11	262.61	316.87	1.45	11279.03	19.47	3354.31	139.00	5027.20	50.07	20403.68	355.55	179750.95	1233.62
EC-10-609	16.09.2010																
EC-10-619	16.09.2010	18.26	2.46	2487.45	5.25	1.47	0.13	1054.50	2.20	175.19	15.43	1777.42	52.52	488.44	13.06	2083.17	51.46
EC-10-624	16.09.2010	18.63	3.35	2520.66	48.67	1.57	0.20	1040.93	4.34	180.10	4.83	1698.18	13.00	515.92	6.02	2121.23	86.46
EC-10-629	16.09.2010	18.21	2.68	2465.55	5.86	1.52	0.12	1017.13	2.58	168.95	12.82	1687.33	8.12	493.58	4.16	2067.44	38.69
EC-10-634	16.09.2010	18.11	2.53	2433.32	0.54	1.51	0.11	1008.11	0.74	181.21	3.07	1677.99	3.86	477.17	13.53	2050.15	45.86
EC-10-639	16.09.2010	18.37	2.53	2442.74	1.85	1.46	0.10	1010.28	0.15	176.80	0.74	1691.33	6.03	491.42	3.08	2051.54	46.91
EC-10-644	16.09.2010	18.61	2.64	2447.97	4.35	1.46	0.14	1003.60	0.36	176.25	16.75	1688.74	0.44	488.95	0.23	2051.50	53.12
EC-10-649	16.09.2010	18.48	2.53	2799.52	1.34	1.55	0.11	1006.38	0.46	175.48	5.10	1689.38	13.94	487.18	2.79	2410.75	36.63
EC-10-659	16.09.2010	18.61	2.49	3152.82	13.16	1.71	0.13	1015.75	3.78	172.05	13.56	1663.28	2.65	483.79	1.37	2805.38	90.37
EC-10-669	16.09.2010	21.30	0.95	3293.12	17.25	1.92	0.12	1031.34	12.06	189.89	5.62	1660.55	7.31	493.25	4.64	2997.00	35.33
EC-10-679	16.09.2010	21.30	1.35	4123.19	22.72	2.87	0.21	1064.87	9.12	211.26	7.42	1626.04	20.81	572.45	33.96	3723.82	45.96
EC-10-689	16.09.2010	12.00	0.15	11737.46	39.09	14.35	0.04	1319.80	2.35	373.28	2.41	2206.63	2.91	1411.71	12.89	10465.09	40.60
EC-10-699	16.09.2010	26.46	1.39	34125.53	165.44	48.74	0.21	2489.24	12.09	685.17	8.04	2050.79	15.00	3319.37	20.38	28785.51	61.72
EC-10-709	16.09.2010	32.28	2.09	74446.19	674.54	110.42	0.80	4469.08	18.59	1325.37	62.72	1751.78	1489.40	6959.09	51.60	61775.69	393.82
EC-10-719	16.09.2010	38.27	2.87	117961.99	394.29	176.84	0.15	6611.90	10.75	1991.75	18.84	3232.03	53.79	10989.45	85.99	97936.91	
EC-10-724	16.09.2010	27.08	0.26	138462.49	29.74	231.86	0.33	6729.42	3.03	2861.17	16.24	4452.72	20.57	13514.71	22.52	124699.86	46.07
EC-11-609	06.10.2010	20.08	2.87	1649.96	4.43	1.08	0.13	893.05	1.32	171.39	5.82	1481.86	12.07	443.84	2.94	1439.97	57.24
EC-11-619	06.10.2010	19.90	2.83	1684.61	3.57	1.13	0.12	902.63	3.14	173.20	5.90	1509.36	4.09	438.08	3.17	1468.50	52.26
EC-11-624	06.10.2010	20.03	3.01	1763.14	1.58	1.18	0.12	931.57	1.21	174.46	6.73	1536.35	5.50	442.40	1.83	1528.66	55.21
EC-11-629	06.10.2010	20.50	2.79	1821.88	1.28	1.28	0.11	948.87	2.13	173.22	5.73	1558.86	20.25	461.02	10.94	1584.68	54.66
EC-11-639	06.10.2010	19.61	2.34	2069.05	0.08	1.38	0.09	1015.91	0.97	178.68	6.11	1653.76	3.12	484.82	3.40	1777.03	59.88
EC-11-649	06.10.2010	18.37	2.53	2863.92	9.75	1.83	0.10	1186.45	3.26	190.61	16.98	1925.77	12.74	546.23	19.26	2331.06	61.12
EC-11-659	06.10.2010	18.21	2.23	3671.66	9.71	2.19	0.11	1245.33	4.15	201.90	8.83	2087.89	10.32	547.83	11.75	2969.39	47.03
EC-11-669	06.10.2010	18.26	2.31	3792.64	0.38	2.18	0.11	1206.90	1.22	188.84	16.73	1981.79	18.42	526.29	3.17	3188.37	78.74
EC-11-679	06.10.2010	18.32	2.68	5492.88	8.78	4.72	0.08	1253.54	1.60	214.05	2.35	1917.06	27.45	661.45	26.74	4724.71	52.04
EC-11-689	06.10.2010	77.69	19.50	17327.22	37.82	22.71	0.08	1744.90	9.27	413.01	30.31	2017.23	7.75	1784.88	8.76	15065.96	18.09
EC-11-699	06.10.2010	79.35	19.76	42273.83	46.27	60.75	0.32	2962.46	9.35	711.90	58.49	2311.87	1.38	4148.22	13.47	36284.77	239.82
EC-11-709	06.10.2010	83.22	19.58	95800.07	135.11	143.61	0.55	5619.01	2.38	1395.01	30.94	3102.94	7.67	9199.73	19.81	82108.13	94.36
EC-11-719	06.10.2010	88.51	19.61	170925.25	187.96	259.62	1.04	9296.29	71.76	2329.92	42.57	4156.94	107.77	16042.01	222.50	146606.82	
EC-11-724	06.10.2010	90.69	19.35	200926.06	505.26	305.37	1.13	10726.64	75.16	2712.24	33.46	4645.43	40.99	18928.02	91.50		
EC-12-609	26.11.2010	23.28	4.60	1983.61	28.59	1.10	0.21	1149.25	20.08	163.69	10.69	1892.43	27.76	547.09	13.14	1739.28	47.81
EC-12-619	26.11.2010	22.80	5.34	1978.85	29.23	1.13	0.24	1123.81	28.59	159.65	3.19	1863.86	22.35	528.66	7.10	1719.11	47.77
EC-12-624	26.11.2010	23.39	4.67	1961.83	60.90	1.18	0.23	1109.75	22.91	157.05	2.96	1847.89	18.63	524.52	5.22	1718.45	48.65
EC-12-629	26.11.2010	21.03	3.31	2026.99	18.51	1.25	0.02	1081.90	10.28	159.51	1.32	1823.89	2.01	532.71	15.16	1761.76	39.65
EC-12-639	26.11.2010	20.98	3.39	2033.33	14.82	1.25	0.04	1076.22	12.63	159.65	3.22	1800.11	6.85	514.67	1.05	1764.02	44.57
EC-12-649	26.11.2010	20.90	3.35	2162.92	15.64	1.39	0.02	1102.61	11.67	166.20	2.89	1822.22	4.59	529.05	5.15	1874.01	38.20
EC-12-659	26.11.2010	21.63	2.78	2988.44	10.32	1.74	0.01	1173.56	16.52	173.37	1.83	1932.48	3.84	540.11	5.48	2645.48	39.85
EC-12-669	26.11.2010	20.86	2.72	3989.58	12.93	2.18	0.02	1245.40	13.83	181.10	3.65	2038.57	13.57	566.19	7.86	3550.68	36.87
EC-12-679	26.11.2010	21.67	2.77	4023.81	15.05	2.26	0.03	1272.68	16.47	184.75	3.39	2091.81	19.93	575.46	12.18	3580.11	36.93
EC-12-689	26.11.2010	21.60	2.75	3904.84	24.81	2.18	0.03	1272.90	15.00	183.59	1.47	2105.87	20.42	584.38	23.55	3484.81	31.36
EC-12-699	26.11.2010	29.53	5.56	4554.29	31.16	2.89	0.05	1306.23	4.86	181.35	7.52	2111.33	23.48	633.60	16.26	4171.48	62.49
EC-12-709	26.11.2010	69.09	11.97	11213.09	29.21	13.55	0.07	1582.29	9.59	254.73	24.47	2137.73	35.82	1346.83	42.32	10174.55	164.19
EC-12-719	26.11.2010	78.09	8.52	47669.01	63.36	69.66	0.14	3323.60	1.77	916.27	1.03	2625.95	37.02	4742.81	20.54	40908.61	39.83
EC-12-724	26.11.2010	97.67	16.79	64424.58	262.22	95.06	0.31	4162.16	0.04	1173.20	36.39	2986.01	218.16	6366.71	16.06	55208.77	113.37
EC-13-609	21.02.2011	9.76	0.41	2204.72	5.11	1.31	0.12	1232.91	3.31	162.54	3.18	3325.24	276.05	375.44	15.13	1534.62	3.29

Overview over major ion composition, part 3 of 3.

ID	DATE	F^-	σ_F	Cl^-	σ_{Cl}	Br^-	σ_{Br}	SO_4^{2-}	σ_{SO4}	K^+	σ_K	Ca^{2+}	σ_{Ca}	Mg^{2+}	σ_{Mg}	Na^+	σ_{Na}
	[dd.mm.yyyy]									[µmol L^{-1}]							
EC-13-619	21.02.2011	10.79	0.97	2209.62	1.26	1.28	0.04	1238.20	9.11	166.53	1.92	3321.15	313.17	371.65	7.33	1549.78	9.97
EC-13-624	22.02.2011	9.47		2200.05	3.93	1.41	0.14	1227.51	2.09	168.68	4.96	3092.33	19.60	364.08	10.71	1526.09	3.04
EC-13-629	22.02.2011	9.74	0.15	2209.35	5.62	1.47	0.19	1231.89	1.82	177.05	16.77	3122.66	30.98	369.00	1.95	1538.01	3.60
EC-13-639	22.02.2011	9.50	0.04	2216.44	1.02	1.48	0.16	1230.19	0.50	171.90	11.72	3088.09	17.52	365.09	2.76	1560.06	10.49
EC-13-649	22.02.2011	9.42	0.07	2356.43	3.33	1.61	0.24	1212.10	2.30	172.42	4.68	3260.78	273.21	381.55	9.63	1698.89	13.78
EC-13-659	22.02.2011	9.76	0.04	2458.21	2.67	1.60	0.20	1214.96	0.59	175.21	0.67	3073.64	20.91	370.52	6.08	1785.95	6.18
EC-13-669	22.02.2011	9.42	0.15	2763.64	4.41	1.67	0.20	1225.18	1.15	160.85	3.76	3299.50	247.87	372.21	20.57	2137.49	21.93
EC-13-679	22.02.2011	6.90	1.41	2671.99	10.93	1.41	0.02	1181.67	1.86	154.03	11.88	3211.18	273.31	366.32	17.31	2123.60	12.49
EC-13-689	22.02.2011	9.47	0.07	2901.95	11.33	2.15	0.14	1191.86	3.76	166.31	3.45	3023.25	98.24	371.78	3.90	2316.05	2.61
EC-13-699	22.02.2011	11.45	0.11	20825.64	0.02	29.10	0.09	2078.92	1.98	504.41	13.04	3595.64	212.74	1559.06	47.19	18230.33	90.37
EC-13-709	22.02.2011	25.03	0.04	169950.36	435.68	253.97	0.65	9338.70	18.02	3197.30	27.56	6898.00	267.54	11190.85	153.81	147302.30	961.42
EC-13-719	22.02.2011	36.35	0.11	293664.94	611.91	434.78	0.96	15062.60	14.02	5340.46	4.23	9324.37		18604.79	29.24	249079.13	488.74
EC-13-724	22.02.2011																
EC-14-609	26.04.2011	11.13	0.11	3646.24	2.35	2.45	0.06	1493.35	0.54	229.98	12.37	3209.17	17.54	460.85	3.37	2943.64	16.52
EC-14-619	26.04.2011	12.71	0.11	3366.54	4.79	2.30	0.02	1460.81	1.99	199.87	1.07	3302.60	31.81	457.91	21.73	2732.54	4.15
EC-14-624	26.04.2011	10.84		3195.95	220.03	2.21	0.13	1437.19	32.25	197.35	1.05	3321.88	32.09	442.48	1.83	2760.88	0.49
EC-14-629	26.04.2011	12.11	0.15	3344.03	6.70	2.37	0.03	1468.32	2.21	212.26	12.01	3368.91	9.67	446.06	1.02	2803.33	41.15
EC-14-634	26.04.2011	11.84	0.00	3342.21	9.71	2.33	0.06	1465.76	4.39	216.16	10.91	3469.48	88.78	437.21	12.89	2811.38	46.07
EC-14-639	26.04.2011	11.66	0.26	3360.39	0.88	2.45	0.10	1468.47	0.27	212.69	4.88	3464.56	23.55	447.67	10.21	2827.41	13.13
EC-14-644	26.04.2011	11.74	0.07	3412.00	4.97	2.46	0.03	1465.14	1.30	212.81	5.95	3491.47	36.73	469.45	3.08	2829.50	40.69
EC-14-649	26.04.2011	11.47	0.22	3622.05	6.72	2.63	0.01	1469.42	2.72	229.52	10.31	3444.61	88.64	459.31	10.50	3022.95	19.19
EC-14-659	26.04.2011	11.58	0.07	4435.72	2.45	3.02	0.10	1472.70	1.55	234.65	10.44	3468.87	23.73	460.87	15.27	3893.10	47.34
EC-14-669	26.04.2011	11.37	0.22	4712.51	7.52	3.08	0.06	1466.91	2.77	229.72	12.32	3339.16	99.16	456.00	7.45	4130.73	18.73
EC-14-679	26.04.2011	11.40	0.11	4966.62	3.81	3.22	0.01	1458.97	0.71	200.10	11.38	3428.09	29.18	457.60	22.63	4431.14	0.98
EC-14-689	26.04.2011	11.32	0.22	5581.62	5.58	4.25	0.08	1446.04	0.04	251.07	33.26	3328.71	24.28	483.89	7.51	4992.89	7.41
EC-14-699	26.04.2011	12.66	0.04	19506.37	12.47	25.51	0.05	2169.92	2.25	466.80	3.04	3681.80	23.18	1392.88	4.25	16809.35	41.89
EC-14-709	26.04.2011	14.90	0.07	45857.85	227.35	66.11	0.36	3481.35	15.82	945.83	11.92	4273.82	36.84	3078.38	5.88	39209.64	270.82
EC-14-719	26.04.2011	20.24	0.04	106930.26	50.00	159.34	0.02	6433.62	2.94	2035.83	0.81	5675.15	50.30	7016.38	0.81	91121.79	62.07
EC-14-724	26.04.2011	23.37	0.00	143202.21	189.36	213.64	0.20	8095.01	12.08	2689.87	2.88	6474.19	90.81	9456.10	89.81	121858.48	101.90
EC-15-609	13.07.2011																
EC-15-619	13.07.2011																
EC-15-624	13.07.2011																
EC-15-629	13.07.2011																
EC-15-634	13.07.2011																
EC-15-639	13.07.2011																
EC-15-644	13.07.2011																
EC-15-649	13.07.2011																
EC-15-659	13.07.2011																
EC-15-669	13.07.2011																
EC-15-679	13.07.2011																
EC-15-689	13.07.2011																
EC-15-699	13.07.2011																
EC-15-709	13.07.2011																
EC-16-609	08.09.2011	3.08	0.78	3957.08	145.60	2.08	0.15	1369.11	63.35	251.33	8.43	2924.73	21.38	683.67	16.75	3076.31	67.04
EC-16-619	08.09.2011	8.07	0.66	3472.57	104.54	1.77	0.06	1214.09	14.68	221.81	5.66	2820.15	27.26	613.10	17.12	2872.41	37.67
EC-16-624	08.09.2011	8.62	0.29	3206.34	97.36	1.86	0.05	1144.47	20.42	235.00	6.00	2830.95	35.05	623.17	14.56	2703.28	63.74
EC-16-629	08.09.2011	9.97	0.37	3646.60	161.19	2.10	0.06	1233.64	23.22	243.87	8.56	2818.70	38.60	671.13	22.04	2918.52	81.14
EC-16-639	08.09.2011	9.82	0.23	3389.56	90.56	2.14	0.05	1218.05	15.37	236.86	6.74	2757.23	9.91	631.87	24.72	2883.09	66.01
EC-16-649	08.09.2011	9.92	0.32	3583.98	96.17	2.16	0.08	1242.22	16.01	234.45	1.69	2769.21	36.82	639.10	11.06	3100.37	69.82
EC-16-659	08.09.2011	10.05	0.05	5044.79	117.22	2.67	0.07	1223.75	11.75	239.18	8.59	2832.48	33.20	658.35	3.44	4477.15	156.96
EC-16-669	08.09.2011	9.84	0.24	4980.07	105.06	2.52	0.06	1181.61	9.78	218.64	7.71	2626.69	27.28	596.42	14.64	4626.92	73.40
EC-16-679	08.09.2011	10.75	0.39	11662.79	115.75	13.07	0.28	1500.93	7.74	374.01	3.12	2658.92	16.39	1333.57	23.25	10524.86	197.36
EC-16-689	08.09.2011	16.33	0.50	86016.55	529.25	127.68	0.16	5357.69	17.91	1720.81	19.71	3648.49	9.90	8534.38	56.05	74422.35	1204.69
EC-16-699	08.09.2011	21.30	0.26	152859.74	1865.39	230.59	1.22	8774.74	63.12	2947.25	94.45	4599.34	43.96	15251.73	302.50	126385.80	3668.41
EC-16-709	08.09.2011	27.40	0.66	235353.67	498.74	358.36	2.56	12767.63	46.52	4339.67	81.52	5932.77	103.05	22810.82	181.54	199404.58	3434.15
EC-16-719	08.09.2011	32.11	0.04	284950.29	3752.26	446.45	4.97	15150.69	211.50	5327.81	108.93	6658.88	102.55	27262.20	349.71	244809.78	3120.37
EC-16-724	08.09.2011																
EC-17-609	25.10.2011	0.89	0.00	3151.93	5.33	1.71	0.04	1307.97	2.30	208.76	6.69	2651.30	24.45	619.19	11.03	2581.08	20.02
EC-17-619	25.10.2011	0.87	0.04	3083.31	3.37	1.78	0.03	1280.99	1.38	209.45	6.29	2643.76	8.45	614.34	13.70	2522.64	1.17
EC-17-624	25.10.2011	0.87	0.04	3145.09	14.80	1.93	0.02	1299.73	5.65	212.91	3.27	2656.59	30.73	622.34	11.70	2566.58	18.09
EC-17-629	25.10.2011	0.92	0.04	3260.58	9.11	2.06	0.03	1320.68	3.57	223.03	0.51	2674.77	31.95	645.03	20.28	2644.11	9.69
EC-17-639	25.10.2011	0.92	0.04	3410.99	2.27	2.19	0.05	1352.55	0.88	222.39	0.22	2765.79	12.72	664.31	20.25	2756.64	1.69
EC-17-649	25.10.2011	0.92	0.04	3738.57	5.05	2.45	0.02	1399.33	1.47	254.87	2.57	2839.95	37.60	666.51	14.46	2986.87	0.15
EC-17-659	25.10.2011	0.89	0.00	4444.57	2.61	2.82		1445.94	1.78	250.51	4.86	2870.37	19.85	724.83	15.77	3651.28	2.71
EC-17-669	25.10.2011	0.89	0.00	5461.22	0.42	3.12	0.01	1395.73	0.42	257.82	8.01	2789.47	20.17	666.41	8.84	4725.82	10.98
EC-17-679	25.10.2011	0.89	0.00	6185.15	8.98	3.54	0.02	1372.47	1.61	255.19	2.12	2709.35	2.06	692.92	8.87	5510.04	10.24
EC-17-689	25.10.2011	1.00	0.00	15629.75	52.95	18.13	0.04	1820.03	4.70	419.97	3.15	2784.31	40.42	1606.32	16.50	13712.43	83.94
EC-17-699	25.10.2011	1.32	0.07	37831.83	3.75	52.26	0.19	2884.70	0.86	828.00	1.14	3153.03		3919.65	22.75	32737.02	10.61
EC-17-709	25.10.2011	2.32	0.45	134128.44	487.95	201.02	0.71	7681.18	34.45	2558.17	24.02	4416.49		13209.61	26.33	114897.84	652.61
EC-17-719	25.10.2011	3.53	0.45	169880.53	637.06	255.63	0.87	9435.21	32.40	3234.78	21.07	5053.21	88.27	16693.91	33.54	146334.11	37.43
EC-17-724	25.10.2011	4.26	0.15	255286.24	1084.96	387.50	1.54	13549.75	58.09	4744.44	24.11	6184.42	9.10	24817.59	24.82	218673.83	791.57
EC-18-609	20.12.2011	3.66	0.04	3323.01	9.63	2.66	0.12	1284.96	4.27	213.72	10.92	2714.17	20.13	597.41	1.75	2706.27	31.90
EC-18-619	20.12.2011	3.66	0.04	3145.67	4.09	2.57	0.08	1272.70	2.33	204.50	5.88	2726.46	9.25	612.75	0.99	2564.71	4.61
EC-18-624	20.12.2011	4.11	0.60	3112.19	53.67	2.12	0.02	1246.96	0.52	200.51	4.76	2606.08	25.04	611.64	41.54	2553.29	2.74
EC-18-629	20.12.2011	3.66	0.04	3303.13	7.98	2.47	0.45	1265.37	3.95	214.77	1.27	2686.71	20.47	600.72	10.74	2737.11	5.20
EC-18-639	20.12.2011	3.63	0.00	3488.39	1.83	3.01	0.12	1288.37	1.30	221.57	0.07	2731.79	3.09	626.66	26.94	2855.25	5.87
EC-18-649	20.12.2011	3.66	0.04	3693.21	9.67	2.83	0.30	1331.98	3.55	241.38	12.32	2756.77	26.71	639.68	1.95	3027.96	8.49
EC-18-659	20.12.2011	3.66	0.04	5152.68	1.64	3.14	0.07	1400.12	0.38	243.76	4.21	2837.73	18.44	653.47	9.16	4416.25	8.09
EC-18-669	20.12.2011	3.68	0.00	6193.10	2.59	3.70	0.03	1435.09	0.78	244.37	0.89	2935.90	62.70	690.93	12.98	5402.77	10.12
EC-18-679	20.12.2011	3.66	0.04	6907.53	5.76	5.26	0.01	1417.01	0.49	264.50	9.02	2790.18	2.61	787.66	4.36	6009.54	11.38
EC-18-689	20.12.2011	3.79	0.00	19700.48	0.44	25.06	0.06	2017.28	1.84	492.75	11.16	2861.82	28.12	2053.45	4.89	17076.83	17.93
EC-18-699	20.12.2011	7.08	0.04	57459.41	107.32	83.33	0.01	3838.83	9.46	1188.39	11.36	3365.39	74.10	5884.92	51.26	49565.85	22.05
EC-18-709	20.12.2011	7.97	0.04	158487.25	387.11	239.10	0.65	8782.53	20.43	3004.41	30.98	4635.75	8.63	15610.99	75.35	135933.07	373.27
EC-18-719	20.12.2011	12.24	0.11	303080.18	419.94	461.62	0.69	15811.76	37.56	5576.07	15.55	6898.39	155.00	29690.35	141.97	259510.88	59.58
EC-18-724	20.12.2011	11.84	0.07	208862.93	351.33	316.45	0.89	11270.79	20.20	3919.70	16.19	5482.04	100.39	20723.72	58.19	179227.93	224.59

C Averaged data from the monitoring programme

1. Seasonal averages for selected parameters in the pre-OMZ and OMZ from the monitoring programme.

	YEAR	MONTH	discharge at Neu Darchau			pH			DO concentration			DO saturation			POC concentration			DOC concentration			POC part of SPM		
			mean	σ	n	mean	σ	n	mean	σ	n	mean	σ	n	mean	σ	n	mean	σ	n	mean	σ	n
										$[\mu mol\ L^{-1}]$			[%]			$[\mu mol\ L^{-1}]$			$[\mu mol\ L^{-1}]$			[%]	
pre-OMZ	1985	May-Aug	505.1	148.8	123	7.5	0.1	24	184.0	22.4	18	68.0	8.0	18	138.8	132.3	15	888.1	107.5	15	5.3	4.4	15
	1986	May-Aug	714.8	403.2	123	7.5	0.1	24	189.7	31.5	24	67.5	10.4	24	161.6	80.5	17	857.1	140.4	17	6.9	4.7	17
	1987	May-Aug	950.4	198.6	123	7.6	0.1	23	257.7	21.1	24	86.6	6.4	24	122.1	61.9	15	716.0	103.4	15	5.7	3.2	15
	1988	May-Aug	522.1	182.7	123	7.7	0.1	24	227.2	50.8	24	82.1	16.1	24	129.5	43.9	9	909.9	100.5	14	5.5	2.5	9
	1989	May-Aug	347.0	146.0	123	7.5	0.1	24	203.0	45.4	23	73.5	15.3	23	90.2	49.7	12	863.8	178.5	12	3.6	1.8	12
	1990	May-Aug	320.8	111.0	123	7.7	0.3	24	227.7	53.4	24	81.7	21.4	19	133.2	68.9	15	649.4	105.3	15	5.8	3.0	15
	1991	May-Aug	354.2	73.9	123	7.9	0.1	24	278.5	35.7	24	97.1	6.7	24									
	1992	May-Aug	350.8	144.0	123	8.2	0.3	20	244.2	100.1	20	90.1	33.9	20	215.5	212.6	18	707.7	64.5	18	8.0	7.0	18
	1993	May-Aug	374.7	64.6	123	8.7	0.4	20	320.9	57.2	20	114.3	22.5	20	489.1	232.9	20	636.5	117.4	20	14.1	6.5	20
	1994	May-Aug	553.3	305.9	123	8.4	0.4	10	288.8	115.3	10	97.7	31.6	10	96.6	68.9	10	574.5	30.4	10	5.7	3.6	10
	1995	May-Aug	811.1	403.6	123	8.3	0.3	20	293.0	80.2	20	100.9	22.5	20	108.7	33.9	20	537.0	104.5	20	4.5	1.7	20
	1996	May-Aug	742.9	298.3	123	8.5	0.3	20	338.8	43.1	20	111.5	8.4	20	64.9	35.7	20	493.7	42.6	20	2.1	0.9	20
	1997	May-Aug	564.6	244.3	123	8.8	0.3	15	344.8	52.9	15	120.2	22.6	15	137.1	69.0	15	491.2	89.6	15	4.6	2.4	15
	1998	May-Aug	343.7	53.7	123	8.8	0.3	20	309.5	50.4	20	105.8	17.6	20	175.7	75.2	20	487.9	46.9	20	6.1	2.5	20
	1999	May-Aug	454.2	117.4	123	8.7	0.2	20	351.3	63.5	20	124.6	22.5	20	309.3	83.8	20	460.4	49.2	20	8.5	2.2	20
	2000	May-Aug	374.5	108.1	123	8.8	0.3	20	365.5	69.4	20	130.7	26.3	20	246.9	127.3	20	505.4	45.0	20	7.0	3.2	20
	2001	May-Aug	461.7	129.2	123	8.8	0.1	20	338.1	47.8	20	115.7	16.2	20	269.3	120.8	20	500.4	29.5	20	7.8	3.1	20
	2002	May-Aug	824.2	710.5	123	8.5	0.6	20	312.8	113.8	20	109.1	39.6	20	306.0	107.8	20	615.7	181.9	20	11.1	1.8	20
	2003	May-Aug	328.1	130.8	123	8.4	0.4	20	301.9	90.6	20	108.9	28.5	20	248.1	159.3	20	570.7	22.0	20	6.7	3.9	20
	2004	May-Aug	422.3	139.4	123	9.0	0.1	20	364.1	48.1	20	133.2	20.0	20	425.5	67.6	20	517.0	34.5	20	10.4	2.3	20
	2005	May-Aug	487.3	113.6	123	8.9	0.2	20	357.0	57.6	20	127.7	21.7	20	461.0	99.6	19	541.6	33.6	19	12.2	2.4	19
	2006	May-Aug	667.0	346.2	123	8.5	0.2	20	331.3	54.7	20	112.9	13.5	20	237.7	88.7	20	533.3	22.8	20	10.8	4.0	20
	2007	May-Aug	431.5	73.0	123	8.5	0.4	20	340.6	114.3	20	123.4	41.0	20	391.7	178.8	20	591.1	26.2	20	9.9	3.8	20
OMZ	1985	May-Aug	505.1	148.8	123	7.3	0.1	31	78.6	46.9	27	28.9	17.0	27	109.3	50.1	16	827.4	56.6	16	5.0	2.6	16
	1986	May-Aug	714.8	403.2	123	7.4	0.1	36	128.8	53.3	36	44.8	16.7	36	131.6	67.2	31	786.9	123.2	31	6.9	4.4	31
	1987	May-Aug	950.4	198.6	123	7.5	0.1	36	222.6	35.5	36	74.3	10.8	36	134.1	111.1	18	721.6	94.7	18	6.1	3.7	18
	1988	May-Aug	522.1	182.7	123	7.5	0.1	36	117.4	66.1	35	41.7	22.7	35	135.3	73.7	16	806.1	64.9	22	4.2	2.7	16
	1989	May-Aug	347.0	146.0	123	7.3	0.1	36	99.4	58.5	36	35.7	20.7	36	78.9	66.4	19	808.5	136.9	19	2.9	1.5	19
	1990	May-Aug	320.8	111.0	123	7.3	0.1	36	117.5	43.7	36	41.9	15.2	35	111.0	40.6	15	627.2	43.0	15	5.6	2.3	15
	1991	May-Aug	354.2	73.9	123	7.6	0.1	36	168.8	57.5	36	58.3	18.2	36									
	1992	May-Aug	350.8	144.0	123	7.6	0.3	28	156.0	83.0	28	55.8	27.7	28	128.6	133.3	27	671.6	40.5	27	4.2	3.6	27
	1993	May-Aug	374.7	64.6	123	7.7	0.2	28	149.8	42.9	28	52.6	15.2	27	229.9	165.7	28	628.0	119.7	28	5.9	3.7	28
	1994	May-Aug	553.3	305.9	123	8.2	0.3	14	258.3	97.6	14	87.3	25.7	14	53.5	54.6	14	578.7	39.3	14	2.6	2.6	14
	1995	May-Aug	811.1	403.6	123	7.9	0.3	28	239.0	96.9	28	81.0	28.6	28	80.9	38.3	28	555.5	121.2	28	4.0	2.9	28
	1996	May-Aug	742.9	298.3	123	7.9	0.2	28	252.1	66.6	28	82.2	18.0	28	46.7	28.5	28	492.1	38.1	28	1.9	1.2	28
	1997	May-Aug	564.6	244.3	123	8.0	0.3	21	211.0	58.6	21	70.6	14.9	21	89.6	30.0	21	490.4	64.0	21	3.9	2.2	21
	1998	May-Aug	343.7	53.7	123	7.9	0.1	28	180.1	36.3	28	61.1	11.8	28	87.1	48.9	28	480.5	47.3	28	3.6	2.4	28
	1999	May-Aug	454.2	117.4	123	7.9	0.4	27	171.3	61.8	28	59.6	20.3	28	154.3	78.9	28	417.8	31.1	28	6.2	2.8	28
	2000	May-Aug	374.5	108.1	123	7.9	0.3	28	177.9	55.5	28	61.4	19.2	28	126.1	50.5	28	481.7	41.6	28	5.2	1.4	28
	2001	May-Aug	461.7	129.2	123	8.0	0.4	28	190.9	82.4	28	63.6	24.4	28	137.2	68.2	27	488.5	30.8	27	5.1	1.7	27
	2002	May-Aug	824.2	710.5	123	7.9	0.4	28	192.4	71.0	28	66.0	22.2	28	158.5	62.1	28	634.9	170.7	28	6.9	2.2	28
	2003	May-Aug	328.1	130.8	123	7.7	0.2	28	159.8	46.1	28	56.5	14.3	28	165.6	122.6	28	536.4	28.3	28	8.6	4.9	28
	2004	May-Aug	422.3	139.4	123	8.0	0.4	28	188.2	79.5	28	65.7	26.3	28	154.3	97.2	28	507.9	36.7	28	6.7	2.5	28
	2005	May-Aug	487.3	113.6	123	8.0	0.4	28	195.0	58.9	28	67.7	20.1	28	198.3	89.4	28	520.7	33.6	28	8.4	2.7	28
	2006	May-Aug	667.0	346.2	123	7.9	0.3	28	246.8	95.0	28	82.9	28.2	28	168.3	66.6	28	532.9	42.9	28	8.4	3.0	28
	2007	May-Aug	431.5	73.0	123	7.8	0.3	28	161.7	73.2	28	56.7	24.7	28	194.8	102.3	28	563.5	38.7	28	7.6	2.5	28

2. Seasonal averages for selected parameters in the pre-OMZ and OMZ from the monitoring programme.

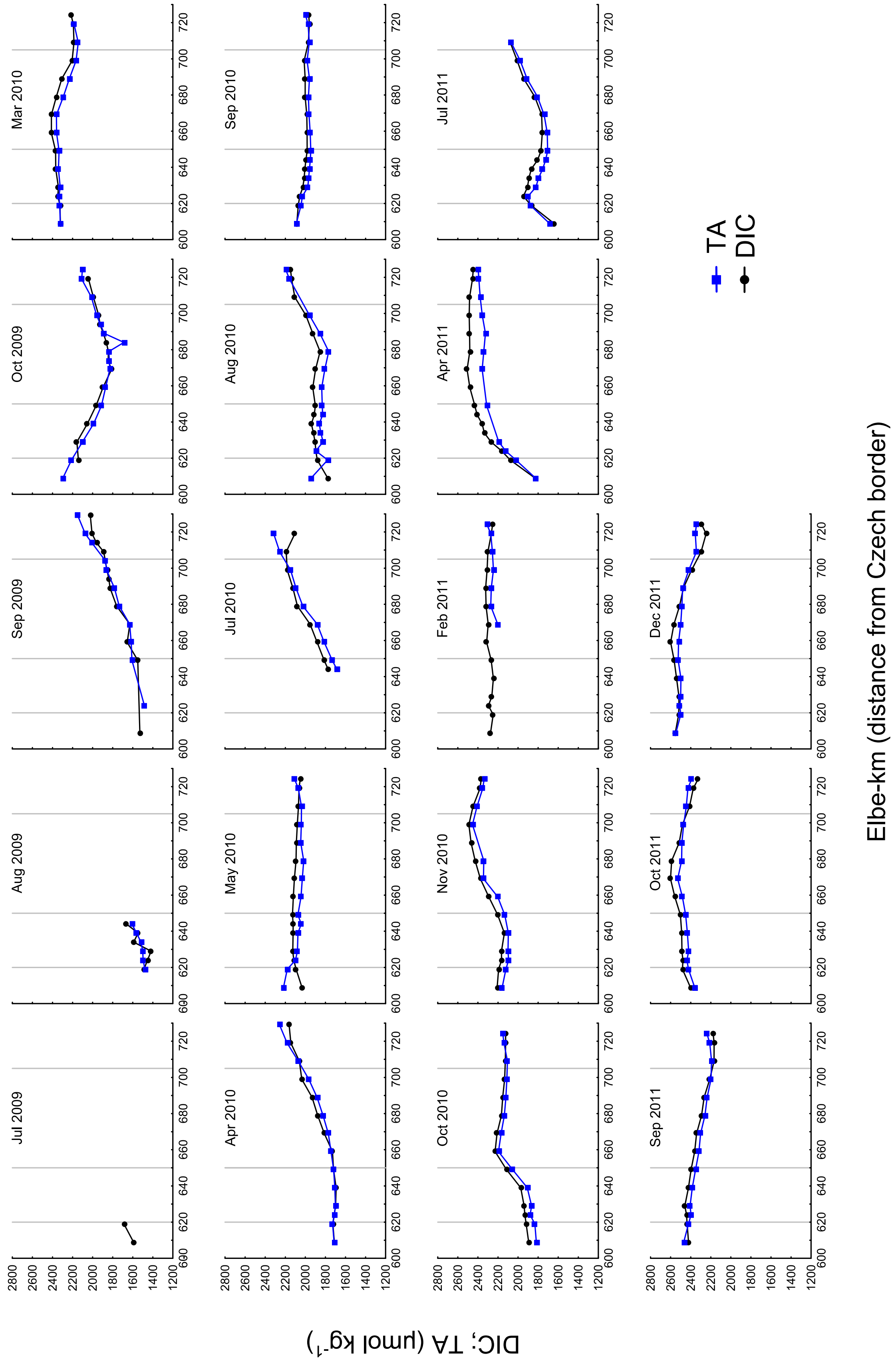
	YEAR	MONTH	DIC concentration			CO_2 concentration			HCO_3^- concentration			CO_3^{2-} concentration			pCO$_2$		
			mean	σ	n	mean	σ	n	mean	σ	n	mean	σ	n	mean	σ	n
			[µmol L^{-1}]			[µmol L^{-1}]			[µmol L^{-1}]			[µmol L^{-1}]			[µatm]		
pre-OMZ	1985	May-Aug	2012.1	152.7	24	171.8	21.7	24	1836.8	146.1	24	3.5	0.6	24	4470.2	520.5	24
	1986	May-Aug															
	1987	May-Aug															
	1988	May-Aug	2133.5	94.5	24	119.9	32.8	24	2007.0	97.3	24	6.6	2.2	24	3143.9	966.8	24
	1989	May-Aug															
	1990	May-Aug	1973.9	265.0	24	110.2	53.8	19	1877.9	284.1	19	10.1	12.8	19	2822.2	1400.0	19
	1991	May-Aug															
	1992	May-Aug	1869.2	186.1	20	35.5	23.0	20	1809.0	180.6	20	24.7	15.0	20	997.2	685.2	20
	1993	May-Aug	1915.0	93.6	20	15.7	16.7	20	1820.7	108.5	20	78.6	51.2	20	405.1	431.7	20
	1994	May-Aug	1690.2	157.2	10												
	1995	May-Aug	1469.5	98.4	20	81.4	56.2	20	1659.6	185.8	20	15.8	18.0	20	653.3	423.9	20
	1996	May-Aug	1544.5	133.6	20	75.7	57.0	20	1606.1	152.3	20	8.3	6.5	20	438.3	396.8	20
	1997	May-Aug	1432.1	178.6	15	69.5	29.0	15	1769.5	80.3	15	9.3	3.6	15	169.9	101.3	15
	1998	May-Aug	1798.4	249.4	15	95.9	36.8	15	2131.3	272.6	15	9.7	3.9	15	293.0	184.2	15
	1999	May-Aug	1798.4	312.0	20	57.9	53.5	20	1834.1	119.0	20	52.2	57.1	20	261.5	124.1	20
	2000	May-Aug	1519.5	320.6	20	85.2	31.2	20	1930.6	304.3	20	11.5	7.7	20	197.4	118.6	20
	2001	May-Aug	1752.6	236.2	20	72.7	33.7	20	2089.7	350.0	20	14.9	7.5	20	193.3	66.3	20
	2002	May-Aug	1985.7	413.5	20	65.6	17.1	20	1872.4	240.2	20	10.3	5.3	20	1110.4	1564.8	20
	2003	May-Aug	1669.3	292.8	20	102.3	23.4	20	1918.1	408.0	20	6.9	5.3	20	760.2	766.9	20
	2004	May-Aug	1494.5	193.8	20	75.3	28.1	20	2041.7	181.2	20	14.5	8.3	20	104.5	46.0	20
	2005	May-Aug	1354.1	258.6	19	66.7	14.0	19	1747.1	116.2	19	9.1	4.2	19	130.5	42.1	19
	2006	May-Aug	1527.8	72.9	20	84.5	35.5	20	1893.3	354.8	20	7.9	2.5	20	359.1	135.0	20
	2007	May-Aug	1869.2	163.1	20	89.5	23.6	20	1748.8	167.6	20	5.9	2.5	20	699.2	983.2	20
OMZ	1985	May-Aug	1966.0	197.8	31	250.6	45.3	31	250.6	45.3	31	2.2	0.8	31	6540.6	1176.3	31
	1986	May-Aug															
	1987	May-Aug															
	1988	May-Aug	2164.7	112.6	36	192.6	47.9	36	192.6	47.9	36	3.8	1.2	36	4900.4	1247.9	36
	1989	May-Aug															
	1990	May-Aug	2017.8	119.6	34	231.4	53.1	33	231.4	53.1	33	2.6	0.8	33	5724.6	1308.2	33
	1991	May-Aug															
	1992	May-Aug	1858.5	143.4	28	147.4	51.6	28	147.4	51.6	28	4.4	3.6	28	3879.0	1443.0	28
	1993	May-Aug	1915.0	106.3	28	109.8	37.8	27	109.8	37.8	27	6.1	3.9	27	2761.7	944.9	27
	1994	May-Aug	1671.1	180.2	14												
	1995	May-Aug	1546.2	129.0	28	54.4	37.0	28	54.4	37.0	28	19.9	15.5	28	1523.9	743.3	28
	1996	May-Aug	1632.5	167.0	28	53.1	29.7	28	53.1	29.7	28	16.2	12.7	28	1435.4	632.5	28
	1997	May-Aug	1772.2	83.9	21	47.2	53.1	21	47.2	53.1	21	78.2	84.3	21	1362.6	810.3	21
	1998	May-Aug	2041.8	130.6	21	56.2	25.4	21	56.2	25.4	21	44.5	40.7	21	1914.5	462.8	21
	1999	May-Aug	1906.0	225.9	28	49.3	25.5	27	49.3	25.5	27	28.4	23.7	27	2105.0	1324.8	27
	2000	May-Aug	1763.3	195.0	28	51.8	46.6	28	51.8	46.6	28	58.5	42.5	28	1885.4	877.7	28
	2001	May-Aug	1825.8	121.9	28	32.5	17.4	28	32.5	17.4	28	72.2	42.3	28	1774.9	1161.9	28
	2002	May-Aug	2022.0	423.8	28	34.4	18.4	28	34.4	18.4	28	67.9	61.9	28	1981.8	1230.9	28
	2003	May-Aug	1819.8	182.3	28	57.5	32.4	28	57.5	32.4	28	42.6	41.0	28	2776.0	921.9	28
	2004	May-Aug	1668.2	129.1	28	36.5	22.4	28	36.5	22.4	28	68.0	42.3	28	1805.6	1216.5	28
	2005	May-Aug	1543.3	138.7	28	33.9	16.2	28	33.9	16.2	28	57.9	43.5	28	1241.8	782.8	28
	2006	May-Aug	1534.3	76.6	28	34.7	17.3	28	34.7	17.3	28	53.2	34.0	28	1595.6	1041.4	28
	2007	May-Aug	1956.6	97.5	28	65.3	30.2	28	65.3	30.2	28	23.4	31.9	28	2583.5	1096.3	28

3. Seasonal averages for Chl-a and resulting ratio of POC:Chl-a at monitoring station Zollenspieker.

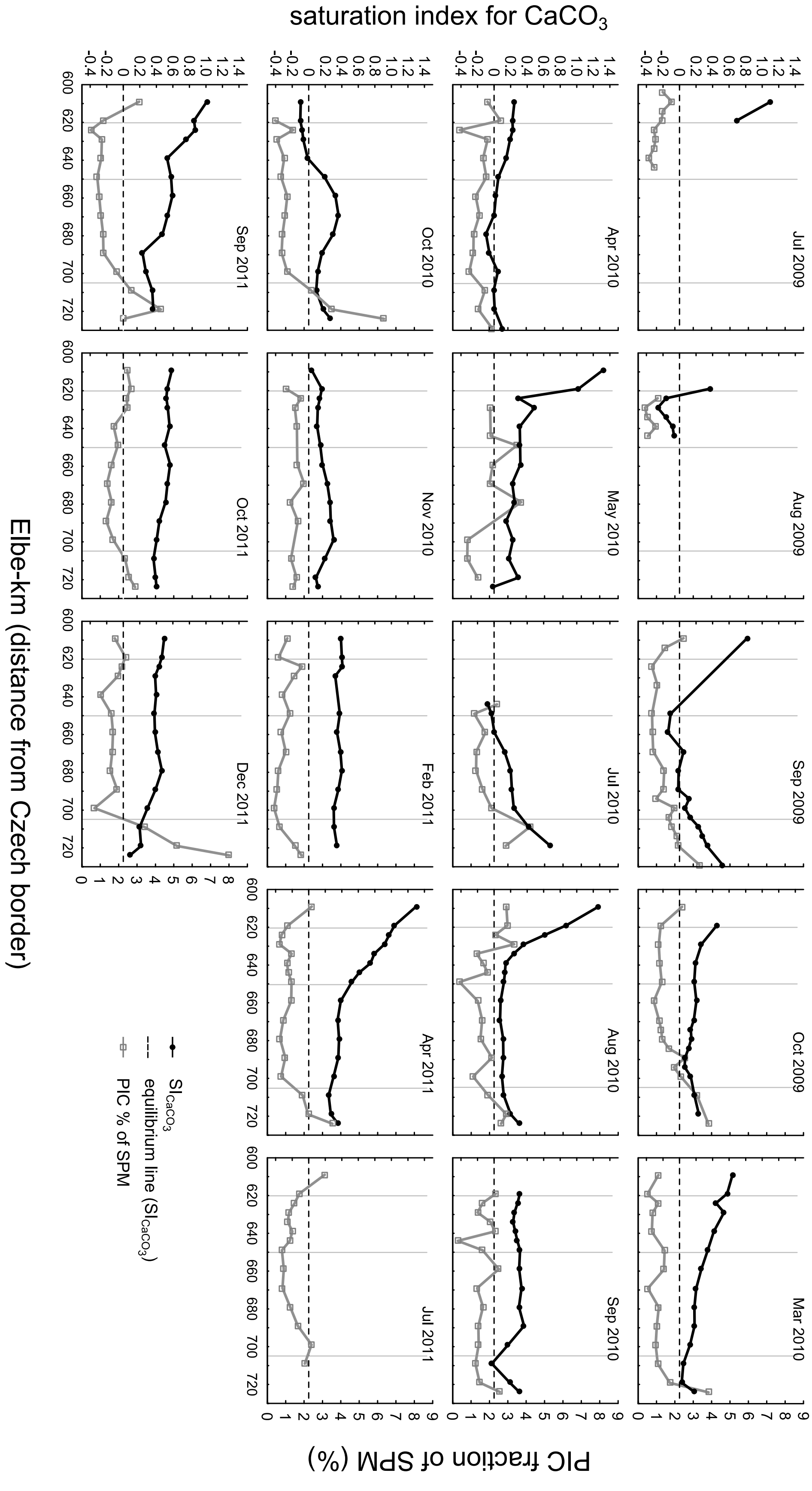
	YEAR	MONTH	Chl-a concentration			POC : Chl-a ratio
			mean	σ	n	
			[µg L^{-1}]			
station Zollenspieker	1993	May-Aug	117.5	73.6	4	14.2
	1994	May-Aug	85.8	56.9	4	22.6
	1995	May-Aug	58.0	17.3	4	25.3
	1996	May-Aug	101.3	57.3	4	15.4
	1997	May-Aug	92.8	40.9	4	11.7
	1998	May-Aug	92.0	63.6	2	17.4
	1999	May-Aug	230.3	50.0	3	
	2000	May-Aug	151.3	20.6	3	17.1
	2001	May-Aug	50.0		1	117.5
	2002	May-Aug	141.1	61.5	8	8.2
	2003	May-Aug	189.5	76.6	4	6.9
	2004	May-Aug	222.5	62.4	4	3.5
	2005	May-Aug	151.9	52.2	7	10.8
	2006	May-Aug	127.0	40.2	9	16.6
	2007	May-Aug	152.5	37.7	4	24.4

D Transect plots of ESTUCARB data

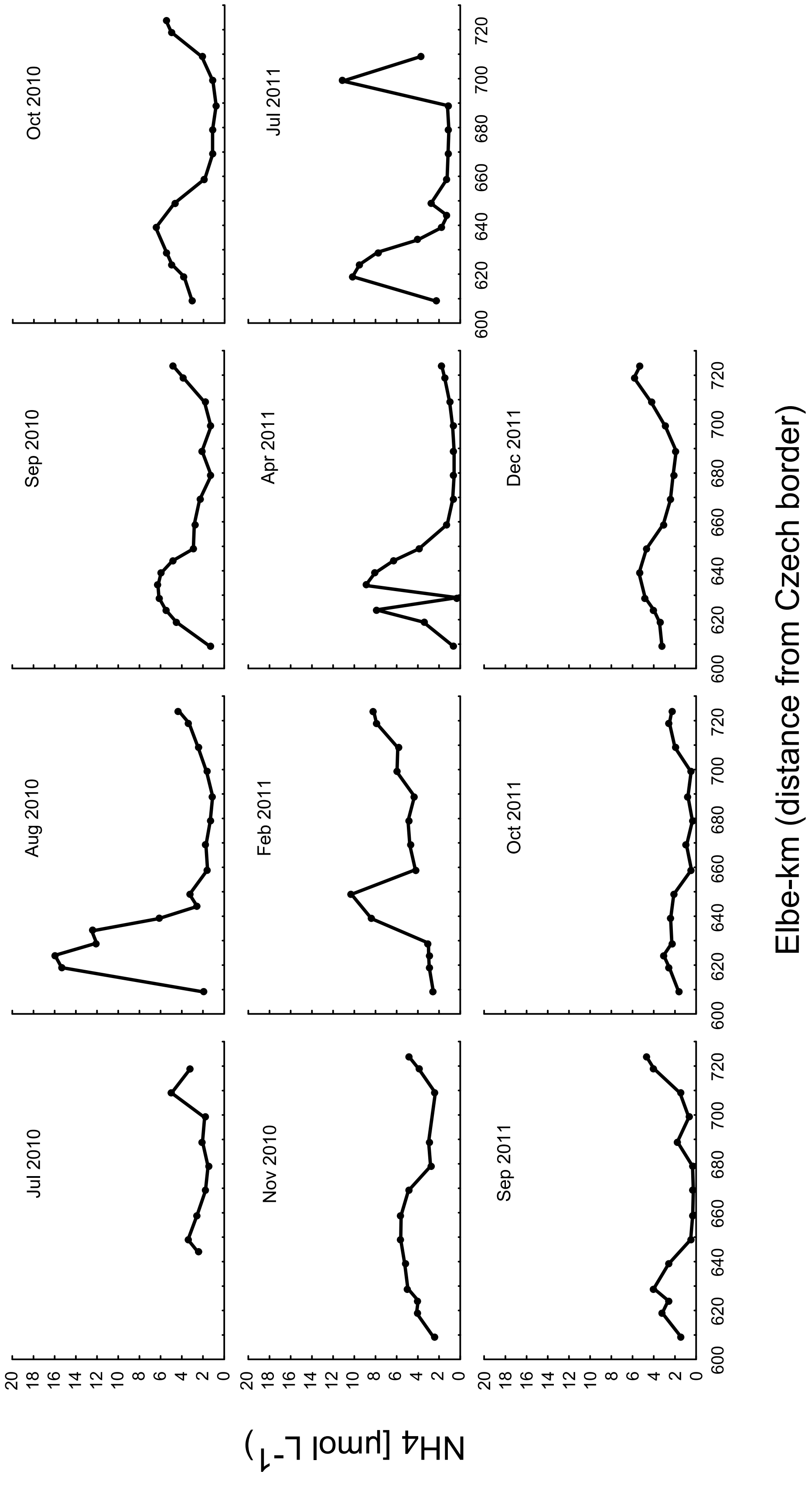
1. Transects data of DIC and TA from ESTUCARB surveys



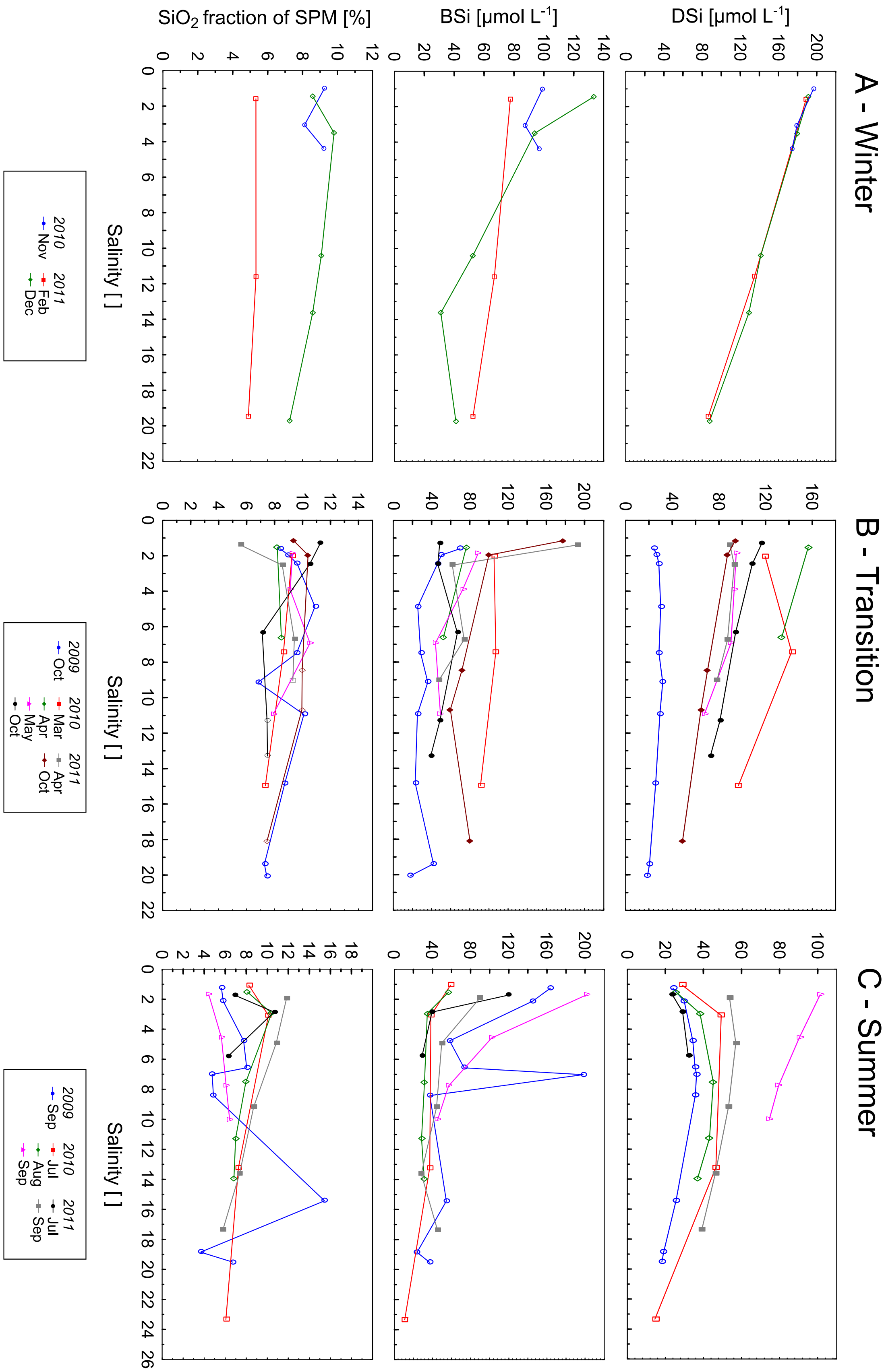
2. Transect data of the saturation index of $CaCO_3$ and the PIC fraction of SPM from ESTUCARB surveys



3. Transect data of the NH_4 from ESTUCARB surveys

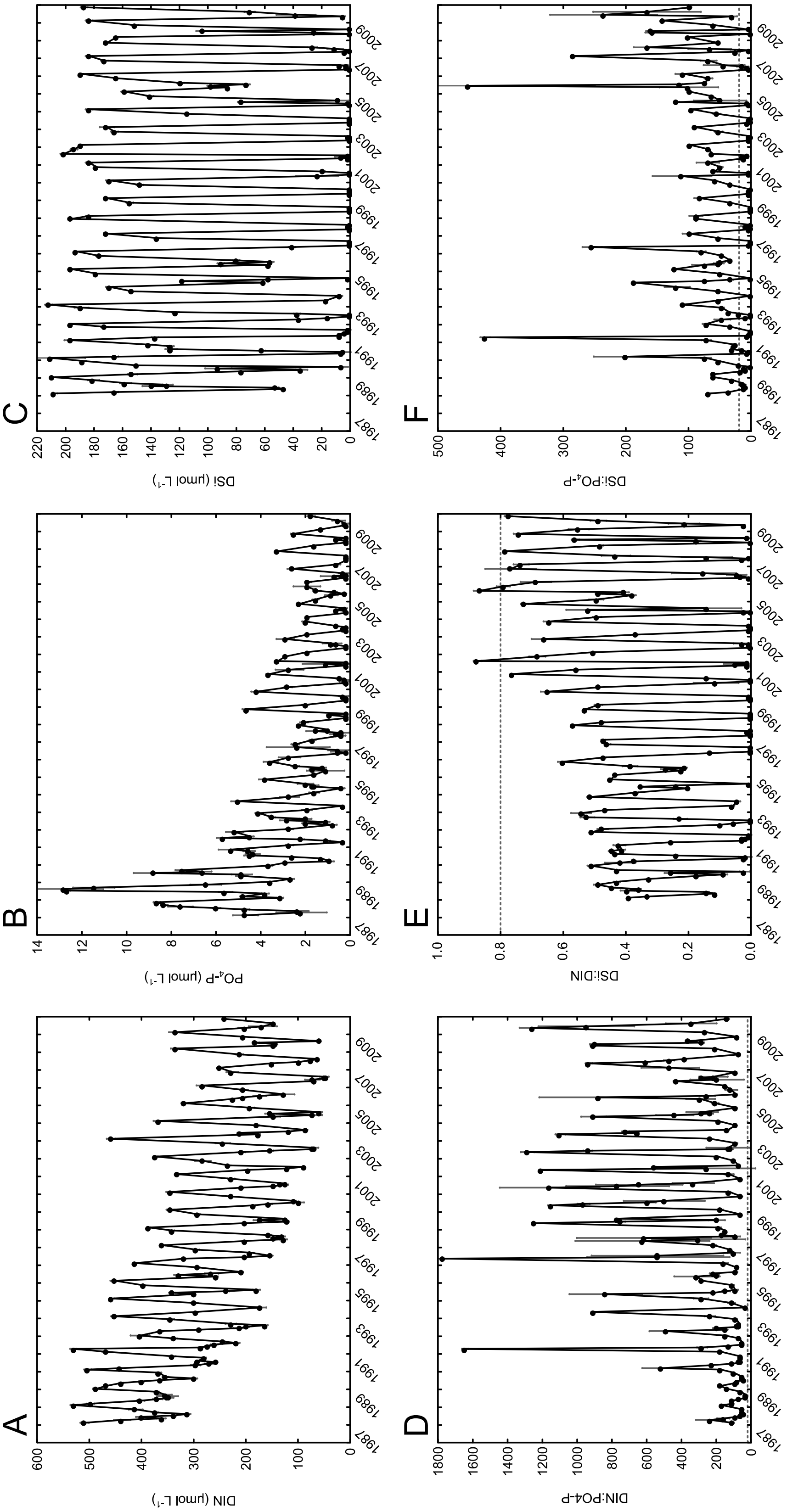


4. Survey data on silica species, grouped by observed situations

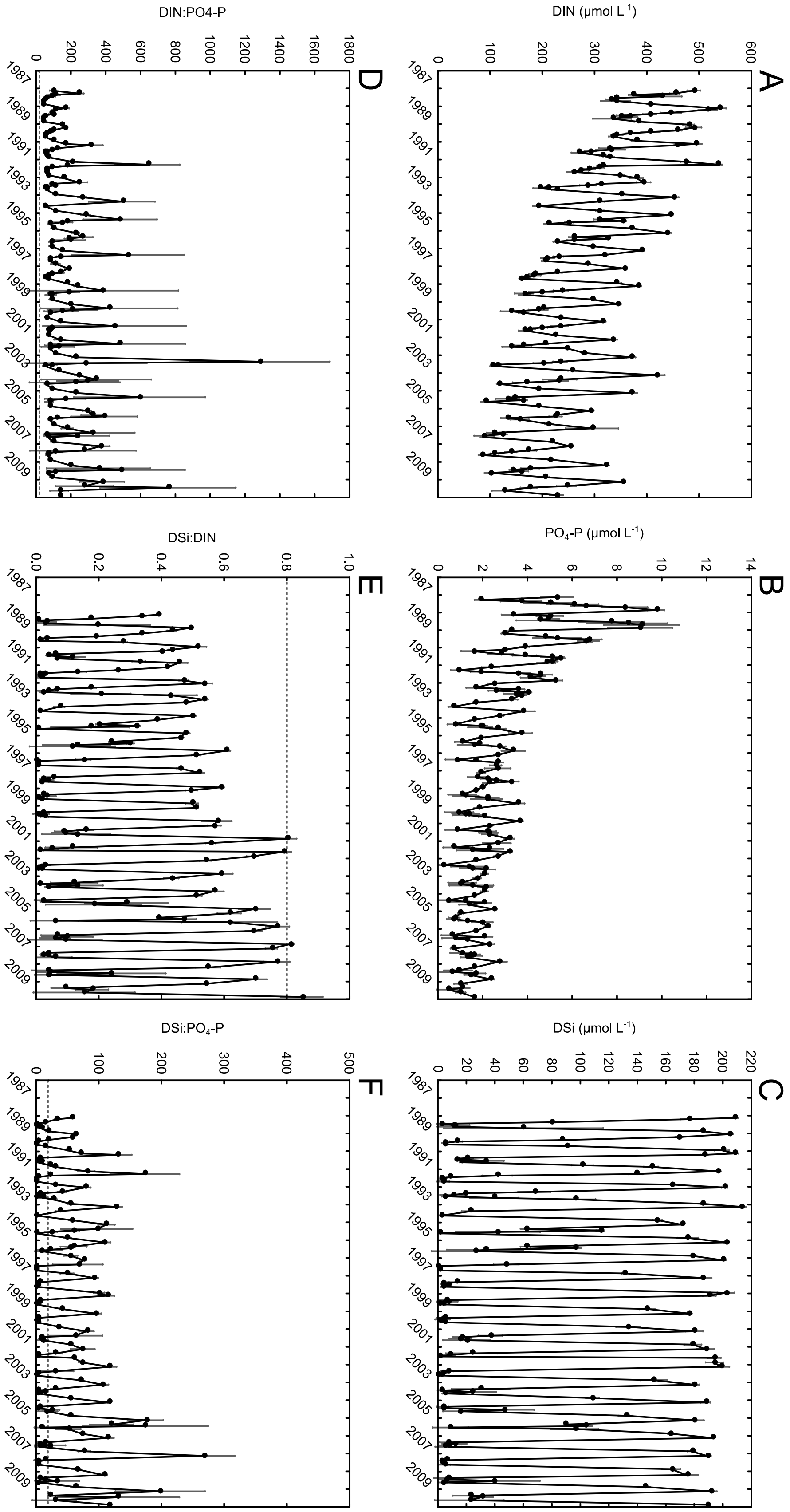


E Plots of historical data on nutrients

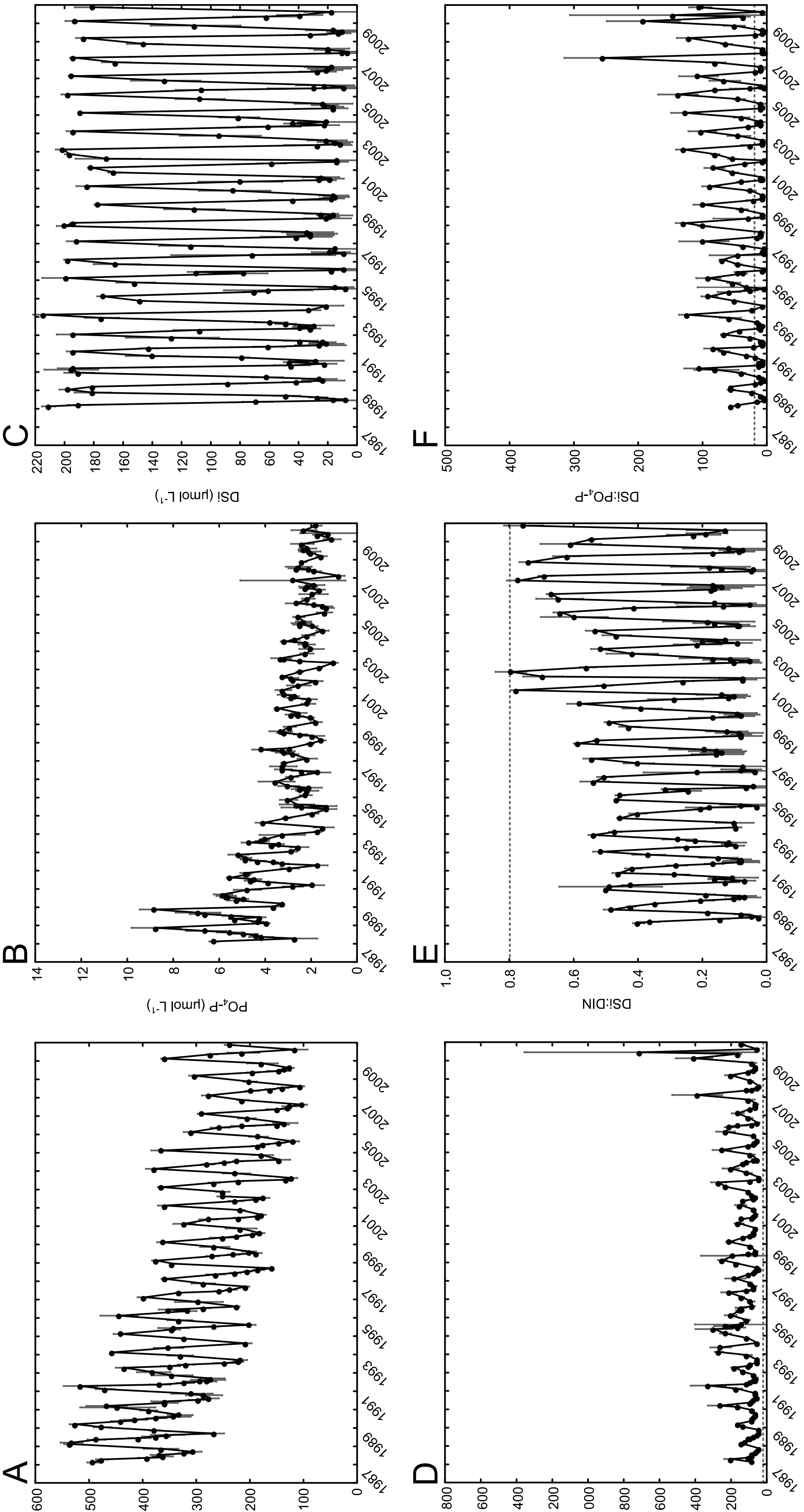
1. Historical development of nutrient concentrations, mean data of the pre-OMZ.



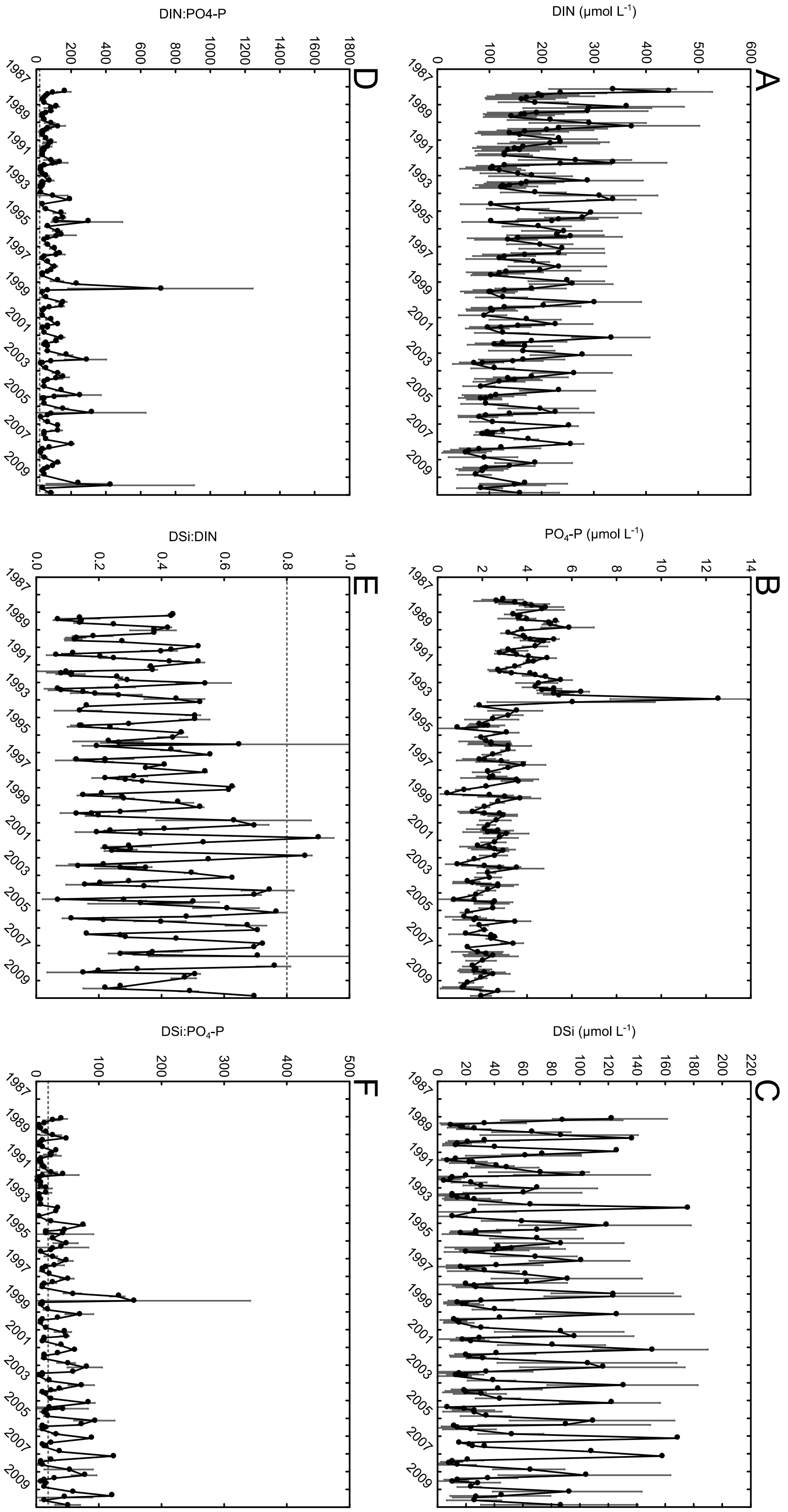
2. Historical development of nutrient concentrations, mean data of the OMZ.



3. Historical development of nutrient concentrations, mean data of the MTZ.



4. Historical development of nutrient concentrations, mean data of the post-MTZ.



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