The Imprint of Anthropogenic Activity versus Natural Variability in the Fjords of Kiel Bight: Evidence *from* Sediments

DISSERTATION

zur Erlangung des Doktorgrades
der Mathematisch-Naturwissenschaftlichen Fakultät
der Christian-Albrechts-Universität zu Kiel

vorgelegt von

Anna Nikulina

Kiel, 2008

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Der Dekan Prof. Dr. Lutz Kipp

To my mama who always knows
the way to cheer me up

SUMMARY

The fjords of Kiel Bight have been inhabited for centuries and thus exposed to long-term anthropogenic influence. The fjords have restricted water exchange as reflected in periodical hypoxia. Overall, the fjords have a high buffer capacity accumulating organic matter and metals in sediments. The sediments contribute to the supply of recycled nutrients for phytoplankton, but they also may be a source of toxic compounds for benthic organisms. The deoxygenation of sediments leads to a diminution of the benthic fauna and a breakdown of the food chain. Therefore, the sediments reflect the state of the local marine system and present a valuable tool for the assessment of the environment, at present time and for the past.

The objective of this study was to determine whether anthropogenic activity over the last century has left the traces in the sediments of Kiel and Flensburg Fjords where sewage discharge, shipyards, and harbours are of major importance. Further questions addressed were how the anthropogenic impact superimposes over the natural variations in Kiel and Flensburg Fjords, and what the main factors controlling the accumulation of pollutants are. To investigate these questions, surface and core sediments were analysed to recover the spatial and temporal distribution and accumulation of organic matter and trace metals in the fjords.

This study revealed that the type of sediments and depositional regime are the main controls of organic matter and trace metals distribution in the fjords. Secondary factors are the gradient of primary productivity, from the inner to the outer fjord, as well as oxygenation of near-bottom water and sediments. Anthropogenic influences appear to be less significant than these factors.

The accumulation of organic matter and trace metals occurs in the inner areas of the fjords. The reasons for that is the depositional regime in the inner fjords where the most intense anthropogenic discharge occurs. Anthropogenic activity does not affect the outer fjords. The only source of exception is the influence of coastal protection measures on cliff erosion and the sediment supply in depositional areas.

In general, the conditions in the fjords are mesothrophic to slightly eutrophic, except for the highly eutrophied innermost Flensburg Fjord. The remediation of the fjords after the cessation of enhanced nutrient input takes more than several decades. Anoxic conditions

promote denitrification, which favours the loss of nitrogen, but the input of nutrients remains high because of redeposition and resuspension of sediments under the shallow water depth.

High concentrations of metals, such as copper and zinc are associated with zones of sediment accumulation in the inner fjords. Only tin, derived from antifouling paints, exhibits extremely high concentrations and only in harbours. Concentrations of lead in the sediments had decreased during the last decades due to the ban on gasoline lead additives.

The enrichment of metals and organic matter for the last 70 years in a core from the outer Kiel Fjord is not clearly apparent due to changes in sedimentation rate and the observed upward coarsening of the sediments. Elevated fluxes of trace metals fell during the 1930s, when the harbours and shipyards flourished in Kiel Fjord. An increase of sewage discharges in the 1940-1970s is recorded in the core as the accumulation of organic carbon and nitrogen. The downcore distribution of redox-sensitive metals showed that no drastic changes in the oxygenation of near bottom water and sediments have occurred in the outer Kiel Fjord, in contrast to the inner fjord.

In spite of expanding anthropogenic activity, its influence is not so pronounced as originally expected and what influence is seen is veiled by natural variability. However, anthropogenic effects are significant for the input of nutrients and acceleration of the natural eutrophication which finally lead to seasonal near-bottom anoxia.

Zusammenfassung

Die Förden der Kieler Bucht werden seit Jahrhunderten bewohnt und durch die Menschen langfristig beeinflusst. Der eingeschränkte Wasseraustausch der Förden mit der Kieler Bucht verursacht regelmäßigen Sauerstoffmangel. Die Förden sind wichtige Puffersysteme und akkumulieren organische und anorganische Verbindungen in den Sedimenten. Die Sedimente setzen wiederum Nährstoffe für das Phytoplankton durch den Abbau der organischen Substanz and außerdem Schadstoffe frei, die die Bodenfauna beeinträchtigen. Die Sauerstoffzehrung in den Sedimenten kann zur Abnahme der Bodenfauna führen und die schließlich Nahrungskette zerstören. Dadurch können die Sedimente den Zustand der ganzen Ökosysteme widerspiegeln, und sind sie deshalb gute Indikatoren des Ökosystems.

Das Ziel dieser Arbeit ist zu prüfen, ob die anthropogen Aktivität während der letzte Jahrhunderte ihre Spüren in den Sedimenten der Kieler and Flensburger Förde hinterlassen hat, besonders weil die Abwässer, Werften und der Havenbetrieb dort von wichtiger Bedeutung sind. Die weitere Frage ist, wie sich der anthropogene Einfluss und die natürlichen Variationen überlagern, und welche Faktoren die räumliche und zeitliche Verteilung und Akkumulation von organischen Stoffen und Spurenmetallen kontrollieren.

Die Ergebnisse dieser Untersuchung haben gezeigt dass der Sedimenttyp und das Sedimentationsregime die Verteilung von organischen Substanz und Metallen in den Förden regulieren. Der Gradient der Primärproduktion von der Innen- zum Außenförde sowie die Sauerstoffanreicherung im bodennahen Wasser und im Sediment sind von untergeordneter Bedeutung. Die anthropogen bedingte Belastung folgt diesen Faktoren ebenfalls.

Die Akkumulation der organischen Substanzen und Spurenmetalle tritt in den innern Abschnitten der Förden auf, wo die Sedimentation vornehmlich stattfindet, und die anthropogene Belastung konzentriert ist. Die anthropogene Aktivität wirkt auf die Außenförden nicht in diesem Maße ein. Die einzige Ausnahme sind die Küstenschutzmaßnahmen. Sie reduzieren die Kliffserosion und ändern dadurch die Zufuhr von Sedimentationsmaterial in die Ablagerungsräume.

Die Stoffumsatz charakterisiert die Förden als mesotroph bis leicht eutroph mit Ausnahme der stark eutrophen inneren Flensburger Förde. Die Sanierung der Förden nach der Reduktion der Nährstoffbelastung braucht voraussichtlich noch mehrere Jahrzehnte. Der

Sauerstoffmangel fördert die Denitrifizierung und den Stickstoffverlust, aber die Nährstoffzufuhr ist immer noch hoch wegen der Umlagerung aus den geringen Wassertiefen.

Erhöhte Spurenmetallkonzentrationen von Kupfer und Zink sind mit den Sedimentationsräumen in der Innenförden verbunden. Zinn, das von den Antifoulingfarben herstammt ist, führt zu überaus hohe Gehalten in den Hafensedimenten. Dagegen haben die Bleigehalte in letzen Dekaden abgenommen, vor allem wegen des Verbots von Blei-Additiven in Benzin.

Die Anreicherung von Spurenmetallen und organischer Substanz während der letzten 70 Jahre ist in einem Kern aus der äußeren Kieler Förde nicht eindeutig wegen der Schwankungen in der Sedimentationsrate und einem deutlichen Trend zur Sedimentvergröberung in jüngster Zeit. Die erhöhten Spurmetallenflüsse während der dreißiger Jahre fielen in eine Zeit, als der Hafen und Schiffbau florierten. Der Anstieg der Abwässerbelastung zwischen 1940 und 1970 ist ganz deutlich in der Sedimentären Überlieferung an akkumulierte organischen Kohlenstoff und Stickstoff zu sehen. Die Verteilung von redoxsensitiven Metallen im Kern hat gezeigt dass es zu keinem langzeitigen Sauerstoffdefizit in der äußeren Kieler Förde während der letzten Jahrhunderte gekommen ist, im Gegensatz zur Innenförde.

Obwohl die anthropogene Aktivität zugenommen hat, ist der Einfluss des Menschen nicht ausgeprägt und wird durch die natürliche Variabilität in den Förden verschleiert. Nur die Nährstoffbelastung, die zu einer Verstärkung der natürlichen Eutrophierung führt, ist ein schwerwiegender anthropogener Effekt in der Kieler und Flensburger Förde.

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CONTENT

INTRODUCTION

The Baltic Sea has been exposed to anthropogenic activity for centuries and at the same time it is highly vulnerable due to the restricted water exchange, long water residence time and overall weak circulation in this marginal sea. The most affected areas in the Baltic Sea are coastal zones where natural variability and anthropogenic activity interfere. Coastal areas themselves present a complex system with gradients in chemical composition, complex hydrodynamic processes, low salinity and oxygen content (Bonsdorf et al., 2002). The high productivity and restricted water exchange lead to natural eutrophication and hypoxia of near-bottom waters. Moreover, nutrients, metals and persistent organic compounds are discharged here. Hence, the coastal areas are also sink of pollutants.

The anthropogenic influence on the Baltic Sea have become significant since the Medieval, but the impact was in the frames of the capacity of the system to regenerate through self cleaning of water and sediments. Only at the end of nineteenth century, the establishment of industry and the growth of towns enhanced the impact to a level, which could not be overcome by the ecosystem. The shallow, partially enclosed Kiel and Flensburg Fjords in the south-western Baltic Sea are a good example for such long-term interaction of humans and nature.

The city of Kiel expanded rapidly in the 19th century with the foundation of the shipyards. The growth of city and the development of agriculture in the surroundings increased the amount of wastewater entering Kiel Fjord (Gerlach, 1996). The elevated levels of nutrients promoted a strong eutrophication with increasing anoxia in the near-bottom waters. Similar processes occurred in Flensburg Fjord (Rheinheimer, 1970). Before the Second World War, the establishment of Navy harbours in Kiel Fjord and intensive activity of shipyards introduced the amount of metals such as copper and zinc. Later, in the 1960s, antifouling tin-based paints and anticorrosive coatings containing lead and cadmium were widely used in civil and marine harbours (Biselli et al., 2000; Förstner, 1980). The sewage discharges and combustion of fossil fuel also contribute to the metal pollution (Förstner, 1980; Schneider, 1987).

The intensified eutrophication and deterioration of environments in Kiel and Flensburg Fjords in the 1940s concerned the inhabitants and authorities. This resulted in the construction

and putting into operation a central sewage plant with an outlet in the outer Kiel Fjord in 1972, and the intensifying of wastewater treatment in Flensburg Fjord. These measures led to a partial improvement of environmental conditions in both fjords.

The discharged nutrients, particulate organic matter and metals, are accumulated in the sediments. Therefore, sediments reflect the integrated characteristic of the marine environment at present time and in the past (Salomons and Förstner, 1984; Harff, 1997). The concentrations of metals in sediments are not dangerous in themselves, but through the bio-accumulation, they can become toxic for benthic organisms and finally find their way into the food chain (Rheinheimer, 1998). Besides the toxicity of sediments, declining bottom water oxygen has negative effects on benthic fauna too (Rosenberg et al., 1991; Nilsson and Rosenberg, 2000). The sediments also play an important role in the supplying of recycled nutrients to the phytoplankton that is more pronounced in the shallow fjords than in the open sea (Zeitschel, 1980). The study of undisturbed sediments may reveal the processes of distribution, accumulation, and remediation in the system in a retrospective.

This study has an objective to look whether an anthropogenic activity was really significant for the functioning of Kiel and Flensburg Fjords, and whether it has left the footprints in the sediments of the fjords. By that, the natural settings and variability of the fjords were taken into account. The study was performed at different time scale using surface sediments deposited during the last five to ten years, and a sediment core covering the past couple of hundred years. The main factors influencing the distribution of organic matter and metals were discussed, and the role and degree of anthropogenic impact was estimated.

Chapter 1 considers the surface sediments of Kiel Fjord in order to discover a current trend in distribution of organic matter, as a measure of primary production and eutrophication, and trace metals sourced from shipyards and traffic. The sampling of surface sediments was performed on seasonal scale. It makes possible to trace how the development of a spring bloom is reflected in the sediment composition. According to the depositional regime, several zones were distinguished by the metal pollution. To answer the question what is more important for benthic organisms – anthropogenic pollution or natural fluctuations in salinity and oxygen, benthic foraminiferal distribution and species composition were studied.

Chapter 2 concerns the monitoring of changes in the sediment composition on a decadal scale. In Flensburg Fjord, the surface sediments were investigated at the same locations as in 1972, that was before the significant decrease of sewage discharges. The relationships

between organic matter and trace metals accumulation, hydrography and sediment properties allow to discern the processes governing the remediation of still eutrophied Flensburg Fjord.

To trace the environmental changes in the region of Kiel Bight on a multidecadal scale, a sediment core from the outer Kiel Fjord was examined (**Chapter 3 and 4**). The chronology of sediments and the determination of sedimentation rates is an integral part of the core studies. The dating of recent sediments is, however, complicated due to the application of different methods. **Chapter 3** describes and discusses the chronological model developed for this core. The distribution of organic matter, trace and redox-sensitive metals together with grain-size composition as referred to this scale (**Chapter 4**) allowed to attribute the variations of sediment components to certain anthropogenic activities or natural events in the fjord. The changes in organic matter reflect the trophic status of the area. Trace metals mirror the pollution history, whereas redox-sensitive metals help to reconstruct the near-bottom water and sediment oxygenation.

The principal results of this study are summarized in **Conclusions**.

Chapter 1

Foraminiferal response to environmental changes in Kiel Fjord, SW Baltic Sea

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Abstract

The living benthic foraminiferal assemblages in Kiel Fjord (SW Baltic Sea) were investigated in the years 2005 and 2006. The faunal studies were accomplished by geochemical analyses of surface sediments. In general, sediment pollution by copper, zinc, tin and lead is assessed as moderate in comparison with levels reported from other areas of the Baltic Sea. However, the inner Kiel Fjord is still exposed to a high load of metals and organic matter due to enhanced accumulation of fine-grained sediments in conjunction with potential pollution sources as shipyards, harbours and intensive traffic. The results of our survey show that the dominant environmental forcing of benthic foraminifera is nutrients availability coupled with human impact. A comparison with faunal data from the 1960s reveals apparent changes in species composition and population densities. The stress-tolerant species *Ammonia beccarii* invaded Kiel Fjord. *Ammotium cassis* had disappeared that reflects apparently the changes in salinity over the last 10 years. These changes in foraminiferal community and a significant increase of test abnormalities indicate an intensified environmental stress since the 1960s.

1.1 Introduction

The previous studies in the Kiel Bight only gave a very short description of foraminiferal distribution, though they were started in the 19th century (Möbius, 1888). Ecological observations of foraminifera were initiated by Rhumbler (1935), who used rather descriptive

than quantitative methods of investigation. Next, Rottgardt (1952) distinguished three different foraminiferal assemblages in the Baltic Sea, which are distributed according to the salinity pattern: marine, brackish-marine (fjords and shallow areas of the Kiel Bight), and brackish faunas. A detailed taxonomical and ecological overview on benthic foraminifera in the south-western Baltic Sea was provided by Lutze (1965), who found out that temperature and salinity rather than substrate were the main ecological controls on foraminiferal distribution in this area. Vice versa, Wefer (1976) observed that the abundances of foraminifera in sediments off Bokniseck (open Kiel Bight) were regulated by substrate features, hydrodynamics and oxygen content of the bottom water. Foraminiferal food preferences in the open Kiel Bight were described by Schönfeld and Numberger (2007b), who reported two reproduction events of *Elphidium excavatum clavatum* following the spring bloom and suggested the "bloom-feeding" strategy of this species.

The benthic foraminiferal distribution in Kiel Fjord has been left out of sight, with the exception of 4 stations investigated by Lutze in 1962-1963, which were taken as reference points for our study. Over the 20th century, Kiel Fjord has experienced a strong anthropogenic impact. For monitoring purposes, the foraminiferal response to environmental changes attracts attention under the aspect of rising ecological problems.

A number of studies addressed the foraminiferal reactions to changing environmental parameters as salinity, temperature, oxygen, food availability, pH, (e.g. Bradshaw, 1957, 1961; Boltovskoy et al., 1991; Moodley and Hess, 1992; Alve and Murray 1999; Stouff et al., 1999ab; Gustafsson and Nordberg 2001; Le Cadre and Debenay, 2003), contamination by trace metals (Ellison et al., 1986; Sharifi et al., 1991; Alve, 1991; Alve and Olsgardt, 1999; Yanko et al., 1998; Debenay et al., 2001) and sewage effluents (e.g. Watkins, 1961; Schafer, 1973; Tomas et al., 2000). A decrease of population density, reproduction capability, enhanced mortality, and increasing frequency of test abnormalities were observed under the high trace metal or organic matter levels (Schafer, 1973; Samir and El Din, 2001; Bergin et al., 2006; Burone et al., 2006; Ernst et al., 2006; Di Leonardo et al., 2007). On the other hand, it was shown that population density of foraminifera may increase in vicinity of sewage outfalls (Watkins, 1961; Tomas et al., 2000). Culture experiments revealed that *A. beccarii* produces abnormal chambers at 10-20 $\mu g\ l^{-1}$ of copper in seawater (Sharifi et al., 1991; Le Cadre and Debenay, 2006) and dies at concentrations exceeding 200 $\mu g\ l^{-1}$ (Le Cadre and Debenay, 2006). Therefore, foraminifera appear to be a rather sensitive tool for the monitoring of pollution, though should be used with caution, because their distribution is

determined by numerous environmental variables (Alve and Olsgardt, 1999; Stouff et al., 1999a,b; Le Cadre and Debenay, 2006).

The aim of this study was (1) to describe the distribution of living (stained) benthic foraminifera in Kiel Fjord, (2) to investigate the distribution pattern of main geochemical parameters of surface sediments, (3) to outline the level of pollution by trace metals, and (4) to assess the foraminiferal response to environmental changes during the past decades.

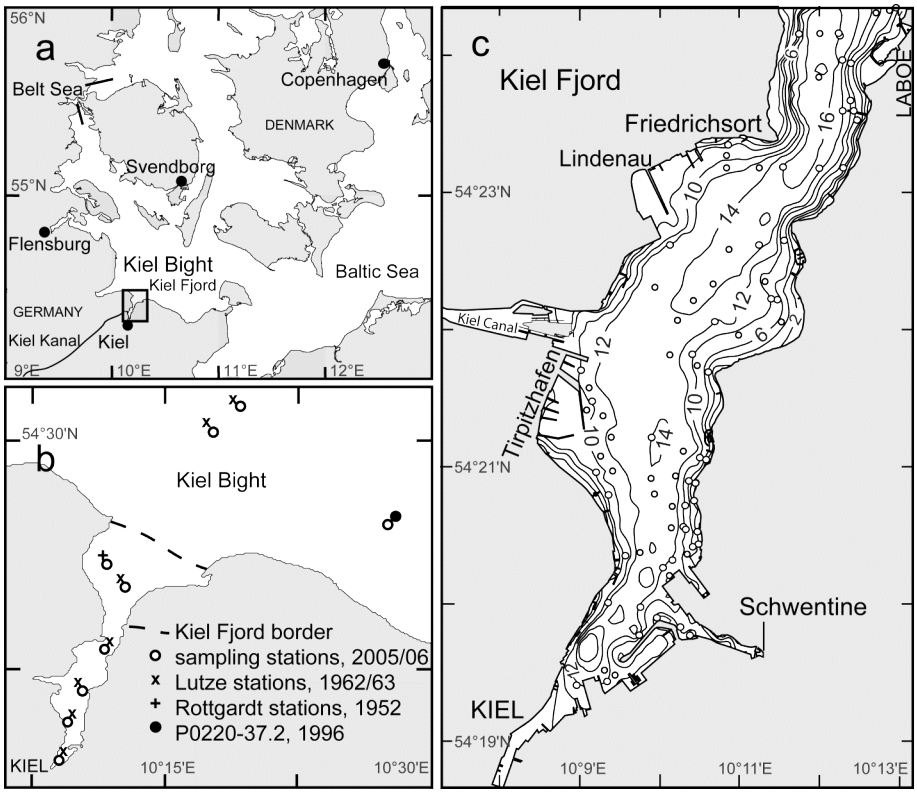

FIGURE 1.1. Study area: (**a**) SW Baltic Sea, (**b**) outer Kiel fjord, (**c**) inner Kiel Fjord with bathymetry (m). Circles indicate here the sampling stations. For station description see Appendix 1.1.

1.2 STUDY AREA

Kiel Fjord is a 9.5 km long, N-S extending and narrow inlet of southwestern Kiel Bight (54°19'– 54°30'N; 10°06'–10°22'E). The Friedrichsort Sound divides the fjord into a southern, inner fjord with width to 250 m, and a northern, outer fjord, which expands up to 7.5 km and passes into Kiel Bight (Fig. 1.1). The inner Kiel Fjord is mostly 10 to 12 m deep. A system of up to 16 m deep channels connects the inner with the outer fjord. The outer fjord itself is more than 20 m deep.

As the entire Kiel Fjord is relatively shallow and isolated, its hydrographical characteristics

weakly depend on the salt-rich inflow water from the Belt Sea. The only river discharging fresh water into Kiel Fjord is the Schwentine.

The water masses of the inner fjord are homogenously mixed, except during summer. Then, surface water has a temperature up to 16°C and a salinity of about 14 units. The underlying deep water has a temperature of about 12°C and a salinity of up to 21 units. In winter, the temperature does not change significantly with depth and may decrease to 2°C. The salinity is constant with depth as well (Schwarzer and Themann, 2003).

Coastal and near-shore erosion of Pleistocene till is the most important source of sediment in this area. Lag sediments with coarse sand and gravel prevail in the shallow coastal areas. They pass into sandy muds and silts in the deeper basins. In the innermost fjord, dark organic-rich muds are encountered even in shallow areas. Sand veneers are found in the Friedrichsort Sound due to relatively strong currents between inner and outer fjord (Schwarzer and Themann, 2003).

Kiel Fjord has seen a strong anthropogenic impact for the last 70 years by town infrastructure, shipyards, military and sport harbours and the intense traffic through Kiel Canal. The shipbuilding industry has led to a substantial trace metal pollution in places. Dredging to keep the seaways clear, and the ship traffic itself have caused a strong disturbance of surface sediments.

1.2.1 Previous pollution surveys

Despite the long-term anthropogenic load in study area, reports on the early history of pollution of Kiel Fjord are rare. Recently, the monitoring of metals concentration at a few stations in Kiel Bight by the Institute for Marine Research, Warnemünde (IOW) indicates no significant temporal trend in trace metal content for 1998-2000 with respect to the observed high interannual variability (e. g. Nausch et al., 2003b, Pohl et al., 2005). Kiel Fjord itself is considered by LANU (The Regional Environmental Protection Agency of the Bundesland Schleswig-Holstein) as one of the most important local hot spots of cadmium, lead, copper, and zinc contamination in the coastal waters of Schleswig-Holstein. In the year 2000 for instance, the concentrations of Cu, Zn and Pb in sediment fraction <20 μm were 82, 300 and 130 μg g^{-1} in the inner fjord correspondingly (Haarich et al., 2003), whereas in outer fjord Cu, Zn and Pb content was estimated to 30, 210 and 60 μg g^{-1} respectively (LANU archive: Ostseemonitoring Programme). No clear temporal trend of metals concentrations in 1995-

2004 was observed in sediments of Kiel Fjord. Extremely high concentrations of organically bound tin (407-2556 µg TBT-Sn kg^{-1}) were found in the fjord sediments; they are supposed to cause the aberrant changes in reproduction system of the periwinkle (LANU, 2001b). High concentrations of Cu and Zn were found in fish (Senocak, 1995) and mussels (ter Jung, 1992) from the inner Kiel Fjord. But the organisms in the outer fjord showed the lowest metals content for all Schleswig-Holstein waters.

Kiel Fjord has been affected by eutrophication induced by a high load of nutrient and organic carbon from the city and surrounding area (Gerlach, 1984). Herein, the nutrient concentrations and primary production showed a southward increase to the inner fjord (Schiewer and Gocke, 1995). The construction of a central treatment plant (Bülk, Klärwerk) in 1972 has reduced the input of nitrogen and phosphorus significantly (Kallmeyer, 1997, Rheinheimer, 1998), but the deep-water oxygenation improved not early than in the 1990s (Gerlach, 1996; Haarich et al., 2003; LANU, 2003). Nevertheless, oxygen deficiency may occur at specific weather conditions in the fjord regularly in late summer due to stable water stratification (Gerlach, 1990).

1.3 Material and methods

1.3.1 Sampling

This study is based on 89 surface sediment samples collected at 4.5-18.1 m water depth between December 2005 and May 2006 on seven daily cruises with RV Polarfuchs. The samples were retrieved with a Rumohr corer with a plastic tube of 55 mm inner diameter and a Van-Veen Grab. The latter was used when sandy sediments were encountered. The Ruhmor corer was deployed three times at each station in order to avoid errors associated with spatial patchiness. The uppermost centimeter of the sediment was removed on each deployment with a spoon, and with cut-off syringes when a Van-Veen Grab was used. The sediment was placed into a glass vial, thoroughly mixed, and subsamples for geochemical analyses were taken from this mixture at first. The remaining sample was transferred to a PVC vial, and preserved and stained with a solution of 2 g Rose Bengal per litre ethanol in order to mark foraminifers living at the time of sampling (Murray and Bowser, 2000).

1.3.2 Hydrographic measurements

The salinity, temperature and dissolved oxygen content of the overlying water in the Rumohr corer tube was measured on board with Oxi- and Conductivity meters (WTW Oxi323/325 and LF320). As the measurements were made within minutes after retrieval, and air temperatures were not substantially higher than the water temperatures, we consider these values as representative for the near-bottom water. In the Schwentine river mouth, at three stations CTD-profiles were done with WTW Profiline 197 TS in 1-m intervals to locate the boundary between riverine fresh water and higher- saline fjord waters.

1.3.3 Geochemical analysis

Subsamples for geochemical analysis were freeze-dried and powdered in an agate mortar. Measurements of C_{org}, total carbon (TC) and total nitrogen (TN) were performed with a Carlo Erba NA-1500-CNS analyzer at IFM-GEOMAR with accuracy better than ±1.5 %. Chlorophyll *a* and phaeopigments were determined after acetone extraction with a Turner TD-700 Fluorometer at IFM-GEOMAR. The precision of the method is ±10 %. Biogenic silica (opal) measurements were done according to an automated leaching method for the analysis of SiO_2 in sediments and particulate matter described by Müller and Schneider (1993) using a Skalar 6000 photometer with precision ±1 %. For trace metal analyses, the sediment samples were digested in an HNO_3-HF-$HClO_4$-HCl mixture solution. The solution was diluted and measurements were performed with an AGILENT 7500cs ICP-MS at the Institute of Geosciences, University of Kiel (Garbe-Schönberg, 1993). Blanks and the international standard MAG-1 were repeatedly analyzed together with the samples in order to evaluate the precision and accuracy of the measurements. The accuracy of analytical results as estimated from replicate standard measurements was better than ±1.5 %.

1.3.4 Foraminiferal studies

The sub-samples for foraminiferal analysis were stored in a fridge for two weeks to effect a sufficient staining with Rose Bengal. The samples were first passed through a 2000 µm screen in order to remove molluscs' shells or pebbles, and then gently washed through a 63-µm sieve. Sediments of the Baltic Sea have a high content of organic detritus. After drying, the detritus creates a film layer on the sample, which has to be disintegrated before picking (Lutze, 1965). In order to achieve a separation of the organic detritus, the 63—2000 µm size fraction was transferred into a cylinder with some tap water and left for a while. Then the

supernatant water was poured through a filter paper to collect the suspended organic debris. During drying, the organic flocks stuck to the filter paper and foraminiferal tests could be easily brushed off (Lehmann and Röttger, 1997). The 63—2000 µm and >2000 µm fractions were dried at 60°C, weighed, and splitted. Well-stained foraminifers that were considered as living at the time of sampling were picked from respective aliquots, sorted at species level, mounted in Plummer cell slides and counted. Both normal and abnormal tests were counted separately. The standing stock was expressed as number of specimens per 10 cm^3 of sediment. The main species were photographed with Cam Scan Scanning Electronic Microscope at the Institute of Geosciences, Kiel University.

1.4 Results and discussion

1.4.1 Hydrography

The temperature and salinity of near-bottom water in Kiel Fjord showed a pronounced seasonality. Temperature decreased from 8°C on average in December 2005 to 2°C in February, and raised again to 7°C in May 2006. In December 2005, the near-bottom water showed the highest salinity with 23.2 units and minimum values of 16.5 units in May.

In the Schwentine river mouth, the boundary layer between riverine fresh water and saline fjord water was encountered at approximately 1 m depth in February. With an average discharge of 7.3 $m^3\ s^{-1}$ (Schulz, 2000), the Schwentine substantially freshens the waters of the inner fjord.

The oxygen concentration mostly exceeded 400 µmol l^{-1} and decreased slightly only in the deep basins. The saturation levels varied from 58 % to 100 %. As such, a sincere oxygen deficiency in the near-bottom waters of Kiel Fjord was not recognized.

The oxygen content of near-surface sediments was measured with a Unisense microelectrode (Revsbech, 1989) in a short core taken from the inner fjord at the beginning of December 2005. The overlying water had oxygen saturation 71 %; the sediments were muddy-sand. At 1 mm sediment depth, the oxygen saturation was still more than 50 %, and a zero oxygen level was encountered at 3.5 mm. As compared with a usual 2 to 5 cm thick oxic layer in normal marine settings, the oxygenated surface layer in this core was quite thin.

1.4.2 Organic carbon and C:N ratio

The organic carbon content in the surface sediments ranged from 1% in Friedrichsort Sound to 7.8 % in muddy sediments of the inner fjord (Fig. 1.2, Appendix 2.1), and it is negatively correlated with the sand content (r=0.793, n=89, Appendix 2.5). Though the changes in mean C_{org} values through the year were not substantial, we observed an increased C_{org} content associated with the spring bloom in February and March (Graf et al., 1982, Wasmund et al., 2005). Generally, the C_{org} content was higher than reported by Leipe et al. (1998) for the open Mecklenburg and Kiel Bights (5 % for the fine fraction).

The mean C:N ratio depicts a substantial input of organic matter from the hinterland (Fig. 1.2). The C:N ratio increases southwards from 4 in the outer fjord to 15 in the inner fjord, which is in the range of values for the southern Baltic Sea (Pertillä et al., 2003). Seasonally, the C:N ratio changed not significantly but has the lower values in February-March that probably mirrors the accumulation of fresh detritus characterized by low C:N values of 5.6 to 7 (Graf et al., 1982).

1.4.3 Biogenic silica

Biogenic silica (opal) content in surface sediments of Kiel Fjord was higher in spring as compared to December (0.1 wt.% to 8 wt.%), and showed a maximum in the inner fjord (Fig. 1.2). The maximum of diatom biomass and biogenic silica flux to the sea floor was recorded in early April in the SW Baltic Sea (Wasmund et al., 2005, 2006). Apparently, the increase of opal in sediments of Kiel fjord in February reflected the spring bloom of diatoms in late February and March. Surface sediment biogenic silica content clearly reflects spatial differences in surface water primary productivity, and at low depths and under relatively high sedimentation rates, it could refer to seasonal changes of primary productivity (Rathburn et al., 2001; Bernardez et al., 2006). At the same time, Schwentine river might also be a source of opal for the inner fjord sediments because in the suspension of its water the opal values exceeded 15 wt. % owing to freshwater diatoms. As the maximum of biogenic silica in the inner fjord sediments was not found in the vicinity of Schwentine mouth, we consider the primary productivity in the fjord as the main cause of seasonal and spatial variations in biogenic silica concentrations.

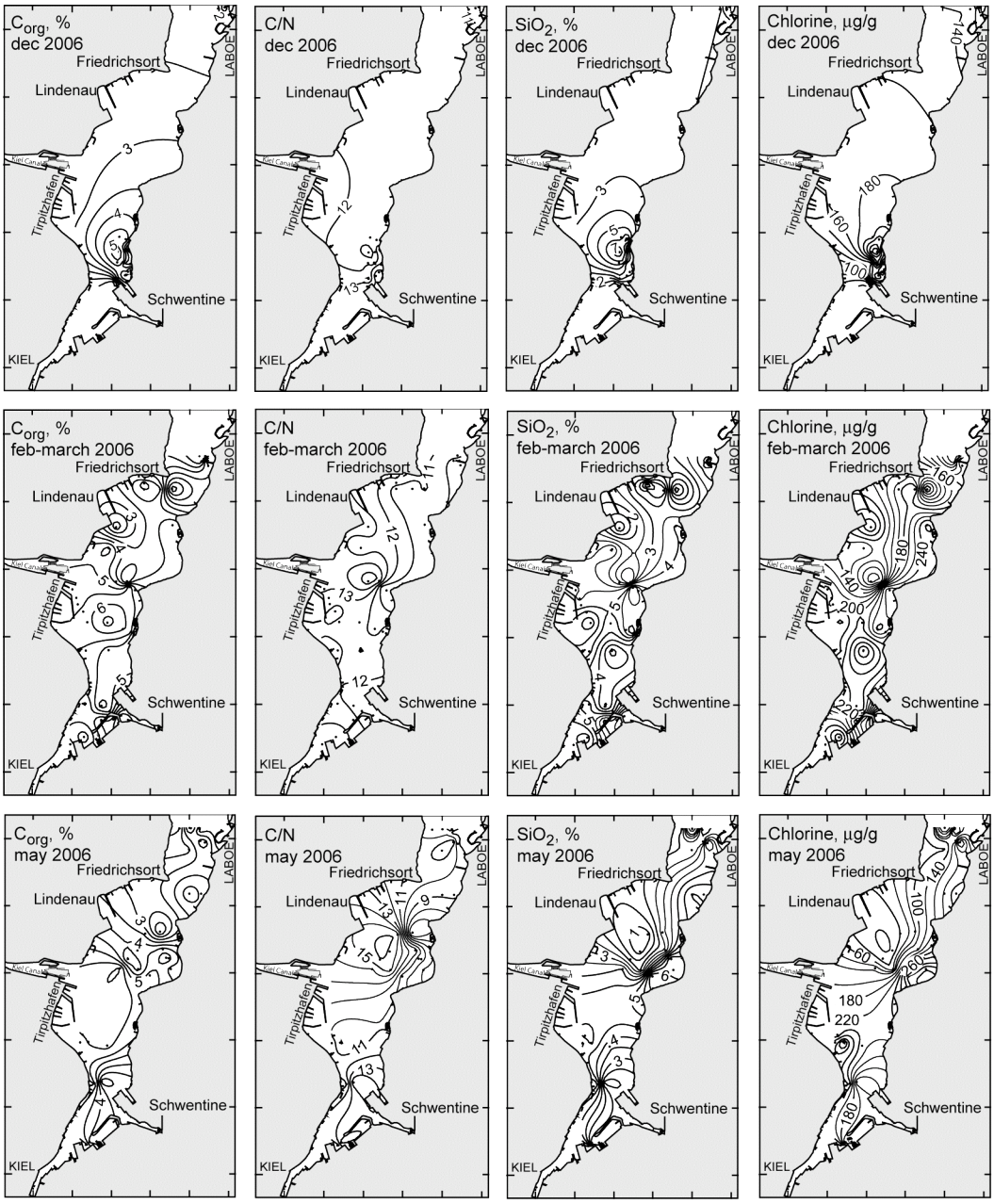

FIGURE 1.2. Seasonal distribution of organic carbon (%), C:N ratio, biogenic silica (wt.%) and chlorine (note: µg g^{-1} instead of ng g^{-1} by other authors) in Kiel Fjord. Sampling stations are shown here as black dots (see Appendix 2.1).

1.4.4. Chlorine and phaeopigments

Chlorine concentrations in surface sediments varied from 7000 to 600 000 ng g^{-1} dry sediment (Fig. 1.2). The values were generally higher in March than in December. The spatial distribution of chlorine concentrations was irregular. In December and February, the highest concentrations were observed in the innermost fjord, while in March and May the chlorine levels were elevated towards the outer fjord. As chlorine content is a proxy for productivity (Harris et al., 1996), this pattern seems to depend on the development of the spring bloom, sequential growth of different algal groups and changes in hydrographical conditions (Graf et al., 1982) as well as terrigenous input. The ratio of chlorophyll *a* to phaeopigments generally increased from February to May, which infers a flux of fresh organic matter to the sea floor (Greiser and Faubel, 1988; Reuss et al., 2005).

1.4.5 Trace metals pollution

The concentrations of copper, zinc, tin and lead in surface sediments of Kiel Fjord show a high variability (Table 1.1). With a sample thickness of one centimeter and presumable sedimentation rate in Kiel Fjord about 1 mm per year (Erlenkeuser et al., 1979, Balzer et al., 1987), one has to keep in mind that the trace metal concentrations present an average over the last 10 years. The concentrations are significantly positively correlated with the C_{org} contents and negatively correlated with the sand content (Table 1.1, Appendix 2.5). The correlation suggests that most of the trace metals are bound to organic matter, that they accumulate in muddy sediments, and that they are winnowed from of sandy sediments. In fact, elevated metal levels were recorded in the innermost and central fjord (Fig. 1.3, Appendix 2.1). Moreover, exceptionally high metal concentrations were found in surface sediments close to Lindenau shipyards at Friedrichsort, and at Tirpitzhafen Navy base.

Table 1.1. Mean (range) concentrations of trace metals (µg g^{-1}) in the surface sediments of Kiel Fjord and their correlation with organic carbon and sand content, number of samples n=53.

Metal	Concentration, µg g^{-1} mean (range)	Correlation coefficient (r) with C_{org}, %	Correlation coefficient (r) with sand content, %
Cu	62.3 (1.79 - 162)	0.726	-0.581
Zn	185 (11.2 - 434)	0.770	-0.621
Sn	4.97 (0.24 – 18.4)	0.549	-0.404
Pb	118 (6.81 - 260)	0.675 (n=52)	-0.579 (n=52)

The long history of human impact in Kiel Fjord suggests that metal concentrations are substantially higher than the regional background (HELCOM, 1993). Except in the innermost fjord, trace metal concentrations are well in the range of values reported from elsewhere in Kiel Bight for the years 1999 to 2004 (Leipe et al., 1998; Haarich et al., 2003; Pohl et al., 2005).

Nonetheless, a trace metal study from a sediment core from Kiel Bight demonstrated that the metal concentrations systematically increased since the 1830s and reached maximum in the 1950s-1970s (Erlenkeuser et al., 1974). The youngest Cu, Zn and Pb contents were estimated as 70, 230 and 80 μg g^{-1} respectively. We found the average values of 62, 185 and 118 μg g^{-1} Cu, Zn and Pb. As such, no significant changes in heavy metal concentrations took place during last 40 years. To the north of Kiel Canal, we found even lower concentrations than in the 1960s presumably referring to environmental protection measures, in particular, a banning of lead additives in gasoline during the last decades. This may explain the today's low concentrations of lead in Kiel Fjord keeping in mind that its main sources in the Baltic region are atmospheric input and surface runoff (Brügmann, 1996). Tin concentrations were not reported in early investigations. In Kiel Fjord the concentration of tin in the sediment fraction <2000 μm (LANU archive: Ostseemonitoring Programme) was 24 μg g^{-1} in 2004 whereas in other fjords and bays of Kiel Bight it varied from 4 to 17 μg g^{-1}. Our measurements range from 0.2 to 18 μg g^{-1} and confirm the elevated levels in the inner fjord. This can be related to sport harbours and shipyards despite the recent restriction of tin-containing antifouling paints (IMO, 2005).

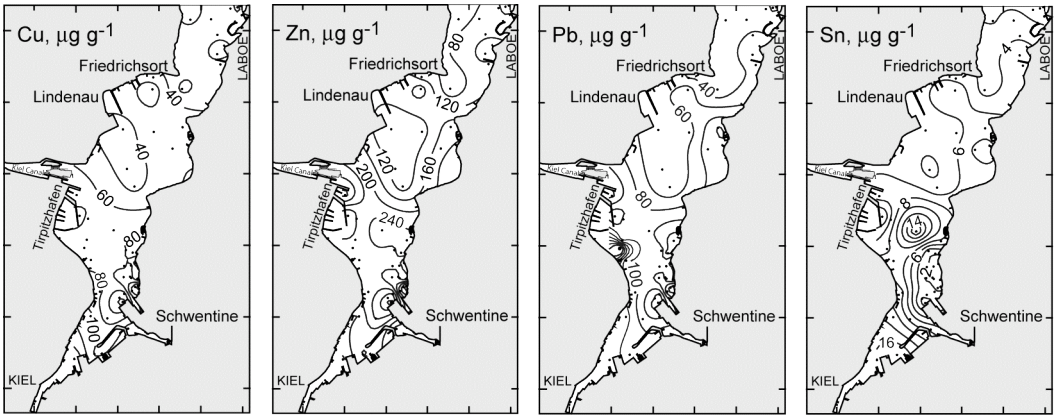

FIGURE 1.3. Trace metals (Cu, Zn, Pb, Sn) distribution in surface sediments of Kiel Fjord.

1.4.6 Foraminiferal population density and species composition

The foraminiferal population density in Kiel Fjord ranged from 3 to 4895 ind./10cm^3, on average 200 to 400 ind./10cm^3 (Appendix 3.1; 3.3). The living benthic foraminiferal communities were dominated by *Ammonia beccarii* (52 % on average) and subspecies of *Elphidium excavatum* (together 44 % on average). *Elphidium incertum, Elphidium albiumbilicatum* and *Elphidium gerthi* were common (5.3 and 3 % on average). *Ammotium cassis, Reophax dentaliniformis regularis, Elphidium williamsoni*, and *Elphidium gunteri* were rare (maximal 2 %). The stations with predominance of *A. beccarii* generally have a lower abundance of *E. excavatum excavatum* and vice versa. We do not recognize any physical, biological or chemical parameter that would explain this spatial change in dominance. But we cannot entirely rule out, that these species occupy different ecological niches. As such, we can presume a substitution of these species. *E. incertum* and *E. albiumbilicatum* co-occurred with moderate abundances to both sides of Friedrichsort Sound. *E. gerthi* and *E. williamsoni* were recorded in shallow and near-shore samples (Fig. 1.4).

The arenaceous species *R. dentaliniformis regularis* and *A. cassis* were recorded only sporadically in our samples. The situation was quite different in the 1960s, for instance, Lutze (1965) reported *A. cassis* with up to 2 % of the living fauna in Kiel Fjord (Fig. 1.5b). We re-examined 4 of Lutze's samples curated at the Institute of Geosciences (University of Kiel) and revisited his stations in February 2006 (Fig. 1.5a, c). The samples taken in 2006 revealed a 5 to 445-fold increase of foraminiferal population densities as compared to the 1960s. We also did not find *A. cassis*. This species was common elsewhere in Kiel Bight until the mid 1990s (Schönfeld and Numberger, 2007a). Our results infer that *A. cassis* has apparently disappeared in the 2000s from Kiel Fjord too, and that it has been presumably replaced by *A. beccarii*.

Positive correlations of population density with biogenic silica (r=0.475; n=21) and chlorophyll *a* (r=0.600; n=21) were found for samples taken in December. This underpins the strong relationship of the availability of food, in particular diatoms, and foraminiferal population density (Altenbach, 1992; Schönfeld and Numberger, 2007b).

In order to reveal the stress response capability of the benthic foraminiferal fauna, we calculated the ratio of the tolerant species *A. beccarii* to the specialized *E. excavatum* (A:E Index), firstly described by Sen Gupta et al. (1996) as a proxy of hypoxia. The highest A:E

values were found in the central part of Kiel Fjord. They coincide with high C_{org} (7 %) and tin concentrations (18 µg g^{-1}).

In the inner part of Kiel fjord, we recorded high frequencies of test abnormalities (up to 17 %). This is considerably higher than the typical value of 1 % under natural undisturbed conditions (Alve, 1991; Yanko et al., 1999). The majority of abnormal tests were observed in *A. beccarii.* A high number of test abnormalities preferentially occurred in the inner fjord, where the highest trace metal levels were marked.

FIGURE 1.4. Foraminiferal relative abundances and occurrence of arenaceous species in Kiel Fjord, here X indicates the stations revisited after Lutze (1965).

E. albiumbilicatum has been described as a typical shallow-water species (Lutze, 1965). Here, it inhabits the transitional area of Friedrichsort Sound where sandy sediments prevailed. The high water turbulences seemingly prevent the accumulation of organic matter bound trace metals here. On the other hand, it was suggested that species living in turbulent waters develop spines (Boltovskoy et al., 1991). Tests of *E. albiumbilicatum* possess the numerous pustules in apertural and umbilical areas making the test surface rough and enabling this species to withstand the higher water turbulences in this sound.

The species composition of dead assemblages at stations revisited after Lutze was the same as the living assemblages. Lutze (1965) reported that thanatocoenoses in the 1960s also resembled the living communities. In 2006, the living:dead ratios varied from 0.3 in the inner part to 3.2 in the outer Kiel Fjord, which is on average 5 times higher, than it was in the 1960s (Appendix 3.2).

The remarkable increase in population densities as compared to previous studies in Kiel Fjord arises a question: why living foraminifera became so abundant since the 1960s, especially in the presence of trace metals? According to Yanko et al. (1999), some foraminifera might respond positively when the environmental impact is continuous. On the other hand, there are no data on trace metal concentrations in Kiel Fjord from the 1960s and therefore one cannot conclude that trace metals are the only factor that is responsible for the observed changes. Moreover, after the setup of sewage treatment plants and strict environmental protective politics in the 1990s (e.g. Danish Action Plan (I); HELCOM), which caused a decrease of industrial discharges and agricultural load, a general decrease of nutrient inputs and stabilization of oxygen levels in the SW Baltic took place (Nausch et al., 2003a, 2004). Despite the slight decline in nutrient levels since the mid 1990s, an increase of primary production by roughly 40 % during the past 30 years has been suggested for the western Baltic Sea (Wassmann, 1990; Schönfeld and Numberger, 2007a). Provided this is applicable for Kiel Fjord too, even a doubling in primary production can not explain a 67-fold increase in foraminiferal population densities from 23 ind./10cm^3 on average in 1963 to 1582 ind./10cm^3 on average in 2005 and 2006.

Re-examination of Lutze's material

Differences in results shown at Fig. 1.5a and 5b may refer to discrepancy in taxonomy, sampling seasons, size fractions (> 63μm in this study and >100 μm by G.-F. Lutze) and study of the whole samples (in 2006) vs. concentrates (1960s). Fig. 1.5b shows *E. excavatum* subspecies, lumped together in 1960s, as the dominant elements of the living fauna. *E. incertum* had higher abundances, whereas *A. cassis* and *R. dentaliniformis* were rare. Lutze did not report *E. albiumbilicatum* and *E. gerthi*, which we found in his samples. Apparently he recognized both species as variants of *E. excavatum*. Lutze's sampling campaign started in spring 1962 and continued until fall 1963. Regarding the difference in sample numbering (342 vs. 239), it well might be that sampling in the 1960s also comprised several seasons per year, as we did in the current study. Concerning the differences in size fractions, it was shown that

there were no living specimens smaller than 80 µm observed in the western Baltic Sea (Schönfeld and Numberger, 2007a: p.85). Therefore it is unlikely that G.-F. Lutze missed or washed away a significant proportion of the fauna. Most residues of Lutze' samples contained a very few or no living specimens whereas the respective flotation concentrates were very rich. Therefore, even if Lutze examined only concentrates but not the whole samples, his results on the population density would not differ by two orders of magnitude to the results we obtained in our 2006 survey. Thus, we finally consider the differences in methods in this study comparing to the 1960s to be of minor influence on the final result.

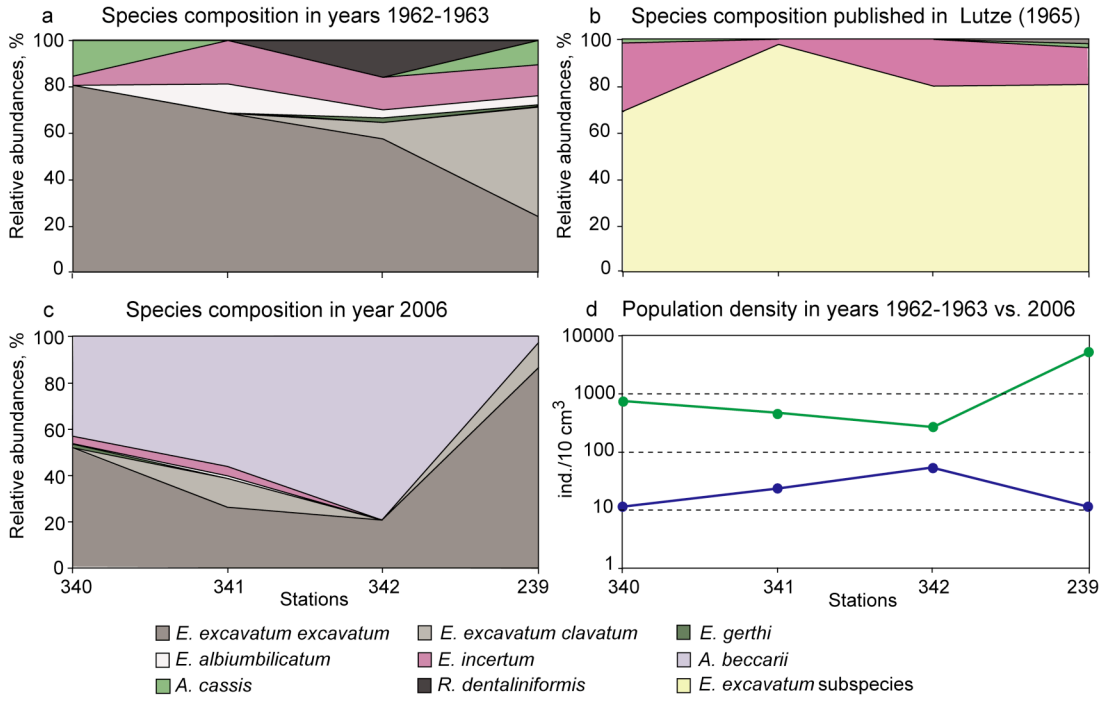

FIGURE 1.5. The species composition in re-examined samples from Lutze collection taken in 1962-1963 (a), described by Lutze himself (b) and at stations revisited after Lutze in February 2006 (c). Figure (d) shows the changes in population density (log scale) since the 1960s (Lutze, 1965).

INVASION AND OPPORTUNISTIC BEHAVIOUR OF *AMMONIA BECCARII*

A. beccarii has an ubiquitous distribution in Kiel Fjord whereas both *E. excavatum* subspecies show avoidance of the central fjord with silty sediments enriched in C_{org} and tin. In the North Sea, Sharifi (1991) described *E. excavatum* as more frequent than *A. beccarii* in sediments polluted by Zn. According to Alve (1995), abundant and geographically widespread species are to be considered as most tolerant to environmental pollution. *A. beccarii* is commonly frequent in coastal and paralic environments (e.g. Stouff et al., 1999ab).

Taking all this into account, we consider that the main reason why *A. beccarii* is so abundant in Kiel Fjord, its opportunistic behaviour and high potential to survive under high input of nutrients and trace metal concentrations.

Disappearance of *Ammotium cassis*

Sample PO220-37-2 taken in the Kiel Bight in 1996 had 90 % of *A. cassis,* but did not contain any calcareous foraminifera. It may well be, that due to bad storage conditions, all the calcareous tests were dissolved in this sample. For this reason, we revisited station PO220-37-2 in December 2005 but we did not find living *A. cassis* any more. Lutze (1965) stated that foraminifera in the Baltic Sea are mainly salinity and temperature dependant, and that *A. cassis* is adapted to a strong halocline between surface and deep waters in Kiel Bight. Schönfeld and Numberger (2007a) suggested cyclic changes of *A. cassis* abundances depending on saltwater inbursts in the Kiel Bight and high salinity contrasts between surface and deep waters. As we observed only isolated specimens in some places, the inner Kiel Fjord is currently almost unpopulated by *A. cassis.* This pattern may be due to the fact that the inner fjord is shallower, more closed and less saline than the open Kiel Bight. As such, the deep boundary layer, which is a necessary condition for nutrition of *A. cassis*, cannot establish in Kiel Fjord (Olsson, 1976).

It is conceivable that with faunal change from very large *A. cassis* to much smaller *A. beccarii*, the total biomass might decrease. However, as the population density increased significantly since the 1960s, we may assume that biomass today is higher than it was in the 1960s and 1990s, when *Ammotium cassis* was abundant in the Kiel Bight.

1.5 Conclusions

The results of the present study showed that labile organic compounds (biogenic opal, chlorine, C_{org}) in sediments of the Kiel Fjord were subjected to a strong seasonal variability. Their concentrations are significantly higher in springtime. The spatial distribution of labile organic compounds is mainly determined by sediment type. Generally, the levels of concentrations of biogenic compounds are comparable to those reported from the open Kiel Bight. Markedly low levels of food in Friedrichsort Sound establish quite unfavourable conditions for many benthic foraminiferal species. The surface sediment pollution by copper, zinc, tin and lead principally could be considered as moderate because the levels of metals are comparable to those elsewhere in the Baltic Sea. Nevertheless the inner Kiel Fjord is

distinguished by a high load of heavy metals. The high tin concentrations in surface sediments apparently depend on its accumulation in muddy sediments for previous decades.

The analysis of foraminiferal population density shows a patchy distribution and a response to food availability, which is depicted by SiO_2 and Chl *a* in the sediments. The strong increase of population density since the 1960s remains enigmatic. It cannot be attributed to an increase in organic matter supply and a slight reduction of pollution. Furthermore, we observed significant changes in foraminiferal species composition in 2005-2006 as compared to the 1960s. The stress-tolerant species *A. beccarii* invaded Kiel Fjord. We suppose that this species is highly opportunistic and can tolerate elevated levels of nutrients and trace metals. *E. albiumbilicatum* apparently is able to withstand the higher water turbulences and therefore inhabits the transitional area of Friedrichsort Sound. Unfavourable salinity conditions in the Kiel Bight and absence of a deep halocline in Kiel Fjord might have caused the disappearance of *A. cassis* during the past decades.

Faunal reference list

Ammonia beccarii (Linné) = *Nautilus beccarii* Linné, 1758; Schönfeld and Numberger, 2007a, p. 52, pl.1, fig.2. (Note: *Ammonia tepida*; De Noijer, 2007, p. 24, pl.1, fig. A; molecular types of *Ammonia* T1 and T2, Hayward et al., 2004, p. 256-258, pl. II-IV).

Ammotium cassis (Parker) = *Lituola cassis* Parker, 1870; Frenzel et al., 2005, p. 75, fig. 4., no. 3.

Elphidium albiumbilicatum (Weiss) = *Nonion pauciloculum* Cushman subsp. *albiumbilicatum* Weiss, 1954; Frenzel et al., 2005, p. 73, fig. 2., no. 10; Schönfeld and Numberger, 2007a, p. 52, pl.1, fig.4. (Note: *Elphidium asklundi* Brotzen, 1943 of Lutze (1965); *Cribroelphidium albiumbilicatum* of Frenzel (2005)).

Elphidium excavatum excavatum (Terquem) = *Polistomella excavata* Terquem, 1875,

Miller et al., 1982, p. 127, pl.1, fig.11-12; Schönfeld and Numberger, 2007a, p. 52, pl.1, fig.12-13.

Elphidium excavatum clavatum (Cushman), 1930; Miller et al., 1982, p. 127, pl.1, fig.8; Schönfeld and Numberger, 2007a, p. 52, pl.1, fig.7-9.

Elphidium gerthi van Voorthuysen, 1957; Lutze, 1965, p. 159, pl. 15, fig. 45 (Note: *Cribrononion cf. gerthi* of author).

Elphidium gunteri Cole, 1931; Frenzel et al., 2005, p. 73, fig. 2., no. 2 (Note: *Cribroelphidium gunteri* of authors).

Elphidium incertum (Williamson) = *Polystomella umbilicatula* (Walker) var. *incerta* Williamson, 1858; Schönfeld and Numberger, 2007a, p. 52, pl.1, fig.5-6.

Elphidium williamsoni Haynes, 1973 (Note: *Cribrononion* cf. *alvarezianum Orbigny*, 1839 of Lutze (1965)); Frenzel et al., 2005, p. 73, fig. 2., no. 8. (Note: *Cribroelphidium williamsoni* of authors).

Reophax dentainiformis f. regularis Höglund, 1947; Schönfeld and Numberger, 2007a, p. 52, pl.1, fig.11.

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Chapter 2

Eutrophication and heavy metal pollution in Flensburg Fjord: a reassessment after 30 years

Together with W.-Ch. Dullo
In revision: Marine Pollution Bulletin

Abstract

A study of surface sediment organic matter and heavy metal content (e.g. Cu, Zn, Pb and Sn) was carried out in 2006 to assess changes in eutrophication and pollution in the periodically anoxic Flensburg Fjord since 1972. Low hydrodynamic activity together with sewage discharges and high primary production in the inner fjord promotes the enrichment of present day surface sediments in organic matter and metals relative to the outer fjord. However, heavy metal contents in the fjord are typical for the western Baltic Sea, although they are higher than in the preindustrial period.

The anthropogenic nutrient load has substantially decreased since the 1970s. Sediments from the inner fjord contain more organic material in 2006 than in 1972 resulting from high primary production supported by internal nutrient loading. Of the heavy metals measured, a decrease in Pb content since the 1970s is distinct, which is explained by the banning on gasoline lead. Taken together, these results suggest that the amelioration of environmental conditions needs time but is indeed related to reduced anthropogenic inputs.

Key words: Baltic Sea, eutrophication, sediments, organic matter, heavy metals, decadal changes

2.1 Introduction

The coastal areas of the Baltic Sea exhibit a high trophic status resulting from high inputs of organic and inorganic nutrients from rivers, as well as local coastal and diffusive sources

(HELCOM, 1993). Moreover, the relatively shallow water depth of the Baltic promotes benthic-pelagic coupling and thus supports enhanced primary production (Zeitschel, 1980). As such, most Baltic coastal areas were classified as being mesotrophic and eutrophic (Nixon et al., 1995). Moreover, the fjords and bays often become anoxic because of the structured topography of these fjords and bays, which leads to restricted or only intermittently restricted water exchange with the Baltic Sea, thus resulting in persistent water column stratification (Jørgensen and Richardson, 1996; Meyer-Reil and Köster, 2000). High production and stagnation of deep waters then leads to oxygen deficiency and to long-term hypoxia, or even anoxia in the fjords and bays, driving the profound changes in the ecosystem structure (Bonsdorf et al, 2002).

The coast of Schleswig-Holstein, in the southwestern Baltic Sea is characterized by long narrow inlets and bays, which have been inhabited for centuries. The more recent municipal, industrial and agricultural activities in the region resulted in a high level of contamination by metals and organic compounds in coastal area for the past 50-70 years. As the fjords and shallow bays possess high filtering and buffering capacity (Schiewer and Gocke, 1996), they are often significantly eutrophied and polluted (Müller et al, 1980; Rheinheimer, 1990; Lange, 1990; Gerlach, 1996; Brügmann and Leipe et al, 1998; Meyer-Reil and Köster, 2000).

Flensburg Fjord is still comparably undisturbed by anthropogenic activities. Nevertheless, severe anoxia and an extremely high primary production in the inner Flensburg Fjord caused concern of local authorities in the 1970s (GKFF, 1973a; GKFF, 1973b). Consequently an extensive monitoring program was established in 1972-1973 to evaluate the fjord's environmental conditions, which was followed by activities to reduce the nutrient input into Flensburg Fjord. After these measures were taken, primary production in the fjord decreased, although oxygen depletion still occurred. In addition, high concentrations of heavy metals in bottom sediments were reported in the 1970s.

The aim of this study was to assess whether the decrease in the inputs of nutrient and other anthropogenic contaminants has affected the eutrophication and pollution levels in Flensburg Fjord over last three decades. Specifically, we measured organic carbon, total nitrogen, chlorophyll *a* and biogenic silica in surface sediments in order to fully constrain both the pattern of surface productivity and the capacity for organic matter preservation in modern sediments. The heavy metals copper, zinc, lead and tin, common anthropogenically sourced pollutants, were also measured. The relationships between all these parameters, as well as the linkages to hydrography and sediment properties, were compared in order to define the main

factors influencing their distribution. Finally, through comparison with similar data from a 1972 study we attempted to predict the future development of the fjord.

2.2 Study area

Flensburg Fjord is a narrow, 50 km-long bay of the northwestern Kiel Bight between Germany and Denmark (Fig. 2.1). The inner fjord is 15 km long and 2.3 km wide with water depths not exceeding 19 m. The inner fjord has only restricted water exchange with the Kiel Bight and the Baltic Sea due to a sill depth of 10 m off Holnis Peninsula. Southward, the inner fjord terminates with the narrow, elongated Flensburg city harbour at 7 to 9 m water depth. The outer Flensburg Fjord comprises Sonderborg Bay (13 to 31 m depth), Gelting Bay (4 to 22 m depth) and open waters eastward of Gelting Peninsula with a depth range from 5 m in the coastal area to 39 m in the Little Belt (Fig. 2.1).

The bottom topography is shaped by current and wave activity that drives erosion of cliffs as well as in shallow water areas, and deposition of the eroded material in deeper waters. In the outer fjord, silt and mud dominates the sediments in deeper areas, while in water shallower than 8 m sand and muddy sand prevail (Exon 1971, Exon, 1972; GFKK 1973a). Dark, sandy mud and soft mud characterize the sediments of the inner fjord (Exon, 1971).

The hydrography of Flensburg Fjord, seen particularly in salinity distributions, is spatially

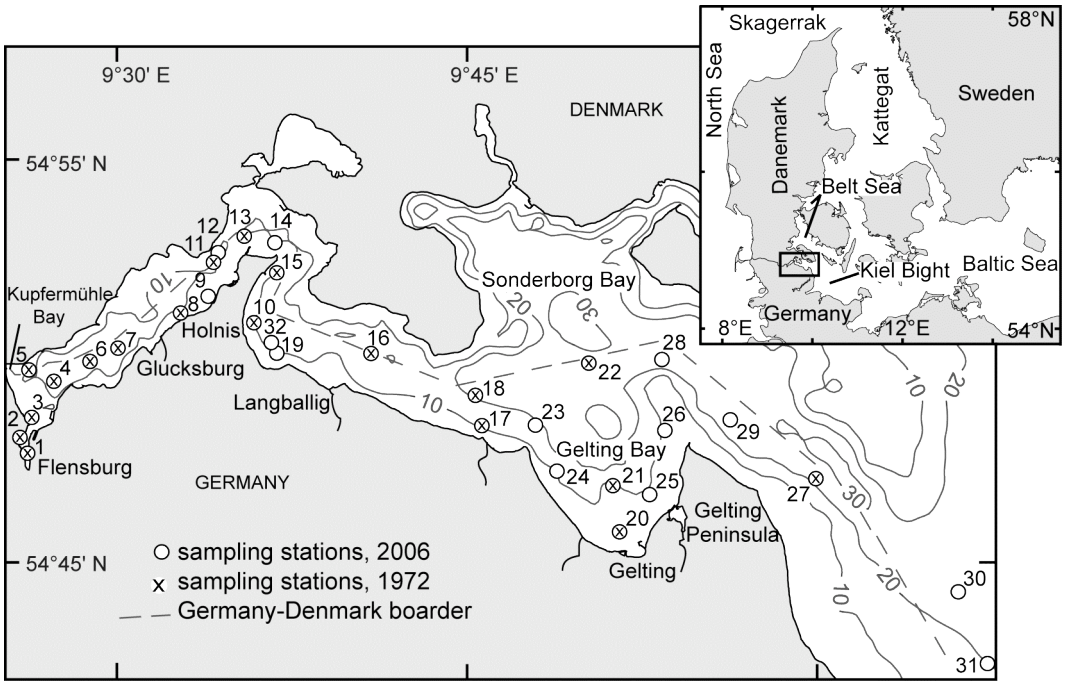

Figure 2.1. Location of sampling stations in Flensburg Fjord. Station prefix PF16- is omitted. Depth contours are in meters. Stations sampled after 1972 are given according to GKFF (1973a).

determined by salt-water inflows from the Belt Sea (GKFF, 1973b). Salty bottom water at the outer fjord in spring and autumn forces its way across Holnis sill and renews the stagnant bottom water in the inner fjord. After such inflow the halocline occurs at 8 to 9 m depth and greatly inhibits vertical mixing between the water layers in the inner fjord. In the outer fjord this pycnocline is found between 16 and 20 m depth (Exon, 1972). In the period between inflows, vertical mixing is the only mechanism of water exchange. Density and wind-induced currents, which occur frequently, are of decisive influence on the rate of water renewal of the whole fjord. Runoff of small rivers and brooks, atmospheric precipitation and sewage discharges input fresh water at rate of about 470 km^3 a^{-1} to the Fjord (average between 1986 and 1997, LANU, 2001a). The annual salinity range is 15-20 psu in surface water, and 20-26 psu in bottom waters (Kändler, 1963; Exon, 1972; Bluhm, 1995). The water temperature of the Fjord varies from 0°C to 20°C near the surface, and from 3°C to 15°C in the near-bottom layer.

2.2.1 Oxygen deficiency events

The combined effects of bathymetry and seasonal temperature stratification on bottom water turnover result in oxygen deficiency (Kändler, 1963; GKFF, 1973b). A short period of oxygen depletion with values less than 90 µmol l^{-1} has been noted in late May-July in the inner fjord and Flensburg harbour (Wahl, 1985). Severe long-term oxygen depletion (less than 4 µmol l^{-1} in bottom water), however, occurs in August and September (Kändler 1963; GFKK, 1973b; Wahl, 1984; Lorenzen et al., 1987; DDTFF, 1992; LANU, 2003). This summer deoxygenation is accompanied by a degradation of the benthic macrofauna (Bluhm, 1995). In winter and early spring, however, the oxygen conditions become favourable again

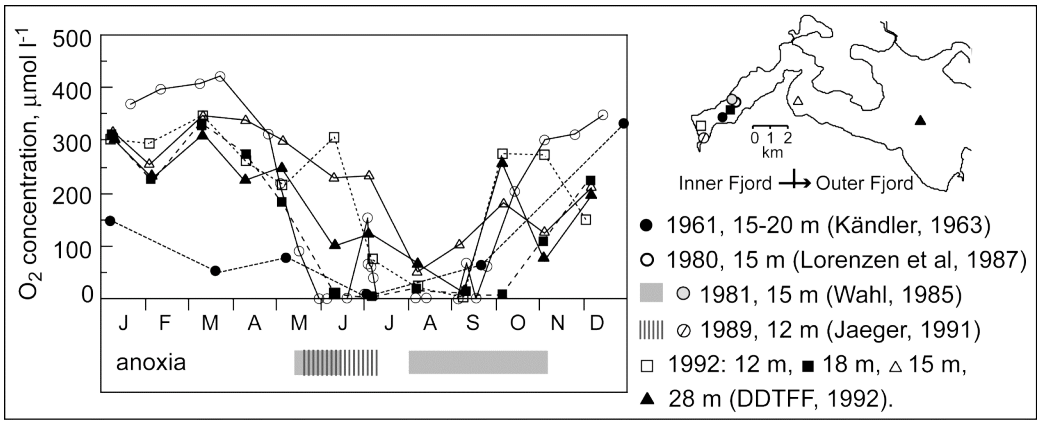

Figure 2.2. Oxygen content in near-bottom water of Flensburg Fjord: year, depth and location of measurement are given for every series. Shadow boxes depict the reported anoxia periods.

for benthic organisms caused by enhanced wind-driven vertical mixing (Fig. 2.2).

A cultural eutrophication in 1960-1980 is purported to have had intensified the oxygen deterioration of the inner fjord due to nitrogen and phosphorous input from open sewage systems (Anonymous, 1985). That is, large amounts of nutrients from the sewage inputs induced an increase of primary production in the inner fjord, thus raising a demand of oxygen in near-bottom water by organic matter-decaying microorganisms. After the installation of the biological cycle of purification of the Flensburg sewage plant in 1967-1969, Rheinheimer (1970) found an improvement of the oxygen situation in the inner fjord. Nevertheless, in the 1980s severe periodical oxygen depletions, even including hydrogen sulphide formation, were reported from the inner fjord (Bluhm, 1995). In 1989, an experimental aeration pump started operating in the inner Flensburg Fjord (Jaeger, 1990). Following stagnant, fully anoxic conditions, oxygen content increased immediately in bottom water after installation of the pump. While this aeration experiment did not intend to rehabilitate the Fjord waters, it lasted only for several months but clearly demonstrated the efficiency of such aeration techniques for oxygenating of stagnant brackish water (D. Jaeger, written comm.). Annual oxygen depletions have been reported for the 1990s and the 2000s (DTFF, 1993; LANU, 2001a; LANU, 2003), despite significant diminution of sewage discharges.

2.2.2 Nutrient input and primary production

The main sources of nutrient input into Flensburg Fjord are the drainage from agricultural watershed and communal sewage. For the most recent decades, the input of phosphorous from sewage has declined: from 169 t a^{-1} in 1986 to 7 t a^{-1} in 1997. Similarly, the total input of phosphorous from all sources has decreased from 305 t a^{-1} in 1986 to 84 t a^{-1} in 1997. As 40 % of the nitrogen comes into the Fjord from diffusive sources, the elimination of nitrogen from sewage alone was not as effective in reducing the source function, which dropped from 2600 t a^{-1} in 1986 to 1600 t a^{-1} in 1997 (LANU, 2001a). Again, the largest part of nutrient load mainly affected the inner fjord.

The changes in nutrient input apparently reduced primary production in the inner fjord from 550-700 gC m^{-2} a^{-1} in 1986-1989 to 225-290 gC m^{-2} a^{-1} in 1995-1997 (LANU, 2001a), although considerable variations were observed between years. In the outer fjord, primary production was consistently at 105-200 gC m^{-2} a^{-1} over this period.

2.3 Material and methods

2.3.1 Samples collection

The sediment samples were collected in June 2006 with RV Polarfuchs (IFM-GEOMAR) at 32 stations in the German area of Flensburg Fjord (Fig. 2.1, Appendix 1.2) by two different sampling devices. A Rumohr corer with a 55 mm inner diameter was used for muddy sediments, and the upper centimeter of the cores was removed with a spoon and kept in plastic vials. A Van Veen grab was used for sandy sediments, and the samples were taken with scaled syringes. After returning from cruise, the samples were frozen at -18°C, then freeze-dried and homogenised manually in an agate mortar. To get comparable geochemical data, samples were taken at the same locations and at the same season as those used in the 1971-1972 studies by Flensburg Fjord Commission (GKFF, 1973a). However, in the 1972 study the upper three centimetres of sediments were taken by a Van Veen grab for geochemical analyses.

Salinity, temperature and dissolved oxygen content of the overlying water in the Rumohr corer tube were measured on board with an Oxi- and Conductivity meter (Oxi323/325Set and LF320/Set). These values represent the near-bottom water properties as the measurements were made immediately after retrieval. At the locations where only a Van Veen Grab was deployed, no data on near-bottom water properties could be obtained.

2.3.2 Geochemical analysis

To assess the productivity and nutrient status of the Fjord, the organic and total carbon, total nitrogen, silica, and pigments were measured. Total carbon, organic carbon, and nitrogen contents of the sediment were determined with a Carlo Erba NA-1500-CNS analyzer at IFM-GEOMAR with accuracy better than ±1.5 %. Total carbon was obtained from bulk sediments, whereas the organic carbon content was measured in decalcified sediments. The atomic C:N was calculated in order to assess the sources of organic matter.

The quantities of biogenic silica were measured by the automated leaching method according to Müller and Schneider (1993). Opaline material was extracted from bulk sediment by sodium hydroxide at 85°C for about 45 min. The dissolved silicon in the leaching solution was determined by molybdate-blue spectrophotometry with a precision of ±1 %. Chlorine contents in sediments were measured with a Turner TD-700 Fluorometer after acetone extraction. The precision of the method was ±10 %.

The heavy metals Cu, Zn, Pb and Sn were measured in the bulk sediment from 20 locations. Powdered samples were completely digested in a mixture of hot nitric, fluoric, perchloric and hydrochloric acids under heat (150°C). Once dissolved, the solutions were dried down and diluted in 2 % nitric acid for analysis. These elemental measurements were performed with an AGILENT 7500cs ICP-MS at the Institute of Geosciences, University of Kiel (Garbe-Schönberg, 1993). The accuracy of analytical results estimated from replicate measurements of the international standard MAG-1 was better than ±1.5 %.

2.4 Results

2.4.1 Physical parameters

Hydrography

In June 2006, the bottom water temperature varied from 8°C in the open, eastern part of the Fjord to 11°C in the sheltered inner fjord, with a maximum of 14°C in Gelting Bay. The bottom water salinity increased from 18.3 psu in Gelting Bay and 19.3 psu in the inner fjord, where freshwater input has a significant influence, to 25.4 units outside the Fjord. The surface water temperature in June fluctuated about 16°C throughout the Fjord and increased to 22°C in Gelting Bight; surface water salinity changed from 18 units in inner fjord, and 16-18 units in Gelting Bight to 24 units in the outer fjord (MAEWEST, 2007).

Oxygen

The dissolved oxygen content varied from 159 to 307 µmol l^{-1} throughout the Fjord (Appendix 2.2). A consistent pattern was not discernable, but the lowest concentration of oxygen with a saturation level of 48-64 % was found in the inner fjord at the depths less than 12 m. In the outer fjord, the saturation was 53-58 % at 25-28 m water depth. In the shallower areas, bottom water oxygen saturation reached values as high as 81 % off Holnis Peninsula and 100 % in well mixed waters of Gelting Bay. Oxygen saturation at most of the stations did not fall below 50 %, therefore presenting favourable conditions for benthic organisms. No significant correlation between oxygen content and water depth was found.

At the inner fjord stations PF16-2; -3; -4 black sediments were recovered, in which H_2S was present and which were barren of any benthic organisms. The cores taken by Rumohr corer at these stations contained very dark sediments covered by few millimetres of light brown oxygenized sediments.

Bottom sediments

Sediment compositions were determined by washing subsamples of the sediments through a 63-µm sieve. Most of the samples contained less than 20 % sand except the samples from Gelting Bay, which all contained 40-90 % sand. Sandy sediments prevail in the coastal areas, whereas muddy sediments were encountered off Holnis Peninsula and to the east of Gelting Peninsula. In the inner fjord muddy sediments entirely dominate. All sediment samples contained ash and coal particles.

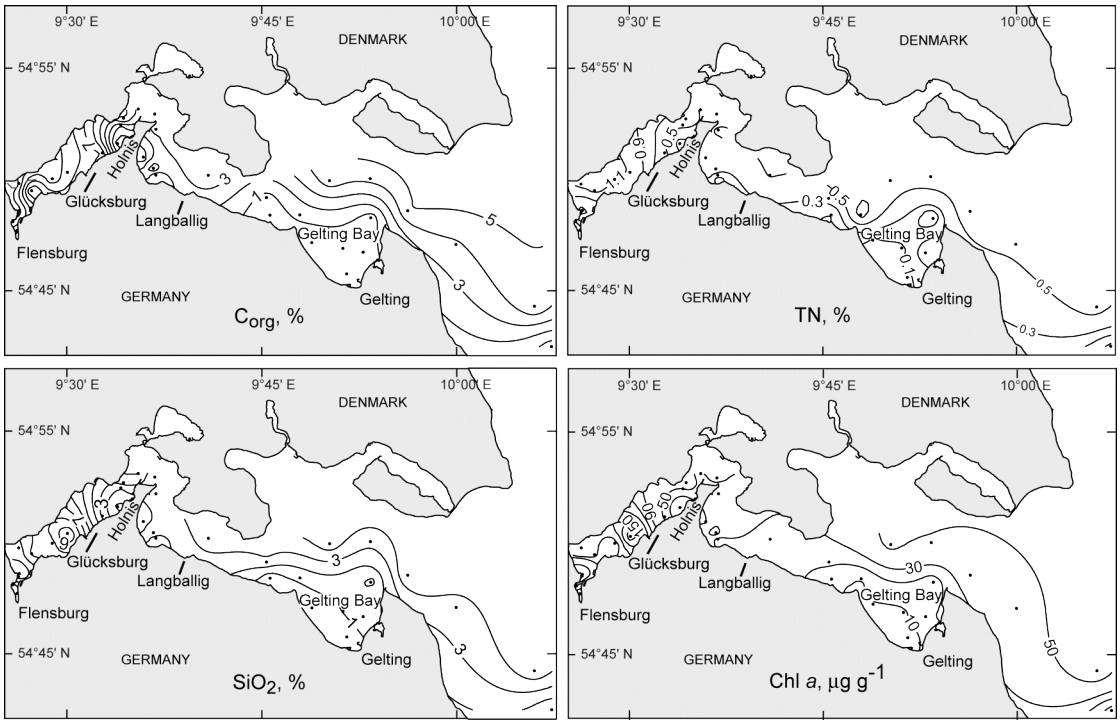

Figure 2.3. Distribution of organic carbon, total nitrogen, biogenic silica and chlorophyll *a* in surface sediments of Flensburg Fjord. Dots indicate sampling stations.

2.4.2 Organic compounds

Organic carbon and total nitrogen

The content of organic carbon clearly increased from the outer to the inner fjord (Fig. 2.3). The distribution of C_{org} is correlated inversely to the sand content of the sediments ($r = -0.685$). With a mean value of 4 %, the highest C_{org} concentrations around 11.5 %, were recorded in Flensburg harbour, around the Flensburg sewage plant, and in sediments of Kupfermühle Bay at the mouth of Krusau river. Towards the Holnis Peninsula, the organic carbon content decreased to 3.3 % and was not correlated to the sand content (Appendix 2.6). Exceptionally low C_{org} values of 0.2-1.3 % characterize the sandy sediments offshore

Glücksburg (stations PF16-8 and -9) and Gelting Bay. Sediments of the outer deep fjord contained 3.8-4.2 % of organic carbon.

Organic carbon accounts for 50-100 % of the total carbon throughout the Fjord, with the exception of Gelting Bay where organic carbon comprised 10-40 % of total carbon. The lower values seen in Gelting Bay are likely the result of intensive wave activity in the bay, which does not favour preservation of organic carbon or enriches the relative content of shell debris.

Total nitrogen concentration in Flensburg Fjord sediments varied from 0.06 to 1.2 % with the lowest values in Gelting Bay and along the shore off Langballig, and with a distinct increase in the inner fjord (Fig. 2.3). The distribution pattern followed the distribution of organic carbon such that total nitrogen also negatively correlates with the sand content (r = -0.749).

The C:N ratio in the sediment had a quite distinct distribution over the fjord, from 14 in the inner part to 6.8 in the outer fjord. The mean C:N ratio of 7.5, differed from the median 8.7 due to a few data fliers. The large difference between mean and median values was observed for virtually all parameters, and seems to be a result of extremely different conditions in the Fjord. Surprisingly low values of C:N were measured in Gelting Bay, despite a substantial allochtonous organic matter input from rivers and agricultural watershed.

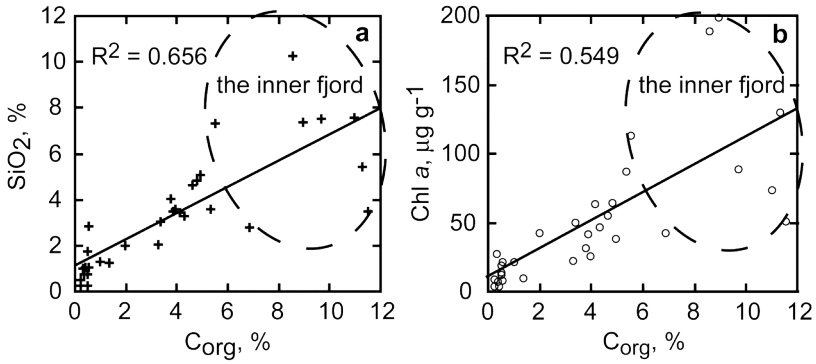

FIGURE 2.4. Relationships between biogenic silica and organic carbon, chlorophyll *a* and organic carbon contents in sediments of Flensburg Fjord.

BIOGENIC SILICA AND PIGMENTS

Sediments of Flensburg Fjord contain biogenic silica between 1.0 and 10.5 % with a mean of 3.4 %. The data show a maximum in the inner fjord with a seaward decrease, and minimal values were found in Gelting Bay (Fig. 2.3). Biogenic silica correlates significantly with organic carbon (Fig. 2.4) and chlorophyll *a* content (r = 0.862).

We observed highly variable chlorine concentrations in sediments of Flensburg Fjord (150 µg g^{-1} to 910 µg g^{-1}), although the highest contents characterized only some stations in the inner fjord while the chlorine content in the rest of the Fjord did not exceed 300 µg g^{-1}. Gelting Bay exhibits low concentrations of chlorine at 20 to 70 µg g^{-1}. The chlorophyll *a* content in sediments ranged from 4.1 to 200 µg g^{-1} with a minimum at Gelting Bay (Fig. 2.3). Chlorophyll *a* concentrations exceeded 100 µg g^{-1} again only in the inner fjord.

The ratio of phaeopigments to chlorophyll *a,* which indicates the degree of chlorophyll *a* decay and preservation of organic matter, varied from 3.3 in the inner fjord to 1.3 in Gelting Bay with 2.7 on average, which means that preservation was high. However at some stations in the inner fjord PF16-2, -6, -14 and –16 at sand portion less than 11 % pigment ratio exceeded 4.2 indicating low preservation.

TABLE 2.1. Concentrations of trace metals (Cu, Zn, Sn, Pb) in the surface sediments of Flensburg Fjord in 2006 (n=20) and correlation coefficients with sand fraction and organic carbon.

Trace metal	Mean, µg g^{-1}	Median, µg g^{-1}	Range, µg g^{-1}	Correlation with sand (%)	Correlation with C_{org} (%)
Cu	45.1	24.4	2.3 – 194	-0.542	0.891
Zn	137	111	10.4 – 438	-0.655	0.831
Sn	4.15	2.45	0.3 – 18.1	-0.595	0.827
Pb	40.3	29.5	6.30 – 158	-0.522	0.826

2.4.3 HEAVY METALS

The heavy metal content in sediments of Flensburg Fjord varies widely (Table 2.1, Fig. 2.5). All the metals measured show significant correlation with organic carbon and the sand fraction (Table 2.1, Appendix 2.6). Consequently, the inner fjord sediments showed elevated metal levels whereas Gelting Bay sediments contain low metal concentrations.

Unexpectedly, normalization of heavy metal content by C_{org} did not reveal any changes in the distribution of the metals (Newman and Walting, 2007). We thus suggest that there are no specific point sources of metals in the Fjord. Nevertheless, the metal content in the inner fjord deviates from the C_{org} -regression model (e. g. Cu; Fig. 2.6). In the outer fjord the metal content is proportional to organic matter and likely represents a natural situation whereas in the inner fjord metals less relate to C_{org}. In particular zinc and tin content could therefore be related to contamination from sport harbours and the shipyard situated in the inner fjord.

Overall, the high concentrations of metals characterize only a few stations (Fig. 2.5). For

example, Cu content higher than 50 μg g^{-1} was encountered at only 25 % of the stations and all of these were situated in the inner fjord. Only 20 % of the stations had Zn concentrations above 200 μg g^{-1} and 60 μg g^{-1} of lead. Tin content did not usually exceed 2 μg g^{-1}, although reaches the levels above 5 μg g^{-1} at four stations in the inner fjord.

The data on near-bottom water properties during the sampling period and concentration of variables in sediments are additionally presented in Appendix 2.2.

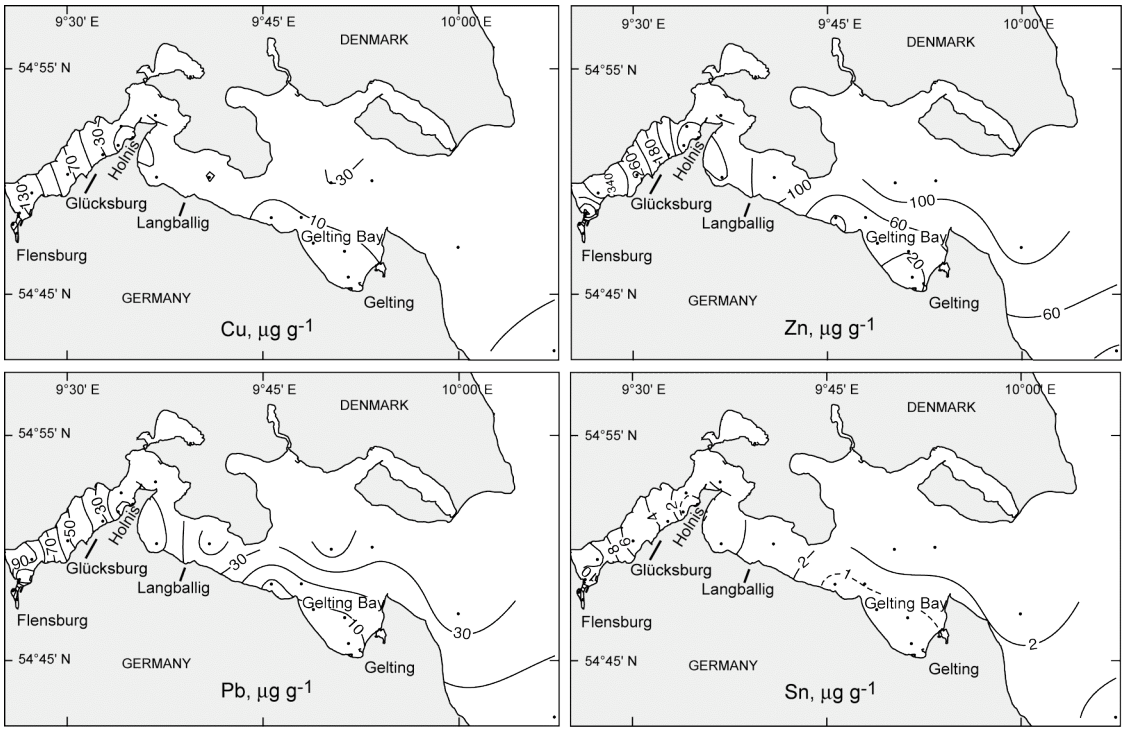

FIGURE 2.5. Distribution of copper, zinc, lead and tin in surface sediments of Flensburg Fjord. Dots indicate sampling stations.

2.5 DISCUSSION

2.5.1 PRESENT STATE

The difference between surface and bottom water salinities in June 2006 points to the formation of a halocline throughout most of the fjord, with exception of Gelting Bay. Furthermore the salinity in 2006 was generally higher than the long-term summer average (Krug, 1963; GKFF, 1972b). These two facts imply that inflow of oxygenated saline water from the North Sea occurred, probably starting in April 2006 (MAEWEST, 2007). A thin oxidized top layer on sediments containing H_2S from the inner fjord also points to oxygen exposure resulting from the inflow of oxygen-enriched salty waters. On the other hand, low oxygen contents in near-bottom waters as well as the presence of some H_2S and the absence

of bottom fauna may be recognized as a consequence of short oxygen depletion after formation of the halocline and water stable stratification. Similar summer oxygen depletions, accompanied by the absence of benthic organisms in sediments, were described by Wahl (1985) and Bluhm (1990) in the inner fjord. Nevertheless winter studies showed the presence of normally structured benthic community in the inner fjord compared to the summer absence (Bluhm, 1990) that was interpreted as recovery of the community under the favourable oxygenated conditions.

The distribution of sediments apparently depends on water dynamics in the Fjord. In the inner fjord and central outer fjord muddy sediments have been deposited whereas in the dominantly erosive regime at Gelting Bay and off Holnis Peninsula one encounters mostly sandy sediments. Following the finer sediment pattern, the accumulation of organic compounds and pollutants is favoured in the inner fjord.

2.5.1.1 Organic matter distribution and sources

The distribution of organic compounds in Flensburg Fjord reflects two features. The first is geographical settings and therefore significant differences in accumulation of organic matter in the outer dynamic fjord and in the restricted inner fjord. The second feature relates to our sampling in late spring, which is reflected in the elevated levels of organic compounds, and which depicts the recent phytoplankton spring bloom. The inner fjord sediments are highly enriched in organic matter compared to the outer fjord and in particular to Gelting Bay. Low levels of organic matter in eastern Gelting Bay are apparently linked to prevailing sandy sediments and strong wave erosion, whereas in the southern and the southwestern parts, they are caused by a lack of water mixture and low nutrients content (Exon, 1971; 1972). Moreover the enrichment of sediments in organic matter in the inner fjord mainly points to a higher productivity in comparison with the outer fjord (LANU, 2001a). Nevertheless organic matter levels in the sediments are still in the same range as organic carbon values of bottom sediments elsewhere in the Kiel Bight (Exon, 1973; Balzer, 1984; Gerlach, 1996; Leipe, 1998).

Organic carbon makes up 80 % of total carbon; though in places a large fraction of total carbon is occupied by the inorganic part, presumably represented by calcium carbonate. The enhanced portion of carbonates in sediments (11 % on average) is higher than usually in the southwestern Baltic Sea (Balzer et al., 1987; Brügmann and Lange, 1990). In particular, the values of 25-59 % carbonate are considered as not reliable. The apparent increase of inorganic

carbon may be caused by additional sources, most likely shell debris or coal and soot.

The total nitrogen concentrations along with organic carbon are also high but of the same order as in other areas of the Baltic Sea (Balzer, 1984; Koop et al., 1990; Carman et al., 1996; Kauppila et al., 2005; Ellegaard et al., 2006). Enhanced concentrations of C_{org} and total nitrogen denote the high rates of sedimentation of organic matter together with high primary production and the high burial potential of sediments.

The biogenic silica content describing the production of diatoms is much higher in the inner Flensburg Fjord than those reported by Emelyanov (1988) for sediments of the open Baltic Sea. Nevertheless, biogenic opal levels are comparable to those found elsewhere in eutrophied bays of the Baltic Sea (Conley and Johnstone, 1995; Carman and Aigars, 1997; Kaupplila et al, 2005; Vaalgamaa and Conley, 2008).

In the Kiel Bight, the spring bloom usually fell on the beginning of March to April (Hickel, 1967; Smetacek, 1980; Wasmund and Uhlig, 2003) but the maximum primary production in Flensburg Fjord was reported to occur in May (LANU, 2001a). The high levels of biogenic silica in the inner fjord in June are apparently linked to both phytoplankton bloom deposition, and the restricted water exchange in this area. The topographical restriction of the inner fjord and the shallow water depth inhibit silica export from this area. Silica is recycled and therefore may be available for diatom production (Raguenaeu et al., 2002), which is usually limited by the availability of dissolved silica in the water column. Moreover, the correlation of biogenic silica with chlorophyll *a* content ($r = 0.862$) in Flensburg Fjord sediment indicates a non-detrital but diatom origin of Chl *a* (Christiansen et al., 2000). Both silica and chlorophyll *a*, as is seen from their high content in sediments, were incorporated in the bottom sediments within a month from production.

On the other hand, the extremely enhanced levels of biogenic silica in the inner fjord could also be explained by the input of fresh water diatoms through rivers and brooks (Conley, 1997; Beucher et al., 2004). This hypothesis is supported by the enhanced C_{org}:SiO_2 ratios in the innermost, high-depositional part of the Fjord (Fig. 2.4) indicating allochtonous organic matter input (Carman and Aigars, 1997). Indeed, the regression of biogenic silica and chlorophyll *a* on organic carbon (Fig. 2.4) showed that in the inner fjord an additional source of organic carbon must exist, either natural (river discharge), or anthropogenic in origin (sewage outlet, nutrient from agricultural drainage area and atmosphere). The same is reflected in high C:N ratios of 10-14 in the inner fjord showing that the organic carbon is mostly of terrestrial origin (Calvert and Pedersen, 1992). The portion of allochtonous organic

matter apparently decreased in the outer fjord where the C:N ratios varied between 7 and 8 and approach the values of marine phytodetritus (Carman et al, 1996) in the outer fjord. These values are fairly low for such an area, but may be influenced by recent spring sedimentation of fresh organic matter (Graf, 1980).

The concentrations of total pigments and chlorophyll *a* in Flensburg Fjord are as high as sediments elsewhere in the Baltic Sea, safe for the strongly eutrophied Danish fjords (Bianchi et al., 2002; Hansen and Josefson, 2003; Kauppila et al., 2005; Reuss et al., 2005). In the inner part of Flensburg Fjord they apparently refer to periodic suboxic conditions. They support preservation of pigments as the grazing by macrofauna is not so efficient because of its periodical diminution under oxygen depletion (Bianchi et al., 2000). On the other hand, good oxygenation and light conditions in Gelting Bay affect the rate of chlorophyll *a* loss by stimulating the activity of microbes and herbivores (Leavitt, 1993).

The mean values of the phaeopigments : chlorophyll *a* ratio for the Fjord characterize sediments, which have been recently enriched by chlorophyll *a*. In the inner part, the values are comparable to those which depict the winter sediments with a high decay level of Chl *a*, or which were affected by resuspension and oxic conditions (Bianchi et al., 2002). However, the low ratios in Gelting Bay, which prevailed under oxic conditions, are enigmatic. The only explanation can be a generally low level of pigments due to the high hydrodynamic activity and also a lower productivity in the absence of nutrient recycling from bottom sediments (Exon, 1973). The latter might be responsible for low total concentration of pigments in sediments of this area (Leavitt, 1993; Reuss et al., 2005).

2.5.1.2 Heavy metals pollution

The heavy metal concentrations in the sediments of Flensburg Fjord have a distinct distribution; they decrease from the inner to the outer part. In the absence of large point sources of heavy metals in the fjord the geographic and the hydrographic settings of the Fjord seems to be the main constraints of metal distribution. In the inner stagnant and restricted fjord, the highest levels of all metals occur, whereas in the dynamic, outer fjord, where sandy sediments dominate, the metal contents are significantly lower (Fig. 2.5). However, the regression model (Fig. 2.6) shows that the regional source of contamination should mainly affect the inner fjord, which is the sewage water, harbours and shipyards of Flensburg and Glücksburg cities. The absence of correlation between high levels of C_{org} and metals in the inner fjord reveals the parallel influence of scavenging by organic matter particle flow and

direct anthropogenic metal pollution.

In the inner fjord the metal contents reach very high values, which are definitely higher than a "background" determined for coastal sediments in the western Baltic Sea (HELCOM, 1993). Sediments provide a temporally integrated indication of ecosystem state and pollution. The mean sedimentation rate derived from a core from the outer, deep Gelting Bay was 3 mm a^{-1} (Müller et al. 1980). Therefore, the obtained concentrations of metals from the surface samples encompass the last 3-4 years, reflecting quite modern conditions. Heavy metal concentrations and distribution patterns of 2006 correspond well to the findings of the State Department for the Environment of Bundesland Schleswig-Holstein (Landesamt für Natur und Umwelt, LANU) in the year 2004 (LANU archive: Ostseemonitoring Programm). Overall, the metal levels are within the range for Kiel Bight (Leipe et al., 1998; Haarich et al., 2003; Pohl et al., 2005). Comparing our results with pre-1880 concentrations from the core from Gelting Bay (Müller et al, 1980), a 6-fold enrichment of sediments in Zn and a 8-fold increase in Pb content were recognised for the inner Flensburg Fjord. However, since 1995 a slight decrease of Cu, Zn and Pb concentrations was observed (LANU archive: Ostseemonitoring Programm).

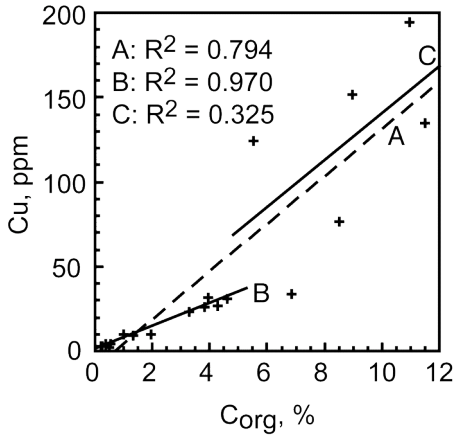

FIGURE 2.6. Relationships between organic matter and copper content in sediments of the entire Flensburg Fjord (A), in the outer fjord (B) and in the inner fjord (C).

The distribution pattern of lead is mostly not affected by sewage outlets and harbours or fine sediment distribution, but mostly by the input from the atmosphere (Brügmann, 1996), and therefore has a more uniform pattern. Copper contents also show some increase above background level (HELCOM, 1993) in the inner fjord, but remained low in the outer fjord and Gelting Bay. Tin levels in the outer fjord sediments are comparable to ones from the western Baltic (Cato and Kjellin, 2005), whereas in the inner fjord the tin concentrations are much higher and even exceed levels of Kiel Fjord (Nikulina et al., 2008). The latter is possibly influenced by yacht harbours and shipbuilding industry because until recent times Sn was used in antifouling paints (IMO, 2005). In this way, Flensburg Fjord can be considered polluted only in its inner part that is determined by diffusive, non-point sources and

hydrographical conditions.

2.5.2 Reassessment of Flensburg Fjord

2.5.2.1 Organic matter supply and eutrophication

In comparison with data from samples taken in 1972 (GKFF, 1973a), organic carbon and total nitrogen concentrations measured in 2006 did not significantly change throughout the Fjord (C_{org}: paired t-test, p=0.225; TN: paired t-test, p = 0.150) although some discrepancies were observed at particular stations. The distribution pattern remains the same and is in good agreement to ones described eventually in different parts of the Fjord (Exon, 1971; Lorenzen, 1987). The median values for C_{org} and TN are very similar. However, the variability of 2006 data was significantly higher (Fig. 2.7). This is probably due to additional stations sampled (Fig. 2.1). Alternatively, the topmost 3-centimeters sampled in 1972 introduce a higher integration over several years and, by that, reduces the noise in the data set as well as represents layers with more decayed organic carbon than in the uppermost centimeter. Nevertheless, a marked increase (up to 200 %) in the amount of organic matter in 2006 comparing to 1972 in the inner part of the Fjord is revealed (Fig. 2.7, Appendix 2.3).

The reason for such changes might be an increase of primary production in this area, enhanced sedimentation and input of organic matter, which cannot be completely decomposed in bottom sediments. Moreover, the preservation of organic carbon in sediments under hypoxic-anoxic conditions may cause organic carbon enrichment (Virtasalo et al., 2005). This is plausible, as in the inner part of the Fjord oxygen depletion events were regularly

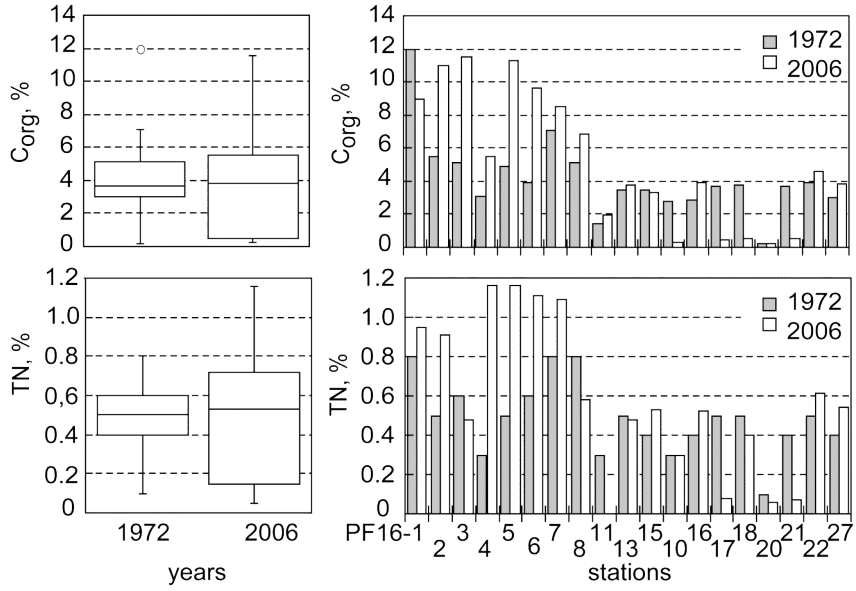

Figure 2.7. Organic carbon and total nitrogen in surface sediments of Flensburg Fjord in 1972 (GKFF, 1973a) and 2006 (this study).

encountered (Kändler, 1963; Kremling et al., 1977; Wahl, 1984; LANU, 2003). On the other hand, the inner fjord also shows an increase in total nitrogen (Fig. 7). However, under anoxic conditions, nitrogen is more efficiently metabolized by denitrifying bacteria leading to a loss of nitrogen as gas or ammonia to the water column and to the atmosphere (Balzer, 1984; Seitzinger, 1988; Koop et al., 1990; Canfield, 1994). Numerous studies showed no significant difference in rates of organic matter decomposition under oxic and reduced conditions (Jahnke, 1990; Calvert and Pederson, 1992; Cowie and Hedges, 1992; Henrichs, 1995). Thus, obviously, still high production stimulates the accumulation of organic carbon even though the external input of nutrients in the Fjord significantly decreased for the last decades (DDTFF, 1993; LANU, 2001a).

An internal forcing may be the alternative explanation. In the restricted inner fjord the settled nutrients may become available again for plankton growth after storm events topping up externally added nutrients (DDTFF, 1993; Meyer-Reil and Köster, 2000; Kauppila et al., 2005). A decomposition of the dead benthic fauna after anoxic events might be an additional source of nutrients, for instance phosphorous (Fallesen et al, 2000). The transition from oxic to anoxic conditions in the surface layer of sediments also induces the mobilization and release of phosphates bound to trivalent iron in the overlying waters (Gerlach, 1988) although this process is reversible under oxic conditions. Indeed, the concentration of nitrogen and phosphorous in the water column did not change in line with the external nutrient input (DDTFF, 1992; LANU, 2001a), which suggests an internal source. Further, the high C:N ratios in the inner fjord suppose that the organic matter contains some compounds (e.g. lignin) which anaerobic microorganisms can not metabolize quickly (Cowie and Hedges, 1992; Calvert and Pederson, 1992; Canfield, 1994). Hence, this terrestrial organic carbon has a higher potential to be preserved in marine sediments and contributes in the generally high content of organic carbon.

2.5.2.2 Heavy metal trends

The comparison of average metal contents as well as t-tests on significant differences between 1972 and 2006 showed that only the lead concentrations had changed significantly (paired t-test, $p=0.027$). Copper and zinc content did not show any changes through time (paired t-test, Cu: $p=0.882$, Zn: $p=0.230$). Although the medians of 1972 and 2006 are very close for Cu and Zn, at isolated stations we observed strong variations of metal content (Fig. 2.8, Appendix 2.2 and 2.3), which was probably due to the patchiness of sediment samples. The distribution pattern of all metals remained constant over the observed period of time,

which means no changes in sources distribution as well as the absence of large point sources for heavy metals. The high concentrations of metals in the inner fjord in 1972 thus had the same causes as at present time. Owing to high water dynamics Gelting Bay showed the lowest metal concentrations, similar to 1972. However, the common enrichment of Baltic Sea sediments by metals leads to enhanced levels of metal concentrations today if we compare 2006 and 1972 values to those from 1880 as being preserved in the nearby core (Müller et al., 1980).

The changes in lead content are noticeable in Flensburg Fjord for the last three decades, though in the Baltic Sea overall, no trend in metal content was detected through time (Pohl et al., 2005). The similar decrease of lead was observed in sediments of Northern America lakes in twenty years after the significant reduction of lead levels in atmosphere (Callender and Van Metre, 1997). Atmospheric transport and surface runoff together with boating and shipping industrial activities are considered as the main sources of lead in the Baltic (Nriagu, 1978; Brügmann, 1996). As such, the decrease of lead in sediments of the enclosed fjord is apparently associated with ban on gasoline lead additives.

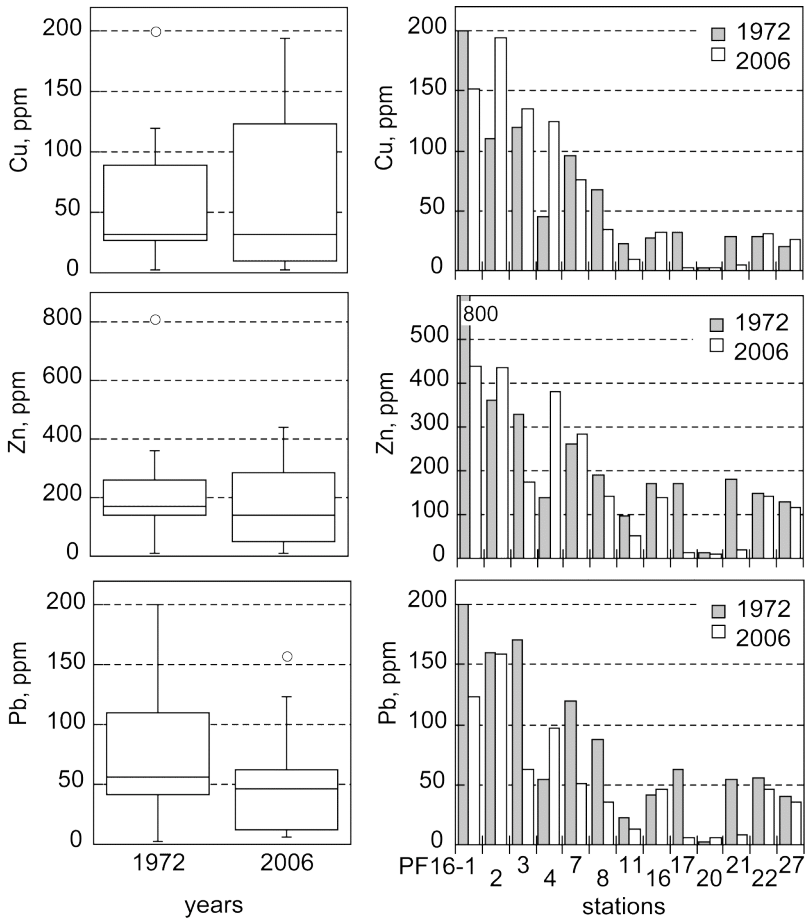

FIGURE 2.8. Heavy metal concentrations in Flensburg Fjord sediments in 1972 (GKFF, 1973a) and 2006 (this study).

2.6 Conclusions

The distribution of both organic compounds and heavy metals in Flensburg Fjord are mostly constrained by natural conditions, such as geographical settings and water exchange. Generally, the high concentration of organic matter in Fjord sediments did not significantly change since the protection measures applied and sewage discharge was reduced in the 1980s and 1990s. Apparently, the high levels of intensive nutrient discharges in the inner fjord until the end of 1970s still support the primary production rates and organic matter supply in the inner fjord. The nutritional conditions in the outer fjord have remained the same over the last decades and are comparable to the open Kiel Bight. The inner fjord is a depositional area, where recycling of organic matter occurs, and not a sealed sink.

We suggest that under the efficiently decreased anthropogenic nutrient input, natural cycles of oxic and anoxic conditions regulate the amount of primary production in the system and mitigate the eutrophication in the inner Flensburg Fjord. Denitrification under suboxic conditions is intensified because nitrate is still available, but oxygen is almost depleted (Nixon, 1981; Gerlach, 1990). This leads to nitrogen loss from sediments, decrease of its availability for phytoplankton and therefore less organic input into sediments and less hypoxia.

The artificial oxygenation of near bottom water may help to support the denitrification and temporarily to diminish anoxia. Unfortunately, the oxygenation technology for brackish and salt water has yet not been developed for long-term implementation and remains energy-consuming and expensive. It seems impossible to prevent anoxic events in the inner fjord and deep parts of outer fjord, where the water exchange processes play the main role.

High levels of copper, zinc, lead and tin were observed in 1972 and 2006 even though no prominent point sources could be identified. The restricted water exchange and prevailing muddy sediments makes the inner part a depositional area favouring metal enrichment and concentration of pollutants. Nevertheless, the levels of lead decreased in the whole fjord since 1972 due to the banning on lead-containing gasoline additives. The outer Flensburg Fjord as well as Gelting Bay may be considered as essentially non-polluted areas for the last three decades. The heavy metal levels in the inner Flensburg Fjord will most likely not substantially improve in the near future. Apparently even the reducing of metal concentrations in the discharges from sewage systems and shipyards will not give a successful result on a short-time perspective.

We speculate that the development of anoxia on seasonal scale in Flensburg Fjord due to

water stagnation and high productivity may be helpful in understanding the development and consequences of anoxia in the Baltic deeps at present time, or on a geological scale, the oceanwide stagnation periods during the Miocene and Cretaceous. Though the reasons for onset of anoxia and eutrophication may be temperature rise due to high CO_2 content (Wilson and Norris, 2001), nutrients input due to sea levels change (Jenkyns, 1980; Filippelli et al, 2003), which leads to high productivity and carbon burial, or water stagnation (Neumann et al, 1997; Matthäus et al, 1999), the processes involved are similar in all scales. Enhanced primary production and/or water stagnation cause a lack of oxygen in near-bottom water. Oxygen deficiency impedes nitrification and favours denitrification in sediments and in the water column. Meanwhile, the demand of nitrate for phytoplankton growth is partially compensated by N_2 fixation in near-surface waters at the absence of external inputs. At greater depths, the return of nutrient nitrogen from deep anoxic waters to the photic zone is cut off by denitrification and anaerobic ammonium oxidation (Kuypers et al., 2004). This discontinuity in the nitrogen cycle together with changes in carbon cycle may decrease productivity in the water column and therefore anoxia. However, apparently only changes in deep circulation may bring down the anoxia induced and maintained by the stagnation itself.

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Chapter 3

Chernobyl and Sellafield events: is it possible tool for age & sedimentation rate determination in Kiel Fjord?

Abstract

The dating of sediments is an integral part of the sedimentary core studies. The recovery of chronology in recent sediments is often complicated by a variety of processes affecting the distribution of ^{137}Cs and ^{210}Pb, used for the age determination within the last hundred years. Several age models were created for a core from the outer Kiel Fjord because of the ambiguous profile of ^{137}Cs and the irregular downcore distribution of ^{210}Pb. The most feasible model showed that the upper 10 cm of sediments cover the last 70 years with slight changes in sedimentation rates. The radiocarbon dating of bivalve shells in the lower part of the core revealed that 40 cm of sediments were deposited during 550 years with 0.3 mm a^{-1} between years 1930 and 1600 and 1.5 mm a^{-1} in the period from 1460 to 1600. Changes in erosion intensity, runoff and primary production induced by eutrophication together with recent anthropogenic coastal protection activity may be the reasons for such variations in sedimentation rates.

3.1 Introduction

The dating of sediments is a tool for time interpretation of geochemical or biological sedimentary records. The determination of the sedimentation rates gives a clue to sedimentary processes in particular area. In recent sediments exposed to different kinds of disturbances, especially in dynamically active areas, the recover of age and sedimentation rates may be a challenge. A number of methods, which can be used for dating of the recent sediments, are

limited. To get a chronology with a high resolution, the several chronological techniques are applied independently or together.

The lead-210 method is generally used (Krishnaswami et al, 1971; Robbins, 1978) for dating and determination of sedimentation rates in recent sediments deposited during the 19th and 20th centuries. In ideal case, the sediments should necessarily be undisturbed for instance by bioturbation or physical mixing, and the complete sediment profile should be sampled without loss of sediments from the core (Geyh and Schleicher, 1990).

^{210}Pb occurs naturally as a radionuclide of the ^{238}U decay series. The decay of ^{226}Ra in soils and crust material produces gaseous isotope ^{222}Rn, which diffuse to the atmosphere and decays through a series of short-lived radionuclides to ^{210}Pb, which in turn is washed out from the atmosphere by precipitation. ^{210}Pb falling directly into the ocean or drained from hinterlands is scavenged from the water column and is deposited with sediments (Appleby and Oldfield, 1992). Excess (unsupported) ^{210}Pb in sediments over those in equilibrium with in situ ^{226}Ra decays according to the radioactive decay law. Thus, the time passed since the particles were at the sediment surface can be calculated from the decrease of excess ^{210}Pb with depth. The excess ^{210}Pb activity is usually determined by subtracting ^{210}Pb supported (the activity derived from ^{226}Ra) from the total ^{210}Pb activity (in Bq kg^{-1}).

However, in order to assess the applicability of the ^{210}Pb chronology an independent dating technique is highly recommended, for instance sediment records of anthropogenic radionuclide ^{137}Cs and ^{241}Am or furthermore completely independent stratigraphic markers as ash layers from steamships, storm layers or specific contaminants introduced to the environment (Cantwell et al., 2007).

In contrast to ^{210}Pb, the ^{137}Cs method is a radiochemical stratigraphical approach where distinct ^{137}Cs peaks are historically identified and used as absolute time marker at the position of highest anomaly. In Northern Hemisphere two distinct ^{137}Cs fallout events are distinguished: the atmosphere fallouts during the nuclear bomb testing from 1957-1964 with a maximum in 1963 and Chernobyl reactor explosion in 1986 (Appleby, 2001). Furthermore, in the North Atlantic, Sellafield radionuclide discharges in 1971-1973 contributed in ^{137}Cs concentrations in sediments (Christiansen and Kunzendorf, 1998; Kunzendorf, 1999). These anthropogenic ^{137}Cs incorporate in sediments and can be detected. However the application of ^{137}Cs as independent marker is sometimes complicated by similar problems as for ^{210}Pb due to broadening of peaks as a result of bioturbation, erosion and resuspension of sediments. This implies to difficulties to verify all potential peaks. The comparison of ^{137}Cs record in

sediments with monitoring data on ^{137}Cs supply to the water column is therefore useful for verification.

^{137}Cs dating technique is limited to the last 50 years. The half-life time of ^{210}Pb constrains the application of this method to 150 years. To estimate the age of sediments deposited earlier, the radiocarbon method is used. Radiocarbon dating is based on the presence of an equilibrium ratio of $R(0) = {}^{14}C/{}^{12}C$ in the carbon cycle. Organisms taking up carbon during their life, for instance molluscs, obtain and fix in their cells the equilibrium value from the environment. The exchange with the environment and also the uptake of ^{14}C stops after the death of the organism. Because of the decay of ^{14}C, the $^{14}C/^{12}C$ ratio decreases exponentially according to the half-life of radiocarbon. From the remaining ratio at a certain time after death, we may calculate the age of the material. However, the equilibrium ratio is not everywhere the same in the ocean, because of the dissolution of old carbonates from sediments or mixing with old or stagnant water masses (Waelbroeck et al, 2001). This causes apparent age differences known as reservoir ages. Although in a marine environment the average reservoir age is 400 years, one should account to regional differences.

Several chronological techniques give a more precise result, but may complicate the establishment of an age model. The objective of this study was to detect whether ^{137}Cs fallout events and discharges left the traces in the sediments of Kiel Fjord and are reliable independent markers to accomplish the ^{210}Pb age model. To extend the chronology in deeper sediment layers, the radiocarbon dating was applied to bivalve shells found in the sediments. The established chronological model helps to attribute the results of my geochemical study to certain time intervals and better interpret causes and consequences of environmental changes in Kiel Fjord.

3.2 Environmental settings

Kiel Fjord is narrow and shallow bay of the Kiel Bight, which is open to the Baltic Sea (Fig. 3.1a). The inner Kiel Fjord is partially isolated from Kiel Bight by shallow Frisdrichsort Sound. Hydrographical conditions of the outer Kiel Fjord are comparable to those for the open Kiel Bight. The water depth in the outer fjord varies from 17 to 25 m. Salt-water inflows from the North Sea almost annually reach Kiel Fjord and refresh water in the deep channels increasing salinity and oxygen content. The near-bottom current carries the water from Kiel Bight in the inner fjord along the west coast, whereas the less saline surface water flows out from the fjord along the east coast (Themann, 2002).

Kiel Fjord was formed during the Saale Glaciation and attained its final shape as glacier tongue basin through several ice advances during Weichselian (Schwarzer and Themann, 2003). The topographical highs surrounding of Kiel Fjord were created by Late Quaternary oscillating ice advances.

The main source of sediments is Pleistocene till. It forms the sea bottom and make up the cliffs in Kiel Bight. Other sources of sediment material are fluvioglacial sands, glacial-lake mud and Holocene sediments. The near-shore transport of sediments is mainly directed into the inner fjord (Fig. 3.1b). Thus, the inner fjord is the depositional area with fine sediments, whereas the outer Kiel fjord has coarse-grained partially sorted or lag sediments on erosive shoals.

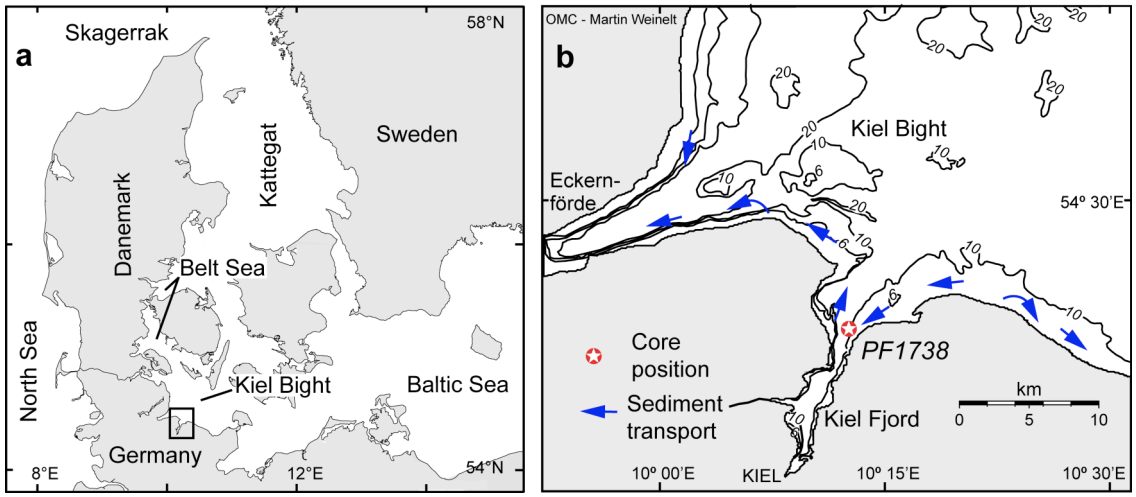

FIGURE 3.1. Overview of the western Baltic Sea (**a**) and location of sampling site in Kiel Bight (**b**). Depth counters in meters. The arrows designate the main directions of nearshore sediment transport in Kiel Bight (Sterr, 1998).

3.3 METHODS

3.3.1 SAMPLING

Three cores were taken at the location 54° 25.235'N 10°12.709'W in the outer Kiel Fjord at depth 14.9 m, PF1738a, PF1738b and PF1838. Master core PF1738b of 40 cm length was used for geochemical investigations related to time (Chapter 4). Core PF1738a of 20 cm length was subjected to chronological analysis to establish the age model and sedimentation rates in the upper 10 cm.

For sampling a Rumohr corer (a type of a lot corer) with plastic tube diameter 5.5 cm was used. A small diameter of tube could result in disturbance of the upper part of the core (Farmer, 1991) and compaction in the lower part. However, the core showed good sequences

of layers.

The core PF1738a was sliced in 0.5 cm down to 5 cm, and in 1 cm down to 10 cm. The slices were frozen and freeze-dried. ^{137}Cs and ^{210}Pb activities were measured in bulk sediment. Considering expected sedimentation rates of approximately 1 mm a^{-1} (Erlenkeuser et al., 1974; Balzer et al., 1987) estimated for this part of the Baltic Sea and the half life of ^{137}Cs (30.17 years) the sub-sampling strategy is aimed for steps integrating 5 and 10 years at maximum, depending on the down-core position. Overall, the sediments shallower than 10 cm should present the beginning of the twentieth century and potentially recover pre-Chernobyl imprints like Sellafield discharges and prior nuclear bomb tests.

Furthermore, two bivalve shells were picked in core PF1738b at 18-20 cm and 38-40 cm depth for radiocarbon analysis. The master core and additional core for geochronology were correlated by their lithostratigraphy (Fig. 3.2). The chronological model constructed for PF1738a was then projected to core PF1738b and expanded to 40 cm. This age model was applied to the geochemical investigation.

3.3.2 ^{210}Pb and ^{137}Cs

The first geochronological approach was focused on the identification of ^{137}Cs anomalies as absolute marker in the sediment sequence, especially of the pronounced and widespread impact of the Chernobyl disaster (AD 1986).

The non-destructive counting of gamma-ray activity was chosen as analytical method. It allows measuring simultaneously several gamma radionuclides in a sample, keeping the sediments undamaged and suitable for further analysis (e.g. geochemical or foraminiferal studies) although this does not give highly precise ^{210}Pb records, at least on that given small sample amounts. The samples were analysed for ^{210}Pb, ^{137}Cs and ^{226}Ra at the Labor für Radioisotope am Institut für Forstbotanik, University of Göttingen, using a low-background coaxial Ge(Li)detector. ^{210}Pb was measured via its gamma peak at 46.5 keV, ^{137}Cs via its gamma peak at 661 keV and gamma peak of ^{226}Ra via the granddaughter ^{214}Pb at 352 keV.

Two standard simple models have been developed to calculate ^{210}Pb dates (Appleby and Oldfield, 1992). The constant initial concentration (CIC) model assumes that sediments have a constant initial ^{210}Pb concentration regardless of accumulation rates, and therefore the supply of ^{210}Pb to the sediment record must vary directly in proportion to the sedimentation rate (Geyh and Schleicher, 1990). The constant rate of supply (CRS) model is usually applied to sites where sedimentation rates are not uniform (Appleby, 2001) resulting in changes in the

initial excess ^{210}Pb concentrations. The dates of older sediments are calculated not from their present concentrations but from the distribution of ^{210}Pb in the sediment record.

The alternative method of age determination with ^{210}Pb is a linear interpolation, in which the constant flux of $^{210}Pb_{exc}$ at water-sediment interface as well as constant sedimentation rate at certain core intervals are assumed. The age between intervals is estimated by using linear interpolation (Sharma et al., 1994; Brack and Stevens, 2001). The activity on top and bottom of a certain interval is determined as x-intercept of a regression line. The age is calculated according to the equation of radioactive decay:

$$T = 1/\lambda \ln (A_0/A_t),$$

where A_0 and A_t are activities on the top and bottom of interval respectively and λ is the constant of radioactive decay equals to 0.0311 s^{-1} for ^{210}Pb.

The validation of lead chronology was based on the profile of the anthropogenic nuclide ^{137}Cs derived from the nuclear tests, nuclear power plants and related hazards. In the Baltic Sea, three ^{137}Cs anomalies are distinguished in sediments: in 1963 related to atmosphere fallouts during the nuclear bomb testing, in 1986 because of the Chernobyl disaster, and in 1971-1973 linked to Sellafield radionuclide discharges (Christiansen and Kunzendorf, 1998; Kunzendorf, 1999). The mean sedimentation rate on intervals was independently calculated from the sediment thickness between assumed dates derived from ^{137}Cs profile.

3.3.3 Radiocarbon

To extend the chronological model deeper in the core, the radiocarbon isotopes were measured in bivalve shells by accelerated mass spectrometry at Leibniz-Laboratory for Radiometric Dating and Stable Isotope Research at the University of Kiel.

To prepare the samples for measurements, the adhering dust, detrital carbonate and organic surface coating were removed by 30 % H_2O_2 in an ultrasonic bath. Then samples were again cleaned with 15 % H_2O_2 in an ultrasonic bath. Cleaned samples were converted to CO_2 by acidification of $CaCO_3$ with 100% phosphoric acid at 90°C in an evacuated, flame sealed quartz tube. The sample CO_2 was reduced to graphite with H_2 on an iron catalyst, and the resulting graphite-iron mixture was pressed into aluminium target holder for the ion sputter source (http://www.uni-kiel.de/leibniz/index.htm).

The ^{14}C concentration of the samples was measured by comparing the simultaneously collected ^{14}C, ^{13}C, and ^{12}C beams of each sample with those of Oxalic Acid standard CO_2 and pre-Eemian foraminifera. Conventional ^{14}C ages were calculated according to Stuiver and

Polach (1977), with a $\delta^{13}C$ correction for isotopic fractionation based on the $^{13}C/^{12}C$ ratio measured simultaneously with the $^{14}C/^{12}C$ ratio. Both the counting statistics of the ^{14}C measurement and the variability of the interval results were used to determine the measuring uncertainty. The larger of the two was taken as measuring uncertainty and completed by the uncertainty connected with the subtraction of "blank".

3.4 Results

The sediments recovered in core PF1738a were perceptibly not disturbed and quite homogeneous. However, random changes in bulk sediment density were noted (Fig. 3.2d). That might indicate an absence of significant early compaction of the sediments in the core. The highest density was found in the uppermost layer apparently due to the artificial washing out of the fine fraction during sampling (Fig. 3.2d). The ship clinker is encountered in the whole sediment column. In the uppermost 8 cm, the amount of ship clinker is negligible, the ash and soot particles are small and not frequent. Below 11 cm depth, ship clinker particles are more common and getting larger, up to 1 cm in diameter (Fig. 3.2a). The occurrence and the size of ash particles from the steam shipping seem to be independent variables and may validate the dating of the core.

^{210}Pb has an irregular profile in the sediments, which does not well fit to logarithmic distribution (Fig. 3.2b, Appendix 4), but concentrations nevertheless rise upwards. In the uppermost centimeter, the activity of ^{210}Pb decreases due to probable loss of sediments during coring. Therefore, the modern lead activity level was assumed as x-intercept of a regression

Table 3.1. The results of radiocarbon analysis of two bivalve shells from depth 18-20 and 38-40 cm in core PF1738b.

Laboratory number	Sample description	Corrected pMC*	$\delta^{13}C$(‰)**	Conventional age, BP	Conventional age, AD	Calibrated age, AD***
KIA 36953	PF1738b-20, 2.2 mg C	92.35 ± 0.29	-1.46 ± 0.24	640 ± 25	1310 ± 25	1530-1650
KIA 36954	PF1738b-40, 2.5 mg C	90.46 ± 0.27	-1.77 ± 0.16	805 ± 25	1145 ± 25	1430-1480

* Corrected pMC indicates the percent of modern (1950) carbon corrected for fractionation using the ^{13}C measurement.

** The $\delta^{13}C$ includes the fractionation occurring in the sample preparation as well as in the AMS measurement and therefore cannot be compared to a mass-spectrometer measurement.

*** Calibrated age was calculated using Marine04 calibration curve and delta R=-67±66.

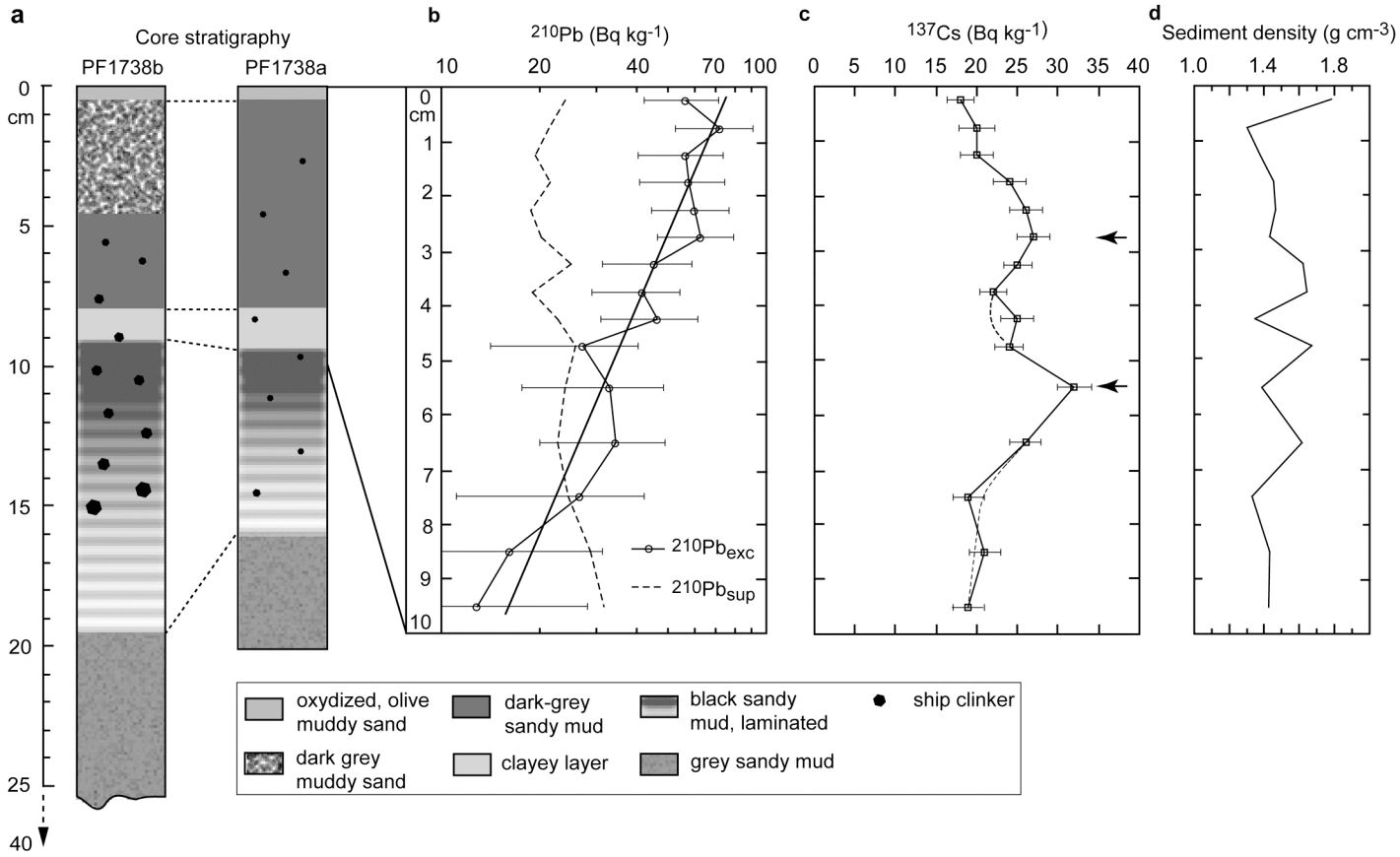

FIGURE 3.2. Composite diagram of visual stratigraphy of uppermost 25 cm of cores PF1738b and PF1738a (**a**), ^{210}Pb activity (**b**), ^{137}Cs activity and potential historical identification (**c**) and sediment bulk density (**d**) in core PF1738 from the outer Kiel Fjord. The error bars on curve $^{210}Pb_{exc}$ (plot b) depict 2σ, the error bars on curve $^{210}Pb_{sup}$ (plot b) are omitted, generally 2σ is 17-34 %. Doted curves (**c**) show at 4 cm a smoothing of the ^{137}Cs profile which is probably a result of sediment disturbances and signal "dilution". The second dotted curve at approx. 9 cm smoothes the profile because of high measurement uncertainties. The arrows designate the main ^{137}Cs peaks, which are discussed later. The size of dots on lithological columns (a) indicates the relative size of ash and clinker particles from steam shipping.

line. ^{137}Cs shows a broad peak at 2.75 cm, a dominating peak at 5.5 cm depth, and two smaller peaks at 4.25 cm and 8.5 cm which are not clearly distinguishable from the baseline within the errors (Fig. 3.2c).

Radiocarbon dating was consistent as both carbonate samples gave enough carbon and produced a sufficient ion beam for AMS measurements. The ^{13}C values were in the normal range of marine carbonates in this area. Thus the results are considered reliable from the analytical side (Table 3.1).

For radiocarbon chronology, the calibration of conventional years to calendar years was made with CALIB 5.0 Radiocarbon Calibration Programme based on the curve Marine04 (Hughen et al., 2004) and delta R = -67±66 for correction on regional reservoir age. This delta R is the mean of data available for the south-western Baltic Sea (Marine Reservoir Correction Database) and is supposed to be reliable for Kiel Fjord too. The calibration revealed an age of AD 1596±25 for the layer 18-20 cm and AD 1460±25 – for the 38-40 cm layer.

However, the uncertainty of plateau/shoulder in the Marine04 calibration curve from about AD 1550 to 1640 includes the calibrated interval. As such, the age of the slice extends from ca. AD 1530 to AD 1650 (P. Grootes, pers. comm.). The Marine04 calibration curve is very steep in the region about AD 1460, which does not allow precise calibration. The date of 38-40 horizon indicates then interval from AD 1430 to 1480.

3.5 Discussion

3.5.1 ^{137}Cs imprint

The uppermost ^{137}Cs peak at the depth 2.75 cm records most probably the Chernobyl accident in 1986. It is the latest one in the profile and the shape of the peak is similar as in the cores described elsewhere for the Baltic Sea (Christiansen and Kunzendorf, 1998; Kunzendorf, 1999; Christoffersen et al., 2007, Fig. 3.3). The shape of the upper ^{137}Cs peak apparently links to upward and downward redistribution of ^{137}Cs due to bioturbation (Farmer, 1990; Brack and Stevens, 2001), or to mobility of ^{137}Cs under anoxic conditions in presence of NH_4^+ as well as in coarse grained sediments (Sholkovitz, 1985; Crusius and Anderson, 1995). The shape of ^{210}Pb profile at this depth also implies some disturbance.

Nevertheless the atmospheric transport and the discharge from the adjacent land contribute significantly to the ^{137}Cs activity in Kiel Bight to create a pronounced peak after Chernobyl fall-out (Kautsky, 1981; Nies and Wedekind, 1987). The sedimentation rate in the upper 3 cm

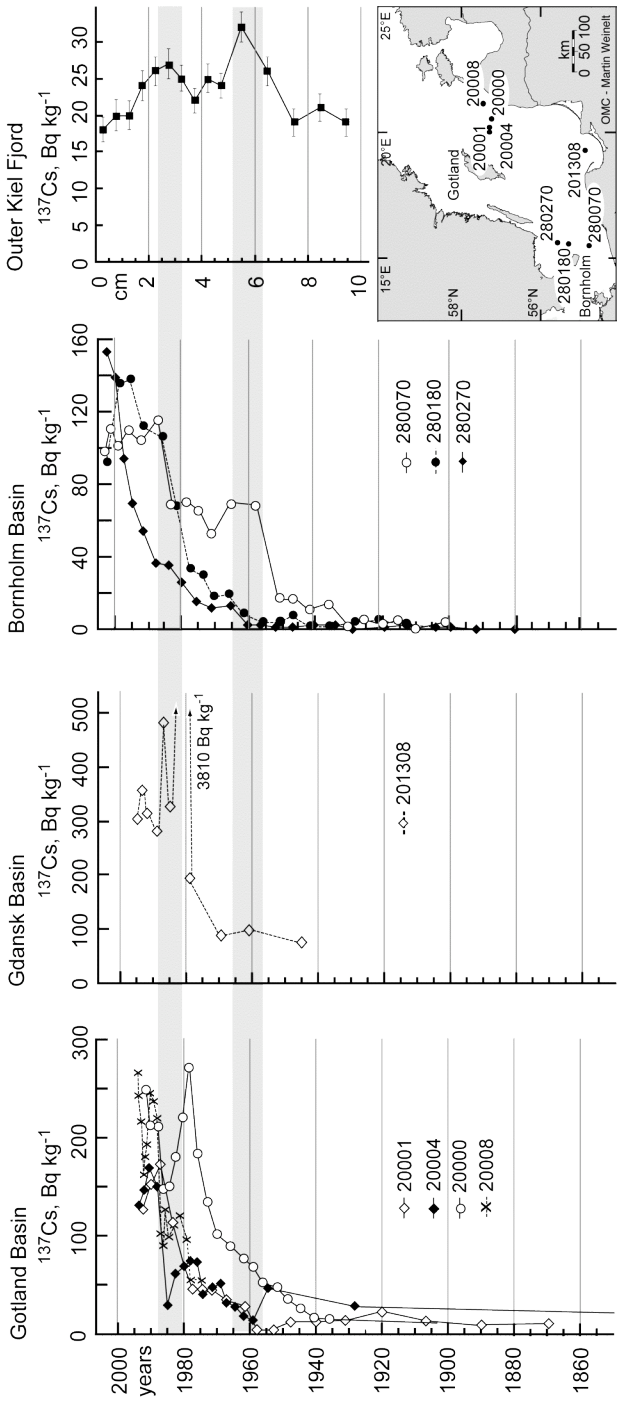

FIGURE 3.3. Variations in ^{137}Cs activities in the cores from Gotland, Gdansk and Bornholm Basins (locations of stations are shown on map) and the outer Kiel Fjord. Shaded areas depict the nuclear bomb testing and Chernobyl accident fallout events (Christiansen and Kunzendorf, 1998; Kunzendorf, 1999; Christoffersen et al., 2007)

is 1.3 mm a^{-1} on average estimated from the time span and thickness of sediments deposited during that time. The second prominent peak at 5.5 cm depth can be explained in two ways: Scenario 1 supposes that the large ^{137}Cs peak at depth 5.5 cm corresponds to the global atmospheric fall-out due to the bomb testing with a maximum in 1963. Thus the sedimentation rate in the middle part of the core from 2.75 to 5.5 cm would be 1.2 mm a^{-1}. Subsequently the small increase of ^{137}Cs activity at 4.25 cm between 1963 and 1986 would correspond to the Sellafield discharges in 1971-1973. Whereas the 8.5 cm increase does not exceed the uncertainties of measurements and would be reduced below 5.5 mm.

Scenario 2 refers the 5.5 cm peak to the year 1973 when the maximum of Caesium was observed in North Sea waters (Vintro et al., 2000). Thus the mean sedimentation rate between 2.75 and 5.5 cm e.g. 1986 and 1973 would be 2.1 mm a^{-1}. The slight increase of radioactive caesium at 8.5 cm sediment depth may be related to 1963 accordingly, and the mean sedimentation rate between 5.5 and 8.5 cm then would be 3 mm a^{-1}. The smooth peak at 4.25 cm in this scenario may be interpreted as formed due to "dilution" of signal.

Some papers (Christiansen and Kunzendorf, 1998, Emeis et al, 2000) described enhanced ^{137}Cs levels in the sediment cores from the Baltic Sea Deeps, a sink of the North Sea inflow water, associated with Sellafield discharges (Fig. 3.3). When elevated activity of ^{137}Cs was observed in the North Sea and the Kattegat, the monitoring of ^{137}Cs in the surface waters of Kiel Bight did not show the increase of ^{137}Cs activity in 1971-1973 (Helcom, 1991; BSH, 2008). In the bottom waters, the increase in ^{137}Cs content was detectable but very low in the Schlei mouth and off Kiel Fjord (Murray and Eicke, 1977, Kautsky, 1981). Indeed, the increase of ^{137}Cs in Kattegat water does not mean obligatory that one had enhanced concentrations of radionuclides in the waters of shallow Kiel Bight and Kiel Fjord because the inflow water bypass this area and is trapped in Gotland Basin and other deeps. Therefore, the first scenario with fallout events at ~3.0 cm and 5.5 cm sediment depth appears to be more plausible and provides the preferred geochemical age model. Scenario 1 reflects rather constant sedimentation rates around 1.3 mm a^{-1} whereas Scenario 2 implies continuous decrease from at least 3 mm a^{-1} to 1.2 mm a^{-1}.

3.5.2 ^{210}Pb chronology

The choice of the appropriate model is crucial for ^{210}Pb chronology. CRS model is the only one taking into account the variable sedimentation rates (Robbins and Erdington, 1975; Appleby and Oldfield, 1983; Appleby and Oldfield, 1992) as well as compaction and dilution of sediments. However, the CRS model cannot be used in the mixed layers (Farmer, 1991). Moreover, the CRS model has two requirements: precise measurements of ^{210}Pb and the exactly identified depth of equilibrium between ^{210}Pb and ^{226}Ra (Joshi et al, 1988; Emeis et al., 2000). Thus, on the one hand for the unconsolidated sediments of the Baltic Sea the CRS model is more appropriate (Emeis et al., 2000), but on the other hand, Baltic Sea sediments are frequently disturbed (Gellermann et al., 1990). The non-monotonic ^{210}Pb profile (Fig. 3.2a) in the core from the outer Kiel Fjord points to the feasibility of the CRS model for age calculations (Appleby et al., 1986). In this case study, however, the use of the CRS model is constrained by the sampling strategy and the analytical method with major aim on ^{137}Cs detection. This results in high depth resolution but little material is available for analysis due to small diameter of the core. The gamma-radioactivity method gave quite imprecise ^{210}Pb concentrations (2σ 15-35 %). In turn, high uncertainty in ^{210}Pb levels (Fig. 3.2a) and shallow measurement depth in sediments made it difficult to designate a level where ^{210}Pb and ^{226}Ra activity are in equilibrium.

The age derived from the activities of ^{210}Pb in the uppermost layer and in the lowermost layer according to the law of radioactive decay (linear interpolation model) showed that the

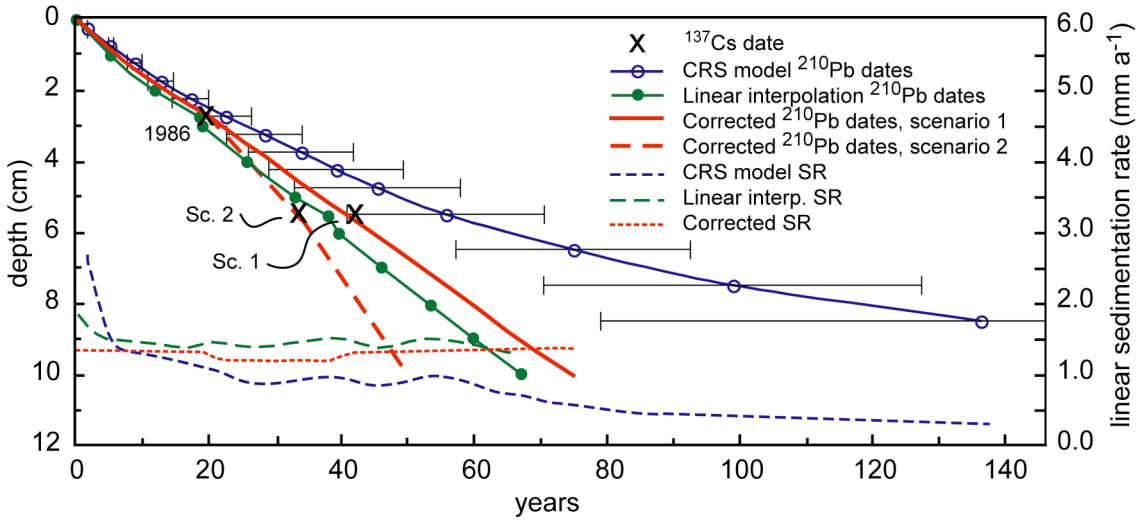

Figure 3.4. The ^{210}Pb and ^{137}Cs chronology of core PF1738a from the outer Kiel Fjord. CRS model dates were calculated according to Appleby (2001). Scenario 1 and Scenario 2 are described in text. SR – sedimentation rate.

10 cm of sediments cover a time span of about 70 years. In contrast, the CRS model with an assumption that at 9.5 cm the activity of ^{210}Pb reaches equilibrium with ^{226}Ra, showed the core bottom age to be 135 calendar years (Fig. 3.4). However the age derived from CRS model does not correlate to ^{137}Cs derived dates in Scenario 1, whereas the correlation with ^{137}Cs in Scenario 2 is even worse. The sedimentation rates and age calculated by linear interpolation also did not well corroborate with the large 5.5 cm ^{137}Cs peak. Therefore, the corrected age model was constructed by linear interpolation of excess ^{210}Pb in the sediments between the known ^{137}Cs dates.

The part below 5.5 cm (year 1963) comprises about 30 years, when sediments accumulated with the rate 1.4 mm a^{-1}. Linear sedimentation rates till 1963 were accepted from ^{137}Cs dates in Scenario 1. Therefore the mean sedimentation rate in 10 cm depth of the core is about 1.3 mm a^{-1}. According to radiocarbon dates, the sedimentation rate below 10 cm decreases to 0.3 mm a^{-1} with a subsequent increase to 1.5 mm a^{-1} from 19 to 39 cm (Fig. 3.5).

The downcore distribution of coal and ash particles from steam shipping period confirms the developed chronology (Fig. 3.2a). After the 1940s only negligible amount of ash was encountered, whereas earlier than the 1920s a lot of ash and ship clinker particles were found. Indeed, the flourishing of the steam shipping fell on the period from the 1840s to 1920s, when steam ships transported the most of goods and passengers (Couper, 1972; Bunker and Ciccantell, 2005). In the 1860s, the amount of coal consumed in steam ships significantly decreased (Marshall, 1995). This decline is reflected in the gradual downcore increase of size and amount of ship clinker particles from depth 12 cm to 20 cm where relatively large (>10 mm) slag pieces occurred.

All obtained sedimentation rates are comparable to those derived from dating of sediment cores retrieved in different time in Kiel Bight and in the adjacent area

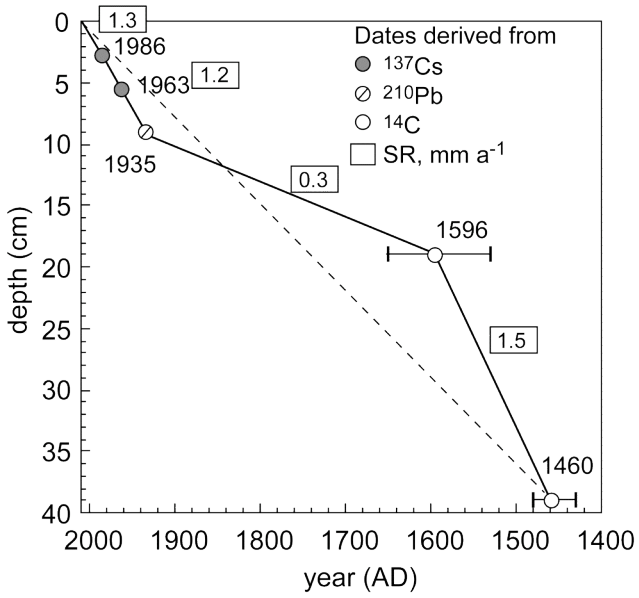

FIGURE 3.5. Composite chronology of core PF1738b based on ^{137}Cs and ^{210}Pb records in sediments and ^{14}C dating of bivalve shells. SR – linear sedimentation rate.

(Erlenkeuser et al., 1974, Whiticar, 1978; Balzer et al. 1987; Müller et al., 1980; Brügmann and Lange, 1990). However the drastic changes in sedimentation rate along the core are unexpected, though an inhomogenity in the recent sedimentation rates was reported, for example by Balzer et al. (1987) for Eckernförde Bay.

The largest part of the period of slow sedimentation fell into the Little Ice Age (Jones and Bradley, 1992; Grove and Switsur, 1994). It is showed (Nesje and Dahl, 2003) that at that time the winter precipitation over the Baltic Sea region was higher than at present time that should principally intensify the land runoff, suspension influx and sedimentation. However, in the cores PF1738 from Kiel Fjord this is not a case. Sedimentation rate variations are apparently induced by variations in erosion intensity while the main source of sediments in Kiel Fjord is erosion and redeposition of material from coastal cliffs built by Pleistocene till (Seibold, 1971). On the other hand, the compaction may partially be responsible for changes of linear sedimentation rates though the fluctuations of bulk density of sediments along the core provide no evidence for it (Fig. 3.1c).

3.6 Conclusions

The irregular distribution of ^{210}Pb through the core together with the ambiguous profile of ^{137}Cs made the construction and validation of age model difficult. The linear interpolation of ^{210}Pb profile between the known ^{137}Cs dates of Chernobyl accident and most probable imprints of bomb testing fall-out was chosen to calculate the age of the core whereas the Sellafield discharges imprint was unclear. Ten centimetres of the core correspond to 70 calendar years. The distribution of clinker and ash from steamship period in the core supports the obtained chronology in the upper 10 cm. The linear sedimentation rate was virtually constant for this time span with a mean value of 1.3 mm a^{-1}. Before the 1900s the sedimentation rate estimated from radiocarbon measurements was much slower on average 0.3 mm a^{-1}, whereas in period from ~1460 to ~1600 the sedimentation rate was maximum for this core 1.5 mm a^{-1}. The fourfold decrease of the sedimentation rate during the Little Ice Age is unclear. At that time the precipitation over the Baltic region was higher, thus the land runoff and erosion of cliffs were more intensive that should lead to the increase of sedimentation rates, but it is not the case for core PF1738.

Chapter 4

Sedimentary record of anthropogenic impact *versus* natural changes in Kiel Fjord

Abstract

The distribution of organic matter, trace and minor elements as well as grain-size distribution were analysed in a core from the outer Kiel Fjord. The organic matter and trace elements, immobile and redox-sensitive species showed an upward decrease from the base of the core corresponding to 1600-1700 AD to the water-sediment interface. This decrease on a first instance is apparently explainable by a dilution effect caused by the upward coarsening of the sediments and the increased sedimentation rates in the twentieth century. The periodical oxygenation of the sediments also contributes to the observed downward redistribution of redox-sensitive metals. The general coarsening of sediments in the upper part of the core might be caused by coastal protection measures reduced cliff erosion, which diminished the availability of the fine-grained detrital sediment.

The intensive eutrophication due to sewage input in the 1940-1970s is reflected in the accumulation of organic carbon and nitrogen in the core. The elevated fluxes of trace metals during the late 1930s correspond to the period before the Second World War, when active shipbuilding and harbour construction occurred in the inner Kiel Fjord. Copper and zinc also exhibit an anthropogenic enrichment in the 1970-1990s, whereas Pb, Sn and Cd concentrations are apparently unaffected by anthropogenic activity during this time. The distribution of redox-sensitive elements in the core implies that no long-term anoxic events have occurred in the outer Kiel Fjord during the last centuries. It is shown that the U:Mo ratio may serve a suitable indicator to reconstruct past bottom water oxygen conditions.

4.1 Introduction

In the Baltic Sea, eutrophication and anthropogenic pollution are major concerns (Helcom, 2002). Pollution in coastal waters results in the accumulation of harmful substances in the sediments, water column and biota (Brügmann and Lange, 1990; Olsson et al., 2002; Gerlach, 1996; Rheinheimer, 1998). Anoxia and hypoxia of the sea bottom and changes in community structure and abundance of biota may also occur (Weigelt, 1987; Bonsdorff, 2002; Wasmund and Uhlig, 2003). Sediments provide a temporally integrated record of such environmental changes and are valuable archives of eutrophication and pollution trends in coastal areas, in particular where high sedimentation rates allow high-resolution sampling. Moreover, rapid sedimentation provides minimal diagenesis and the preservation of the signatures of the pollutants (Callender, 2000).

In the western Baltic Sea one of the first studies of recent sediments (Erlenkeuser et al., 1978; Balzer et al., 1987) was carried out in Eckernförde Bay and revealed strong anthropogenic enrichment in copper and zinc in comparison with the preindustrial background as a result of contamination by ship clinker and combustion of fossil fuel. Later, Brügmann (1990) and Borg and Jonsson (1996) investigated the cores from the Baltic Sea and showed the enrichment of trace metals and organic carbon near the surface of the cores but the degree of enrichment varied between the sites depending on their depositional regime. A core from Lübeck Bight (Leipe et al., 1998) revealed synchronously enhanced levels of organic carbon and lead, copper, and cadmium in a distinct subsurface layer indicating the remediation of environmental conditions during the last decade after the diminution of pollutant discharges.

Early studies focused on trace metals as main pollutants, but in the 1990s Danish estuaries (Clarke et al., 2003), Swedish fjords (Blomqvist et al., 1992), Norwegian fjords (Brack and Stevens, 2001) and the Gulf of Finland (Kauppila e al., 2005; Vaalgamaa and Korhola, 2004) have received attention by studies to assess the sewage history, eutrophication and to quantify changes in nutrient concentrations. Recent studies in the Baltic Sea use a multi proxy approach comparing the chemical composition of sediments with organic remnants and the history of human disturbance (e.g. Ellegaard et al., 2006).

Many studies assumed rapid transport of organic matter and metals associated with the settling of inorganic particles and biogenic detritus from the water column to the bottom, as well as a little or no postdepositional disturbance of the sediments (Farmer, 1991). However, the distribution of contaminants under anoxic conditions (Piper, 1971; Paetzel et al., 1994;

Adelson et al., 2001) showed that redox changes in the sediments can lead to a redistribution of trace elements. This can be misinterpreted as human impact, for example, extremely high levels of copper and cadmium appeared of diagenetic origin rather than anthropogenic. Therefore, some trace elements such as Cd, U, Mo, V have attracted attention as potential tracers of past redox conditions in the sediment and the water column (Calvert and Pedersen, 1993; Rosenthal et al., 1995; Crusius et al., 1996; Morford and Emerson, 1999; McManus et al., 2005; Tribovillard et al., 2006).

The sediments of bays and fjords of the western Baltic Sea has been extensively investigated (Müller et al., 1980; Balzer et al., 1987; Leipe et al., 1998), but Kiel Fjord was not addressed by complex studies despite a long history of human impact.

Here I study the geochemical composition of a sediment core taken from the less anthropogenically disturbed outer part of Kiel Fjord. To analyse the eutrophication trend in comparison with sewage discharges in Kiel Fjord, organic matter compounds were traced in the core. The development of shipbuilding, harbours growth, ship traffic and urban runoff are supposed to be reflected in the abundance of trace metals such as copper, zinc, lead, tin and cadmium. The record of manganese, iron, uranium, molybdenum and vanadium is interpreted to reflect the oxygenation of water column. These records and the chronostratigraphy of the sediments help to understand, which factors have mainly governed the distribution of anthropogenic metals and the overall accumulation of substances in the sediments of Kiel Fjord. The degree of correlation between pollutants and the activity of the local industry and urbanization combined with the natural variability provide insights into the sensitivity of the system to different perturbations.

4.2 Environmental settings

4.2.1 Bathymetry and hydrology

Kiel Fjord is a shallow narrow bay within the Kiel Bight (Fig. 3.1, Fig.4.1). Although the Kiel Bight is enclosed to the west and south, it is exposed to the influx of highly saline Kattegat waters from the northwest and less saline waters from the Baltic proper. Water in Kiel Bight is mesohaline and due to the relatively shallow depths the density structure of the water column is salinity- rather than temperature- dependent. The water depth in the outer fjord varies from 17 to 25 m. Inflows from the Kattegat reach Kiel Fjord almost annually and refresh the water bodies in the deep channels by increasing their salinity and oxygen content.

Kiel Fjord is well stratified during the summer period and less stratified during winter and

spring. During May and June, a clear halocline at 8 m depth separates bottom- from surface-water. While the inner fjord is dominated by relatively fresh and stagnant waters, hydrological conditions in the outer fjord are similar to those in Kiel Bight. The near-bottom currents transport water from Kiel Bight into the inner fjord along the west coast, whereas the less saline surface water flows out of the fjord along the east coast (Themann, 2002).

During the season from September to March when winds from northeast prevail, the influence of waves and erosion are significant along the western coast of the outer Kiel Fjord while along the eastern shore the wave effects are poor (Schwarzer and Themann, 2003).

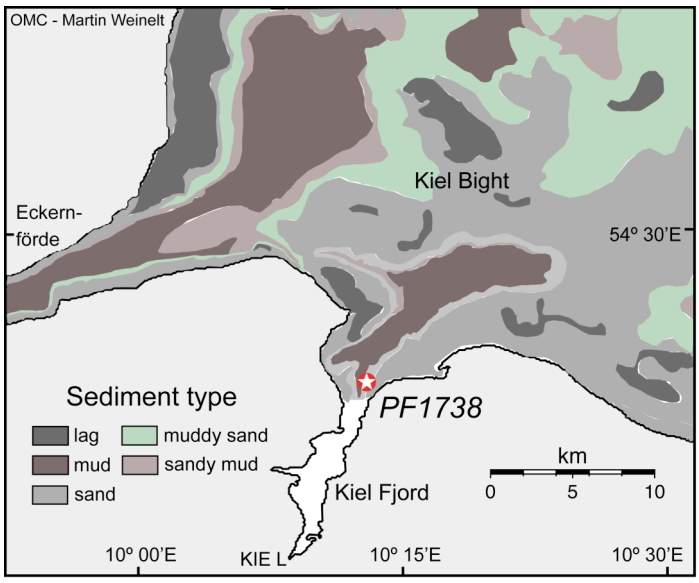

FIGURE 4.1. Location of the sampling site and distribution of sediments in Kiel Bight. The sediment type map is modified after Babenerd and Gerlach, 1987 and Kögler and Ulrich, 1985. For bathymetry and nearshore sediment transport see Fig. 3.1.

4.2.2 SEDIMENTS

The coastline of the inner fjord is overbuilt and used for shipyards, ferry terminals and harbours. Nevertheless some natural coast sections exist along the outer fjord comprising active and inactive cliffs, lowlands and some sandy beaches. The nearshore sediment transport is mainly directed from North and South into the fjord (Kachholz, 1982; Schwarzer and Themann, 2003, Fig. 3.1).

Pleistocene till forms the sea bottom and builds the cliffs surrounding Kiel Bight. The till is the most prominent source of sediment in this area. It consists mostly of quartz, feldspar and clay minerals. Additional sources of material are fluvioglacial sands, glacial lake mud, and

Holocene sediments (Seibold et al., 1971).

In general, two types of sediments occur in the outer fjord (Fig. 4.1). At water depth of more than 15 m, sediments contain up to 70 % of silt and clay with high contents of organic compounds prevailing. At shallower depth sandy sediments with a silt and clay content less than 35 % dominate (Seibold et al., 1971). The heavy ship traffic is supposed to affect sediment distribution in the shallow parts (Schwarzer and Themann, 2003) but at depth of 15 m and below the sediments should not be affected.

4.2.3 PRODUCTIVITY

In terms of productivity, Kiel Bight and Kiel Fjord are considered as mesotrophic areas with an annual primary production of 125-175 g m^{-2} y^{-1} (Wassmann, 1990; Smetacek, 1980). Only a third of this organic matter reaches the sea floor and is incorporated in the sediments (Smetacek, 1980).

4.2.4 ANTHROPOGENIC LOAD

The human activity on the coasts of Kiel Fjord started early (Fig. 4.2). At the beginning of the 19th century Kiel was a small town with 30 thousand inhabitants, living mostly of fishing and agriculture. In 1838, the foundry was established together with a ships' repair workshop which was the beginning of Howald Deutsche Werft, one of the largest shipyards in Germany. In the 1870s Kiel was chosen as a center of Prussian Navy and started to grow and develop the harbours. In the 20th century the population of Kiel increased by a factor of eight in comparison with the beginning of 19th century.

However, all domestic wastewaters were still released directly in the fjord without treatment. The increase of particulate organic matter and nutrients input stimulated primary

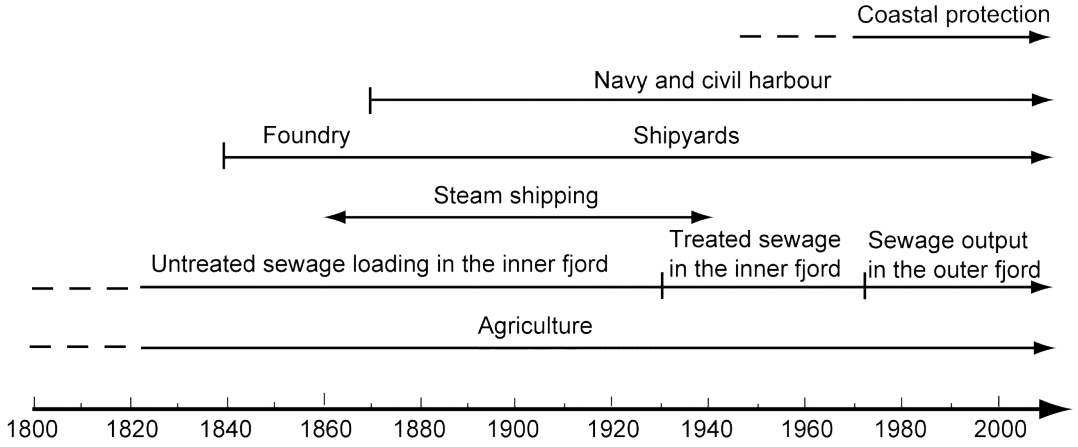

FIGURE 4.2. Timescale showing the time period of sewage loading, construction activities and industries in the vicinity of Kiel Fjord.

production, which was the reason why bottom water oxygen deficiency and hydrogen sulfide formation occurred (Kallmeyer, 1997; Rheinheimer, 1998). A centralized sewage system was introduced in 1929, but nevertheless treated domestic waters were discharged into the inner fjord. After 1972 the central city treatment plant came into operation and output of sewage discharges started in the outer fjord. The environmental situation of the whole fjord improved, primary production declined and oxygen deficiency has occurred seasonally due to the lack inflows originating from Kiel Bight (Gerlach, 1984, Gerlach, 1996, Haarich et al, 2003). In 1972/73 the sewage plant Bülk Klärwerk discharged 2427 t a^{-1} of nitrogen and 252 t a^{-1} of phosphorous, whereas by 1990 the amount of nitrogen had been reduced to 1306 t a^{-1} and 9 t a^{-1} phosphorous. Nevertheless, no declining trend in phytoplankton production as derived from chlorophyll measurements was recognizable in the nearby Eckernförde Bay (Gerlach, 1996). In the 1980s, an increase in the abundance of phosphates was recorded in Kiel Bight (Gerlach 1990), and between the 1960s and 1990s, the nitrogen portion from atmosphere sources doubled in water of Kiel Bight (Gerlach, 1996).

The discharge of trace metals into the fjord apparently started with the sewage input as some metals namely zinc, copper and cadmium are enriched in sewage water (Förstner, 1980; Bricker, 1993). A flourishing of steam shipping in the middle of 19th century and the active shipping through Kiel Canal may also have contributed to the metal input. The influence of shipping is undoubted because a lot of ship clinker particles were found in the near-surface sediments. Ship clinker contains extremely high concentrations of trace metals such as Zn, Cu, Pb and Cd (Erlenkeuser et al, 1974). At the same time the shipbuilding industry was established, and the input of metals such as lead, tin and zinc, which were or still are widely used in anticorrosive coating and antifouling paints, increased. Burning of fossil fuels and municipal transport (Förstner, 1980) are additional sources of lead, cadmium, zinc, and copper. The main fraction of anthropogenic lead is considered to enter the water column and sediments from the atmosphere and urban surface runoff. Nowadays, in general, the metal input into Kiel Bight mainly occurs through the atmosphere (Schneider, 1987), while river input is negligible. Under natural conditions a large part of metals were introduced by erosion of glacial clays.

The surface sediments of the inner Kiel Fjord contain increased concentrations of copper, zinc, lead and tin in comparison with the open Kiel Bight (Nikulina et al, 2008). An investigation of cores from the different bays of Kiel Bight in the 1980s showed surface maxima or substantial subsurface increase of metal concentrations in Eckernförde Bay

(Erlenkeuser et al, 1974), Flensburg Fjord (Müller et al., 1980), nearby Lübeck Bight (Leipe et al., 1998) and the Greifswalder Bodden (Rösel et al., 1996). Therefore it is reasonable to assume the increased anthropogenic metal concentrations together with organic matter, as marker of production have been recorded in sediments of Kiel Fjord.

4.3 Materials and methods

4.3.1 Sampling

Two double cores were taken in the outer Kiel Fjord in May 2007. These sediments have presumably never been disturbed while in the inner fjord a lot of dredging and transport activity have occurred. The sampling site was placed in the outer Kiel Fjord and is supposed to represent the conditions between the eutrophic fjord and the open Kiel Bight. The location of cores PF1738a and PF1738b is 54° 25.2348'N and 10°12.7092'W at 14.9 m water depth.

I used a Rumohr corer with a plastic tube 5.5 cm of diameter. It is necessary to note that such a small diameter of the tube could result in disturbance of the upper part of the core and compaction in the lower part (Farmer, 1991). However, both cores showed well-preserved sequences of layers by which they were correlated to each other.

Immediately after returning to the laboratory, the master core PF1738b (40 cm length) was sliced in 0.5 cm sections down to 10 cm and in 2 cm intervals from 10 to 20 cm depth for the geochemical analysis. The samples then were washed on 63 μm sieve. The clay and silt fraction was collected in jars, frozen, freeze-dried and powdered with an agate mortar.

The organic compounds and heavy metals were measured from the fraction < 63 μm. It was done, firstly, to avoid contamination by coal particles, soot and ash, which were encountered in all core layers, and secondly, to reduce bias from large particles with a low surface area in order to increase sensitivity in detecting contamination (Luoma, 1990; Irion, 1994).

The second core (PF1738a of 20 cm length) was taken for geochronological analysis based on ^{137}Cs and ^{210}Pb that described in Chapter 3. Knowing the sedimentation rate of about 1 mm a^{-1}, which is typical for Kiel Bight (Erlenkeuser et al, 1978; Müller et al., 1980; Balzer et al, 1987), the sediments from depth around 10 cm must represent the beginning of twentieth century when the most intensive human activity in the area of Kiel Fjord took place. The presence of coal and ship clinker particles throughout the core (Fig. 4.3) confirms that the core covers a time interval within the steam shipping era.

4.3.2 Grain-size analysis

In June 2008 a third 25 cm long core (PF1838) was taken at the same location as the previous two cores to analyse the grain-size distribution. It was dissected in 0.5 cm intervals. The samples were dried in the oven at 50°C. With known volume of the samples (0.5 cm x square of corer tube) and weight loss after drying, the bulk densities and water contents were calculated. Then the samples were washed through a 63 µm sieve to collect the fine fraction in jars. The fine fraction was further separated into grain size distributions of silt (2-63 µm) and the sortable silt (10-63 µm). Sodium polyphosphate solution was added to the fine fraction samples to facilitate sufficient homogenization of the suspension. The suspensions were thoroughly homogenised in a rotating carousel and were exposed to an X-Ray beam in Micrometric Sedigraph 5100. The attenuation of X-rays indicates the concentration of settling particles. The grain size analysis ranged from 1 to 63.1 µm and was performed with a density of quartz (2.654 g cm^{-3}) at a constant temperature of 35°C. Where the amount of sample was not enough for reliable measurement, two or three subsequent samples were combined.

4.3.3 Organic compounds

Concentrations of organic carbon, total carbon, total nitrogen, biogenic silica and pigments were measured as markers of primary production in the water column and preservation conditions in the sediments.

Measurements of organic carbon, total carbon and nitrogen were performed with a Carlo Erba NA-1500-CNS analyzer with a precision of ±1.5 %. The organic carbon was determined after removing carbonate carbon by acidification with 0.01 M hydrochloric acid. The inorganic carbon was derived from the difference between total and organic carbon. The carbonate fraction was determined according to their atomic weight ratios as $CaCO_3$ = 8.33•(TC-TOC). To investigate the sources of organic matter, the atomic C:N ratio was calculated.

The automated leaching method by Müller and Schneider (1993) was used to determinate the biogenic silica content. The opaline material was extracted from sample using sodium hydroxide at 85°C for about 45 min. The dissolved silica in the leaching solution was continuously measured by molybdate-blue spectrophotometry with an accuracy better than 1 %.

Chlorophyll *a* and phaeopigments abundances reflect the primary productivity (Harris et al., 1996) and terrigenous input of organic matter and were determined after acetone

extraction with a Turner TD-700 Fluorometer at IFM-GEOMAR with an uncertainty of ±10 %.

4.3.4 Metals

An array of elements was measured in the fine fraction: Cu, Zn, Pb, Sn and Cd represent those influenced by anthropogenic sources; V, U, Mo, Cd are redox sensitive metals enriched in the sediments under particular redox conditions; Ti is a marker of heavy mineral input; Ba is a marker of productivity; as well as Al, Fe and Mn serve to normalize the other elements to natural background.

The sediments were totally digested in a mixture of hot nitric, perchloric and hydrofluoric acids at 150°C. The solutions were dried and dissolved in 2 % nitric acid to be measured for trace metals with an AGILENT 7500cs ICP-MS (inductively coupled plasma-mass spectrometry) at the Institute of Geosciences, University of Kiel (Garbe-Schönberg, 1993) and for Al, Fe and Mn with an ICP-AES JY 170 ULTRACE (IFM-GEOMAR).

The reproducibility of replicate analyses of the samples is better than 4 % for trace elements and better than 1 % for minor elements. To evaluate the precision of measurements, a blank and the international standard BIR-1 and BHVO-2 were analysed together with the samples. The accuracy of analytical results as estimated from replicate standard measurements was better than 5-10 %.

4.4 Results

4.4.1 Stratigraphy and age of the cores

Three cores were taken at the same location in 2007 and 2008. They showed distinct bedding that allows correlating them. This lithostratigraphical correlation facilitated to develop a composite chronological model for the cores PF1738a and PF1738b. Cores were correlated to depth and age using Analyseries 2.0 (Paillard et al., 1996). The time scale thereafter is applied to the master core PF1738b (Fig. 4.3).

The age model developed for the cores was based on the high-resolution records of ^{137}Cs and ^{210}Pb in the upper 10 cm of core PF1738a. Radiocarbon dating was performed at bivalve shells picked at 18-20 cm and 38-40 cm in core PF1738b. The composite age model is discussed in Chapter 3, Fig. 3.5.

The ^{210}Pb chronology relates the sediments at the depth of 9 cm to year 1935. In the upper ten centimeter, the sedimentation rate varies around 1.3 mm a^{-1}. The linear sedimentation rate

decreases to 0.3 mm a^{-1} between 10 and 20 cm, and increases again to 1.5 cm a^{-1} between 20 and 40 cm. The distribution of ship clinker from the steam-shipping period (1860-1940) in three cores is in agreement with age model. The application of this age model allows me to describe the variations of organic matter and trace element contents over the last 400 years.

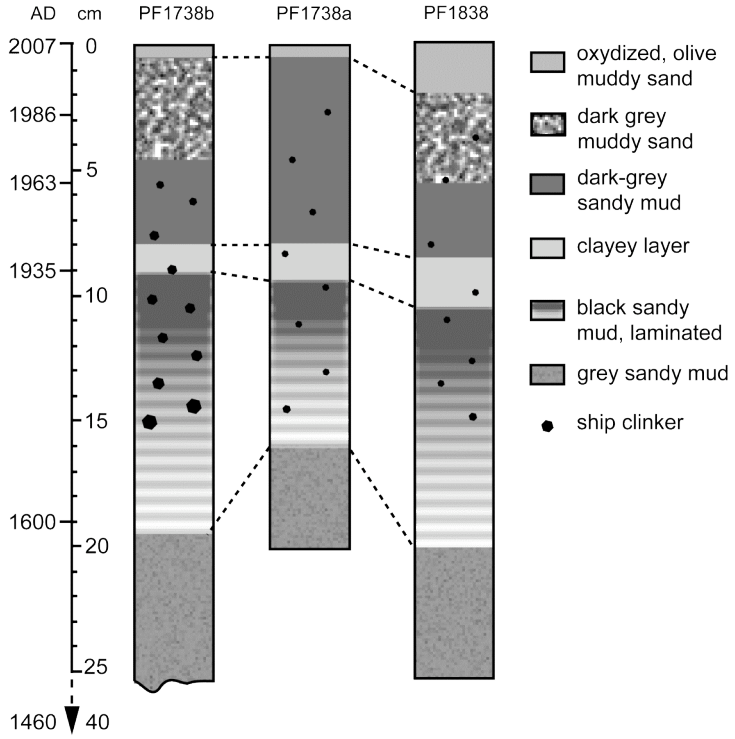

FIGURE 4.3. The visual stratigraphy of the upper 25 cm of the cores taken in the outer Kiel Fjord in 2007 and 2008. The size and frequency of the dots reflect the relative size and abundance of ship clinker particles encountered in the cores. The time scale refers to the age model described in Chapter 3.

4.4.2 GRAIN-SIZE COMPOSITION

Core PF1838 shows abrupt changes in sediment composition. Sand-rich sediments characterize the uppermost 8 cm, while silt and clay abundances are distinctly higher at 62 % and 19 % below, respectively (Fig. 4.4a, Appendix 5.1). The portion of clay particles remains rather constant throughout the core but the silt fraction shows two types of distribution of particles. At the base of the core a polymodal pattern of particle distribution prevails that indicates currents of variable strength. Above 7 cm, the polymodal distribution passes into an unimodal (Fig.4.4c, Appendix 5.2), which indicates that the sediments were deposited beneath high velocity current, which prevented the accumulation of fine-grain material at the site. The mean sortable silt exhibits a pronounced increase at the top of the core and a thin deeper layer

of coarser sediments is also distinguishable at 12 cm (Fig. 4.4b).

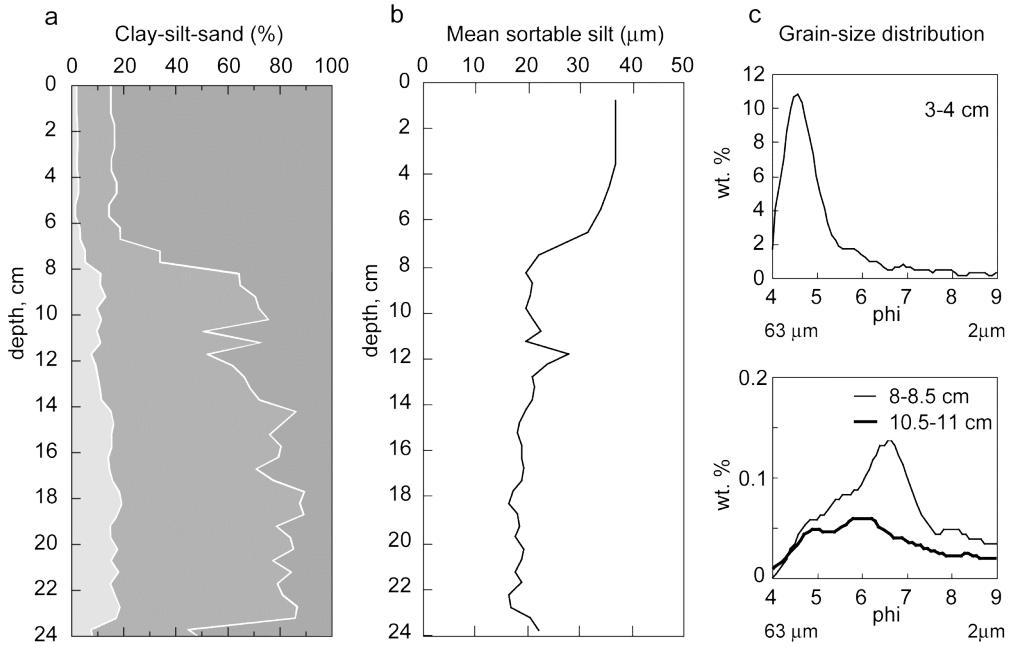

FIGURE 4.4. Sediment characteristics along core PF1838: (**a**) abundance of clay, silt and sand fractions in bulk sediment in %; (**b**) fraction of mean sortable silt; (**c**) typical particle distributions in the fraction 2-63 μm.

4.4.3 ORGANIC MATTER ACCUMULATION

The abundance of organic matter compounds changes along the core in a way similar to the grain size distribution (Fig. 4.5, Appendix 2.4). The mean content of organic carbon is about 2 %. Organic carbon represents 37-64 % of total carbon. Changes in total nitrogen concentration through the core are also pronounced from 0.19 to 0.49 % with an average of 0.27 %.

Organic carbon and total nitrogen show the upward decrease of concentrations from 20 cm to 9 cm depth, followed by slight increase from 9 cm to 5.5 cm depth. Above 5.5 cm, the concentrations subsequently decrease to 0.5 cm depth (the 1970s-2000s). Total carbon varies differently in the core. The increase is found again at the bottom part with the lowest concentration recorded at ~ 8 cm. Higher levels of total carbon are found in the upper 6 cm.

The biogenic silica content shows small variability but steadily decreases (Fig. 4.5) from 4.38 % at 20 cm depth to 1.63 % at the surface. The profiles of pigments closely resemble the biogenic silica distribution. Chlorine and chlorophyll *a* as well as phaeopigments contents decrease upward in the core too (Fig. 4.5).

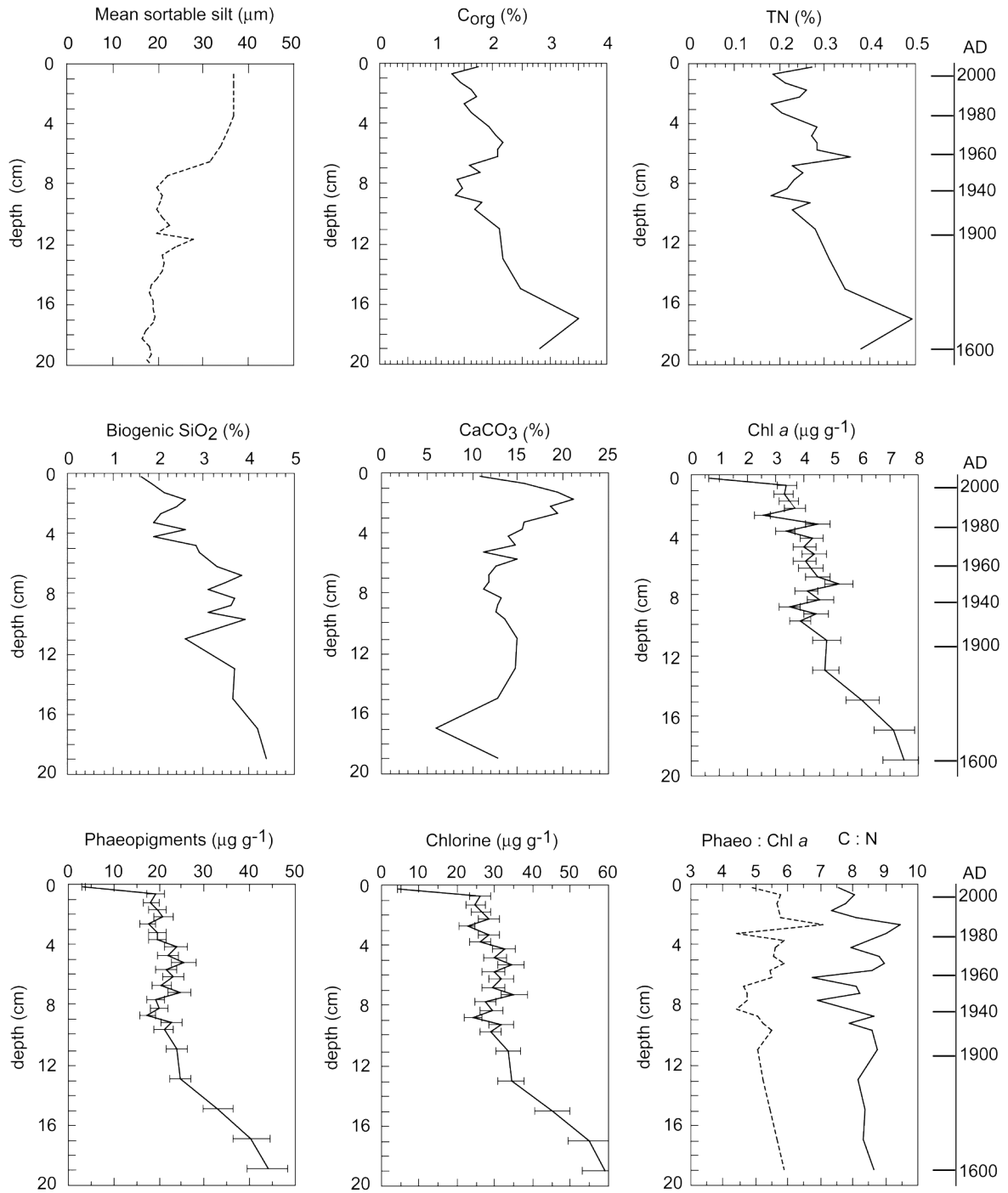

FIGURE 4.5. Variations of organic compounds and mean sortable silt for comparison within core PF1738 from the outer Kiel Fjord. The error bars indicate the measurement uncertainties (standard deviation) and are only displayed when they are significant for the interpretation.

TABLE 4.1. Variations in trace metals, organic compounds and sediment fraction percentage in the core PF1738. RSDm – uncertainty of measurements.

Component	Mean	Std. Dev.	RSD, %	RSDm, %
Ti (μg g^{-1})	4366	217	5.0	3.8
V (μg g^{-1})	70.3	5.86	8.3	3.4
Cu (μg g^{-1})	55.0	33.1	60.2	2.4
Zn (μg g^{-1})	165	37.8	22.9	0.8
Mo (μg g^{-1})	2.28	1.04	45.5	0.7
Cd (μg g^{-1})	1.08	0.15	13.5	0.9
Sn (μg g^{-1})	5.23	1.16	22.2	0.5
Ba (μg g^{-1})	397	17.0	4.3	0.4
Pb (μg g^{-1})	62.2	17.1	27.4	0.5
U (μg g^{-1})	2.81	0.28	10.0	0.6
Al (μg g^{-1})	37520	4201	11.2	3.8
Fe (μg g^{-1})	24472	2616	10.7	2.4
Mn (μg g^{-1})	457	58.3	13.0	0.4
TC (wt %)	3.57	0.43	12.1	1.5
TN (wt %)	0.27	0.07	25.9	1.5
Corg (wt %)	1.88	0.50	26.5	1.5
$CaCO_3$ (wt %)	14.08	3.20	22.7	1.5
SiO_2 (wt %)	2.97	0.79	26.7	1.0
Chl *a* (ng g^{-1})	4232	1353	32.0	10
Phaeo (ng g^{-1})	22739	7499	33.0	10
< 2 μm (wt %)	15.0	2.1	14.0	-
< 20 μm (wt %)	50.3	20.5	40.9	-

Taking into account the measurement precision (Table 4.1), the pigment abundances between 4 and 9 cm can be considered constant. The marked upward decrease from 20 cm to 9 cm is, however, significant. The upper 0.5 cm of the sediment contains very small amounts of all types of pigments in comparison with the underlying sections, even though the core was taken in the summer. The ratio of phaeopigments to chlorophyll *a* fluctuates about a value of 5 along the core (Fig. 4.5) and decreases in the uppermost centimeter of the core indicating the input of fresh detritus. Core PF1738 reveals similarity between the records of the C:N ratio and the pigment ratio.

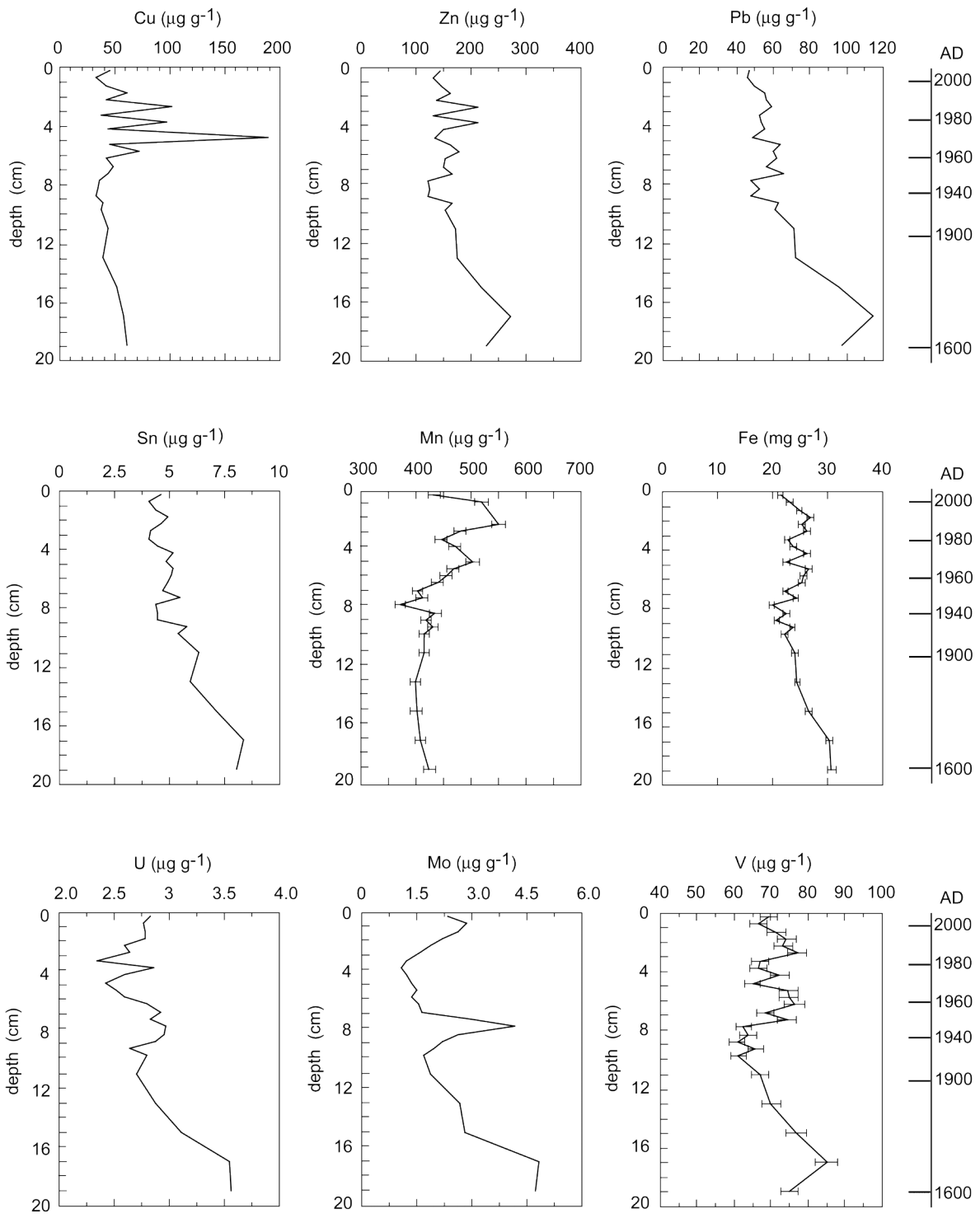

FIGURE 4. 6. Downcore variations in the concentrations of trace and minor metals in core PF1738. The error bars (1 St.Dev.) are shown only when they are significant for the interpretation of the variability.

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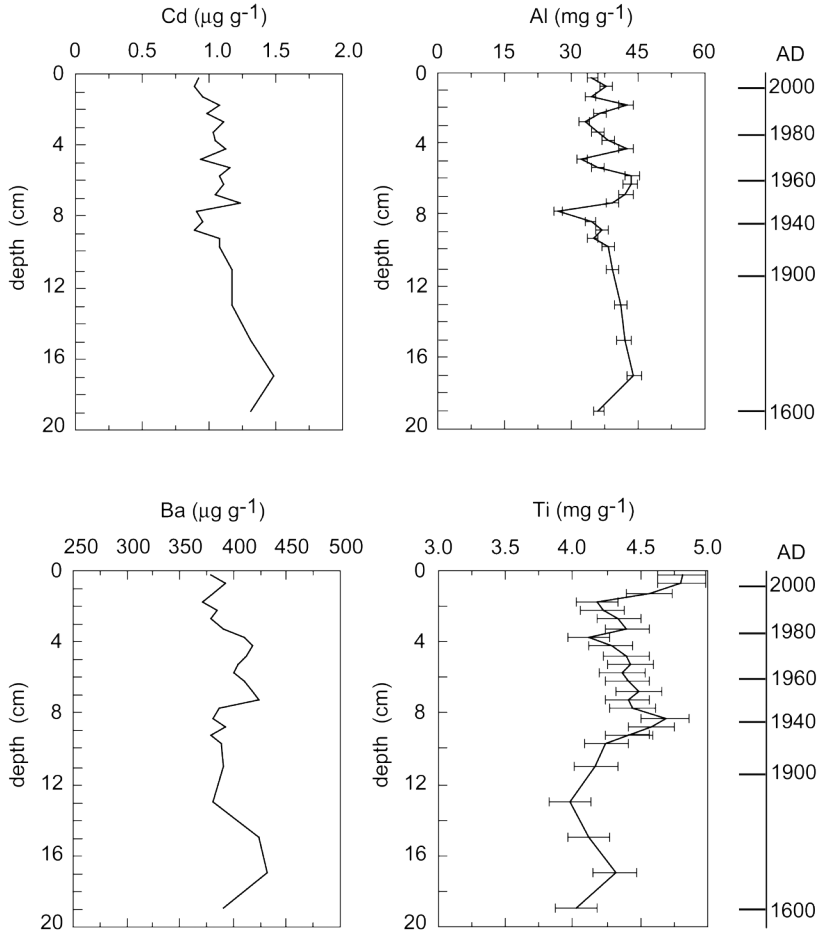

FIGURE 4. 6. Downcore variations in the concentrations of trace and minor metals in core PF1738. The error bars (1 St.Dev.) are shown only when they are significant for the interpretation of the variability.

4.4.4 DOWNCORE VARIATIONS IN METAL CONCENTRATIONS

Minor element and trace metal concentrations follow a general trend with distinctly high values at 16-20 cm core depth and a steady upward decrease (Fig. 4.6). Aluminum has the most invariant profile with value around 37 mg g^{-1}. Variations in barium content are also negligible. Trends in titanium concentrations are opposite to the other metals. It gradually increases from 4023 µg g^{-1} at the bottom of the core to 4808 µg g^{-1} at the surface sediments (Fig. 4.6, Table 4.1). However, taking into account the measurement errors, the variations of Ti are close to insignificant.

Those metals (Pb, Sn, Cd), which may potentially be introduced anthropogenically, do not show a consistent increase in concentration in the upper part of the core as may have been expected. Instead, high levels are observed at 19 cm for lead and tin. Their contents decrease from the bottom to the surface with some fluctuations in the upper 10 cm.

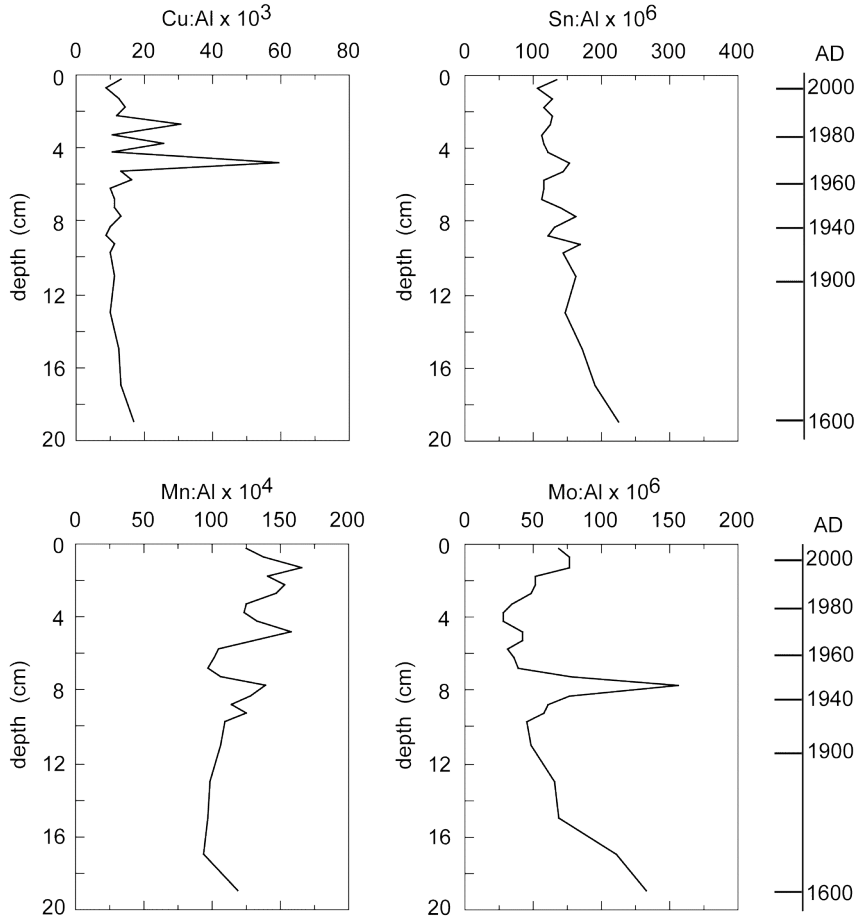

FIGURE 4.7. Distribution of some elements normalized to aluminum through core PF1738.

Zinc shows a similar distribution, except for two small peaks at 2.75 and 3.75 cm, which are ~25 % higher than the mean concentration. Copper content is quite constant throughout the core, though it shows peaks similar to Zn, and it is highly enriched at 4.75 cm (Fig. 4.6).

Manganese concentrations are constant with 400-430 μg g^{-1}in the bottom part of the core and increase in the upper sections. Manganese forms two broad peaks at 1.75 and 4.25 cm. Iron content does not show pronounced peaks. It decrease continuously from 31 mg g^{-1} at 20 cm to 10 cm. Iron levels vary about 24 mg g^{-1} in the uppermost ten centimeter. A similar downcore distribution characterizes vanadium and uranium (Fig. 4.6).

Cadmium exhibits the same features as vanadium and uranium, but with more pronounced relative increase of concentrations at the base of the core and lower concentrations in the 7-8 cm layer. Molybdenum concentration decreases from the base of the core to the upper part, than forms a sharp peak at 7.25 cm. The enhanced Mo levels in 15-19 cm depth are probably also a part of a subjacent peak.

All metals except Cu and Mn have significant linear correlations with organic carbon content (Appendix 2.7). Excluding outliers the correlation between copper and organic matter was also recognised (r=0.600, n=22). The strongest correlations with organic carbon characterize zinc, cadmium, tin and lead. Apparently, these metals are supplied to the sediments either together with organic matter or adsorbed and bound to organic matter.

Lead, Cu, Zn, Cd, Sn, V, and Fe correlate well with the aluminum (Appendix 2.7). Therefore metals were corrected to aluminum (Fig. 4.7) because Al content is more or less constant in the sediments of a region and in the core sampled. Normalized Sn, Pb, Fe, Cd and V show similar steady downcore concentration trend. Uranium and molybdenum show a tendency to accumulate at 8 cm, whereas, only Mn shows enrichment in the upper part of the core. Copper and Zn still show pronounced peaks at 2-4 cm but do not vary a lot otherwise in the core (Fig. 4.7). As aluminosilicates are constituents of the clay fraction, such distribution of metals indicates that the part of metals is absorbed on clay.

4.5 Discussion

4.5.1 Grain-size composition

Prevailing currents carrying fine-grained sediments from Kiel Bight to the inner, depositional part of Kiel Fjord explain the sandy character of the sediments in the outer Kiel Fjord. These general sedimentation dynamics, however, do not explain the coarsening of sediments in the uppermost part of the investigated sediment core.

The distribution of particle sizes in the fraction 2-63 µm allows to attribute the coarsening pattern to changes in the strength of currents. The polymodal distribution of particles (Fig. 4.4c) is associated with low energy currents and partial accumulation of the fine fraction. The unimodal distribution in upper 7 cm suggests that stronger currents prevailed during sediment deposition, which did not allow settling of fine particles (Höppner and Henrich, 1999; Rüggeberg et al., 2005). The SEM images of sediments from different core sections confirm the results of grain-size analysis (Fig. 4.8).

According to Seibold (1971), half of all winds and three quarters of the storms in Kiel Fjord are westerly. During strong winter storms, wave erosion is enhanced on the shallows, and compensating currents can carry sandy sediments at 6 m to 12 m depth (Seibold et al., 1971). Thus, the increased storminess in the 1980s (Alexandersson et al., 2000; Bärring and von Storch, 2004) can explain the upward coarsening tendency of the sediments of the outer fjord. Furthermore, an increase of sedimentation rates in the 20th century (Chapter 3) also

invokes an increased supply of sediments, which was accompanied by an increase in the sand content. Moreover, coastal protection in the 1970s increased the capture of fine particles in the inner fjord obviously contributed in the upward coarsening of sediments.

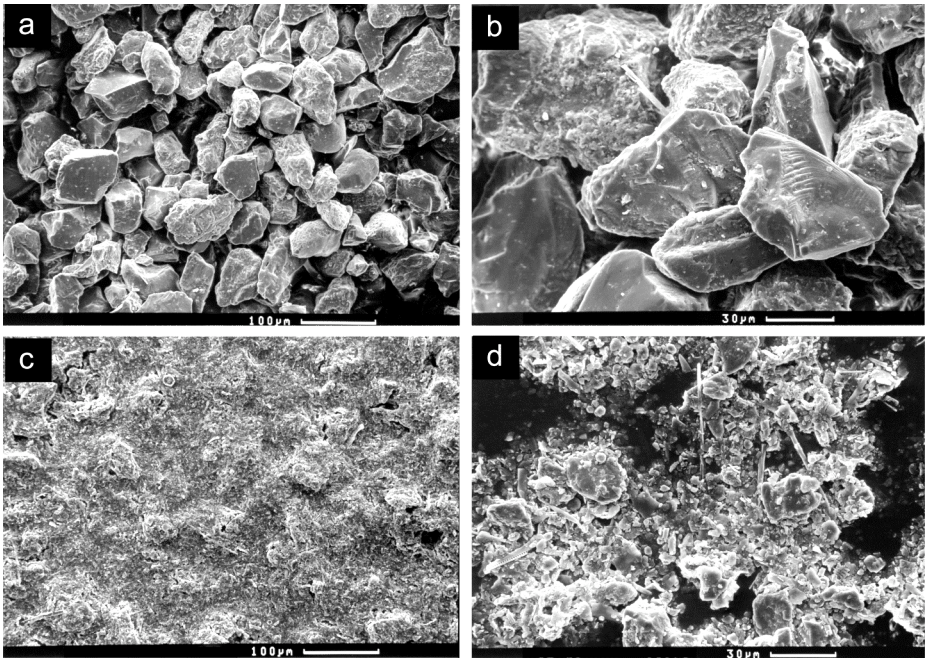

FIGURE 4.8. SEM photographs of the sediment fraction <63 µm: (**a**) at 12 cm depth, magnification 200, (**b**) 12 cm, × 600, (**c**) 20 cm, × 200 and (**d**) 20 cm, × 600. The images show a clear difference in the grain size distribution between core sections. The sediments have apparently glacial origin.

4.5.2 ORGANIC MATTER: SEWAGE INPUT *VS.* NATURAL VARIATION

The pattern of organic matter accumulation in the core from the outer Kiel Fjord is quite unusual because most of the Baltic Sea cores, including those from the fjords and bays of Kiel Bight, exhibit downcore decrease of organic matter (Müller et al., 1980; Balzer, 1984; Kauppila et al., 2005; Damm, 1992; Emeis et al., 2000; Clarke et al., 2006; Vaalgamaa and Conley, 2008). Such changes in the Baltic Sea are considered to be caused by a combination of increased organic matter input during last decades due to natural and anthropogenic eutrophication and decomposition of organic matter in the underlying sediments (Canfield, 1994). In cores from the Greifswalder Bodden, the accumulation of organic matter in the upper sediments was referred to changes in sediment sources (Rösel et al., 1996). Thus, the decrease of organic matter towards the water-sediment interface in the Kiel Fjord core might be a result of changes either in sedimentation rate or primary production. The role of productivity and oxygen availability in preservation of sedimentary organic matter has been discussed, but no consensus has been reached (Canfield, 1989; Fenchel and Finlay, 1995).

With sedimentation rate of about 1-1.3 mm y^{-1}, anaerobic conditions seem to have no significant effect on preservation (Calvert and Pedersen, 1991), which means that the organic carbon record in the sediments mainly reflects the productivity through time.

It is known that primary production in the inner Kiel Fjord increased as a consequence of high nutrient input in the middle of the 20th century (Rheinheimer, 1998). However, Stienen (1986) showed that nutrient status and phytoplankton dynamics in the inner part of Kiel Fjord differ considerably from those in the outer part. A substantial fraction of the nutrients entering the inner fjord is retained there by sedimentation and never reaches the open Kiel Fjord. Schiewer and Gocke (1996) also mentioned the gradient of nutrients and chlorophyll *a* as a measure of primary productivity from the inner to the outer Kiel Fjord.

The observed decrease of organic carbon from deep to surface sediments is not monotonic (Fig. 4.5). In the layer 5-9 cm (AD 1940-1970) an upward increase of C_{org} and TN values is observed, whereas in the section above 5 cm, which corresponds to the 1970s-1980s, levels of organic matter decrease. This part of record agrees with the history of sewage discharges in Kiel Fjord. The amount of sewage waters increased in the first half of 20th century with the growth of population in the city and diminished after the introduction of the central sewage plant in 1972. Therefore, the 1940-1970s accumulation rates of organic matter in the sediments are plausible because of the excessive input of particulate organic matter, the high availability of nutrients for phytoplankton growth, and a slow degradation of settled organic matter under anoxic conditions (Fenchel and Finlay, 1995). The remediation of environmental conditions obviously followed the intensification of the sewage treatment.

Although there are not a lot of data about the content of organic matter in the silt fraction, our values, at least organic carbon, appears to be slightly lower in comparison with data from other bays (e.g. Gerringa et al., 1990). This implies that the outer Kiel Fjord by trophic conditions is closer to the open Kiel Bight than to the eutrophied inner Kiel Fjord.

Biogenic silica as marker of diatom and dinoflagellate abundance and thus phytoplankton productivity (Conley, 1988; Conley and Schelske, 2001), does not change in line with organic carbon in core PF1738. A common response to increased nutrient loading, however, indeed is an increase of diatom biomass that leads to increased accumulation of biogenic silica in sediments and to a decrease in the dissolved silica reservoir in the water column (Conley et al., 1993; Beucher et al., 2004). Possibly, a lack of dissolved silica limited the diatom production, and therefore the contribution of this group of organisms in the total biomass decreased with time. Indeed, a decrease of the cold-water phytoplankton (diatoms) portion in

the bulk algae linked to warming was recognized during last decades in the Baltic Sea (Bonsdorf et al., 2002; HELCOM, 2007).

The weak fluctuation of chlorophyll *a* and total pigments around the mean in the upper 10 cm and then increase to the bottom of the core in general resembles the organic carbon record. Chlorophyll *a* and total pigments are marker of primary production and an indirect measure of oxygenation of the bottom waters and sediments, which governs the decomposition of pigments and herbivore digestion (Furlong and Carpenter, 1988; Leavitt, 1993; Sun et al., 1993; Meyers, 1997; Bianchi et al., 2000). In the Kiel Fjord core, chlorophyll *a* and overall pigments levels are lower relative to those from eutrophied bays of the Baltic Sea (Bianchi et al., 2002; Reuss et al., 2005). However, one has to keep in mind that they account only for the fraction finer than 63 μm. In the bulk sediments they are most likely even lower.

The ratio of phaeopigments to chlorophyll *a* is commonly used to estimate the degree of pigments decomposition because the parent compound chlorophyll *a* is readily degraded while the degradation products are more stable. Anoxic conditions in the water column and sediments preferentially prevent the decay of chlorophyll *a* in comparison with the decomposition of other pigments (Bianchi et al., 2000; Reuss et al., 2005). The phaeopigments to chlorophyll *a* ratio varies from 4.4 to 7.5 within the core (Fig. 4.5), suggesting an oxygen regime that favored the degradation of chlorophyll *a*. A small peak at 2.75 cm hints to the anoxic event at the beginning of the 1980s. Indeed, Kiel Bight waters frequently suffered depletion of oxygen in 1980-1983 (Gerlach, 1984). Probably, the outer fjord area, where the core was retrieved, was not substantially affected by extended anoxia with an exception of the strong event in the 1980s.

A similarity of fluctuations of the C:N ratio and the pigment ratio observed in the core is unclear. The C:N ratio mainly depends on the sources of organic matter, and it can also decrease under anoxic conditions due to preferential nitrogen loss during organic matter decomposition. The phaeopigments : chlorophyll *a* ratio in sediments mainly depends on their oxygenation. Under oxic conditions chlorophyll *a* decays faster than phaeopigments, and the ratio increases. Thus, the ratios should change in opposite directions under certain conditions, but it is not a case in the core from Kiel Fjord.

As sediments were sampled in spring, the low content of pigments as well as biogenic SiO_2 and total carbon in the uppermost centimeter is unusual because sampling fell into the production season. This pattern therefore may be related to a loss of the fine sediment fraction

during core sampling (Farmer, 1991), which is, however, unlikely with Rumohr corer. The other explanation would be an active remineralisation of fresh detritus in the uppermost oxidized centimeter of the sediments prior to establishment of steady state conditions (Balzer et al., 1987).

The reason for the decrease in concentration of all biogenic parameters toward the surface of the core is unclear. Anthropogenic disturbances can be excluded given that 20 cm core depth correspond to the age of about 400 years (AD 1600). Therefore, the non-anthropogenic background seems to be higher than can be predicted based on changes recorded in the upper part of the sediment core. Obviously, two facts may elucidate this feature. Firstly, the low sedimentation rates and thus slow accumulation at the time interval when the core section 10-20 cm was deposited may fairly elevate the amount of organic matter in those deposits. Secondly, the observed upward coarsening of sediments may be responsible for the reduced levels of C_{org}. Changes in grain size with time may strongly affect the analytical data. Indeed, when the main part of organic matter and trace elements is brought from the inner fjord to the outer fjords with the silt fraction, the coarsening of sediments in last 60 years may have led to an effect of "cleaning" of the sediments (dilution of concentrations in sediments) of the outer fjord. Christiansen et al. (2002) observed the similar record of organic carbon due to the increased portion of coarse silt fraction in bulk sediments from Danish estuary.

4.5.3 Evolution of the metal accumulation and input

The steady concentrations of Al imply that no change in sources of clastic material such as river inputs or erosion occurred. The record of titanium, as a marker of heavy minerals input, also indicates no variations in the sources of deposited material. Barium content varies negligible. Given that barium is assumed to be an indicator of paleoproductivity and also shows redox-sensitive behaviour (McManus et al., 1998; Brumsack, 2006), its profile suggests that neither significant changes in productivity nor diagenetic remobilisation linked to the migration of redox boundaries occurred.

4.5.3.1 Metals potentially introduced anthropogenically

In the bays of the western Baltic Sea, many workers observed a clear accumulation of trace metals in the sediments deposited in the 20th century (Erlenkeuser et al., 1974; Müller et al., 1980; Brügmann and Lange, 1990; Rösel et al., 1996; Leipe et al., 1998). In these studies metal enrichment was attributed to an increased anthropogenic load of metals since the beginning of industrialisation. Obviously, the sewage discharges, foundry, steam shipping

and shipyards, harbours, and municipal transport introduce some amount of metals to the

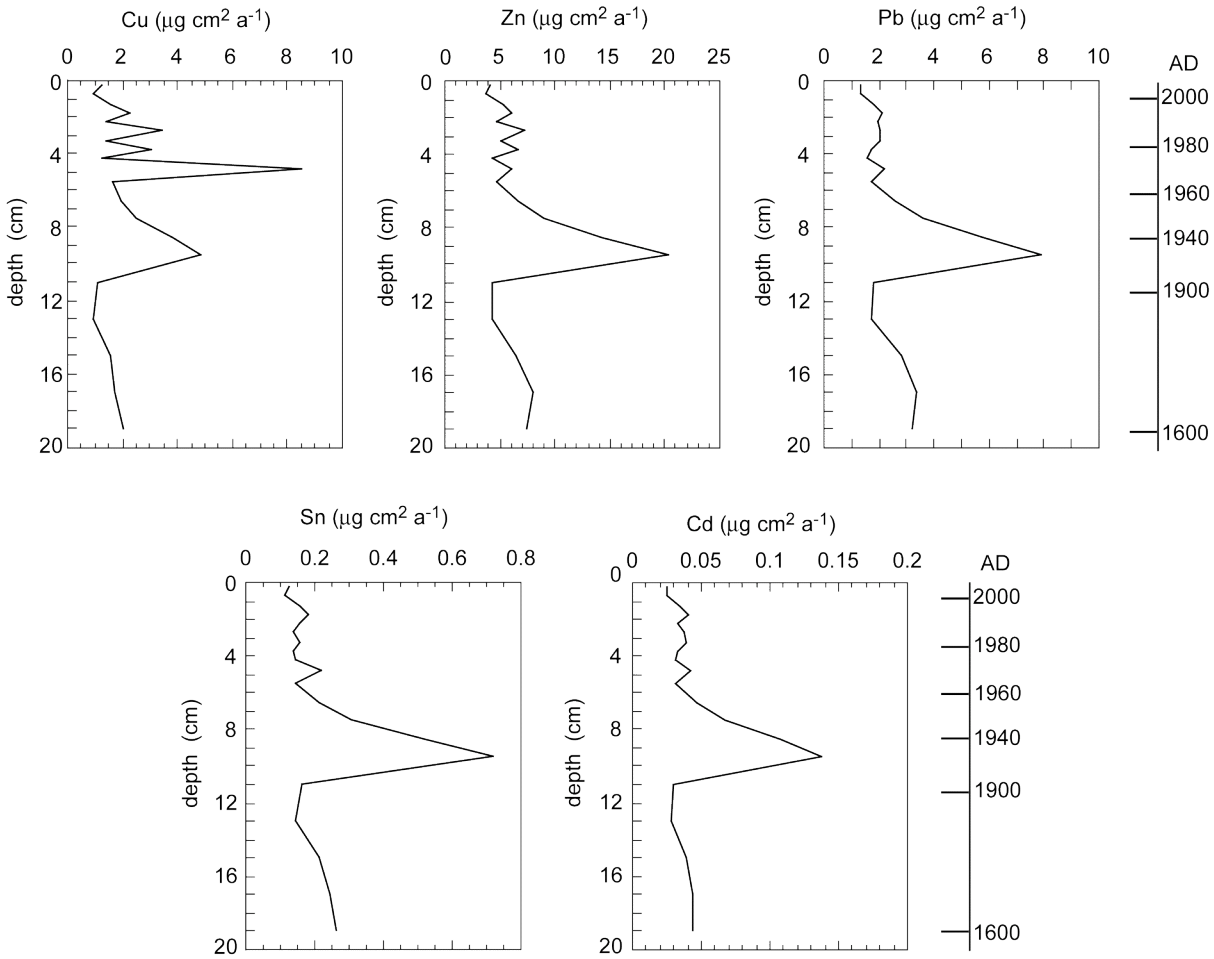

FIGURE 4.8. The fluxes of anthropogenically introduced metals within the fraction finer than 63 µm in core PF1738.

sediments of Kiel Fjord. In spite of these settings, copper, Zn, Pb, Sn and Cd concentrations are virtually constant with some variations in the upper 10 cm of the core studied and regularly decrease from 20 to 10 cm depth (Fig. 4.6). Referring to the quite uniform profiles of these metals normalized to aluminum, they apparently have not been modified by redox changes as evidenced from the difference to Mn, U and Mo distributions. This finding is in agreement with Calvert and Pedersen (1993), Gobeil et al. (1997) and McManus et al. (2006).

However, the increased rates of sedimentation in the 20th century as well as grain-size variations could affect the record of metals. Even if trace metal concentrations increase due to anthropogenic activity at the fjord watershed, they might be easily masked by natural changes through time and may show as a result constant or even depleted values in the core respective intervals. The generally stable concentrations of metals in the deposits from the 20th century may also be due to the fact that environmental conditions in the outer Fjord are closer to the

open Kiel Bight than the depositional inner fjord.

To compensate the effect of higher sedimentation rates, the fluxes of metals, whose distribution is presumably not modified by diagenesis, were calculated within the fraction finer than 63 µm. The distribution of metal fluxes through the core revealed that the input of metals significantly increased from the late 1930s to the mid 1940s. In that period of time, the intensive building of large warships and the expanding of harbours occurred in Kiel Fjord before the Second World War, followed by the period of depression of the city of Kiel and shipyards till the 1960s.

The peaks of zinc and copper between 3 and 5 cm appear to reflect later pollution as this horizon was deposited between 1970 and 1990. The fact, that copper (extreme values omitted), Zn and Cd correlate significantly with organic carbon content (Fig. 4.9) imply that they accumulate concomitantly with organic matter, or, these metals are bound as micronutrients with organic matter. The positive x-intercept of the regression line reveals another additional source of these metals, possibly anthropogenic influx or background sedimentation of outwash of glacial till. Lead and tin also correlate with organic carbon content because apparently they are able to build stable complexes with organic matter (Förstner, 1981). For instance, high concentrations of tributyltin, enough to induce aberrations in reproductional system of periwinkle, were found in near-coastal surface sediments in the vicinity of the site investigated here (LANU, 2001b).

The hydraulic and mineralogical fractionation of deposited particles leads to increasing natural trace metal concentrations with decreasing grain size in most estuarine and coastal

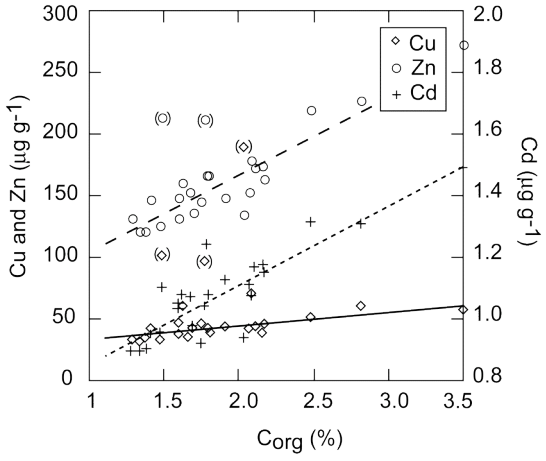

FIGURE 4.9. Relations between copper, zinc and cadmium content and organic carbon percentage in core PF1738. The parentheses designate values considered as outliers, which were excluded from the linear regression.

sediments. Metals are associated with clay minerals and organic matter. Anthropogenically derived non-detrital metals also become associated with fine-grained inorganic and organic material during transportation and deposition (Förstner, 1981; Loring, 1991). Therefore, metal concentrations usually decrease in the sand and coarse silt fractions because of the dilution of the fine-grained carriers adsorbing trace metals by coarser grained quartz, feldspar, and other components with low surface area on only little trace metal content. Although I already accounted to this grain size effect measuring the metals directly in the fraction finer than 63 µm (Förstner and Salomons, 1980; Irion and Müller, 1987), the particle size distribution in this fraction also varies between the sediment layers and they affects the total metal concentrations (Damm, 1992) Therefore a normalisation of metals to the fraction finer than 20 µm was done (Fig. 4.10).

Normalized to < 20 µm concentrations, all metals display a tendency to become enriched in the sediments deposited after ~1945. From anthropogenic trace metals, tin exhibits the greatest increase in concentration, as with zinc and cadmium. High tin concentrations in the sediments in the 1960s are connected with the extended use of antifouling paints containing tin in shipyards of Kiel Fjord. Tin additives were prohibited since the 1990s (IMO, 2005), but the concentrations of Sn in sediments of the inner fjord are still high compared to the open Kiel Bight.

The copper and zinc contents of the fine silt and clay fraction are constant downcore and only slightly elevated between 2-4 cm layer. The excessive metal concentrations point to an anthropogenic origin of these peaks. Lead and cadmium concentrations are fairly constant. Therefore these elements must be linked to a large extent to the fine fraction and do not depend on external sources. However, the surface sediments of the innermost fjord show elevated Pb content that was related to municipal transport and surface runoff (Nikulina et al., 2008).

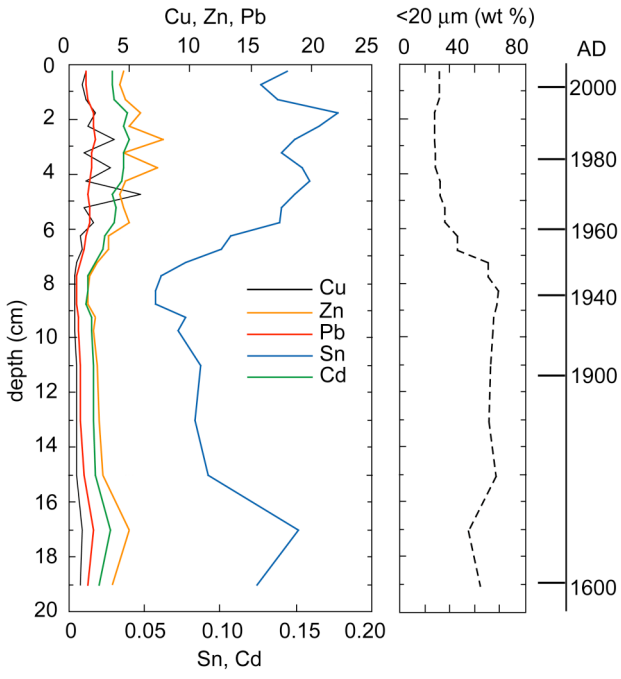

FIGURE 4.10. Downcore variations of elements normalised to percentage of fraction finer than 20 µm.

The trace elements were determined in

the fine fraction. If the sand fraction carries no trace metals at all, and the concentrations in silt fraction were proportional for the bulk sample, one would obtain values lower by factor 5 than reported in Table 1 in the subsurface sediments and lower by factor 1-2 below approximately 7 cm. Such concentrations are, however, within the background levels for the Baltic Sea (e.g. Brügmann and Lange, 1990). Nevertheless, the normalised concentrations of metals along the core constrain the human impact only to specific elements as tin, zinc and cadmium. They are closely related to the shipyard industry.

4.5.3.2 Redox sensitive elements

Kiel Bight has been exposed to periodical hypoxia or even anoxia once the inflow of salt and oxygen rich waters from the North Sea was diminished, a stable water stratification was established and organic matter decomposition led to complete consumption of oxygen in near bottom water (Gerlach, 1988). In the inner part of Kiel Fjord, the anoxic events have occurred to a different degree from June to September, whereas the outer fjord did not experience an oxygen deficiency regularly (Gerlach, 1990). The change of oxic conditions at the water-sediment interface, as well as within the sediments causes a redistribution of redox-sensitive elements through the sediment column. Elements are ordered around the actual oxidation front in sediments according to their different redox potential (Thomson et al., 1993). If this pattern is presented, it gives a possibility to recover the depositional or postdepositional conditions in a particular area. Furthermore, the formation of hydrogen sulphide associated with anaerobic bacterial sulphate reduction is an important factor for trace metal fixation due to the formation of sulphides (Rosenthal et al., 1995; Sundby et al., 2004).

Manganese

Among all redox sensitive metals measured in core PF1738 only manganese shows a small subsurface peak at 1.75 cm, which corresponds to the base of the oxic layer. Manganese is prone to upward reductive remobilisation (reduced Mn^{2+} is mobile and oxidised Mn^{4+} is immobile) and therefore gets enriched in the upper oxygenated sediment layer forming stable oxides (Calvert and Pedersen, 1993; Fig. 4.11a). The subsurface peak in core PF1738 therefore suggests that pore water oxygen does not penetrate below 2 cm (Froelich et al., 1979).

The slight peak at 5 cm depth may reflect the past redox conditions, when oxygen penetrated deeper in the sediments (Fig. 4.11b). Manganese from a peak formed earlier at the redox boundary diffuse upward after the setting of reducing conditions and redox upshift. The

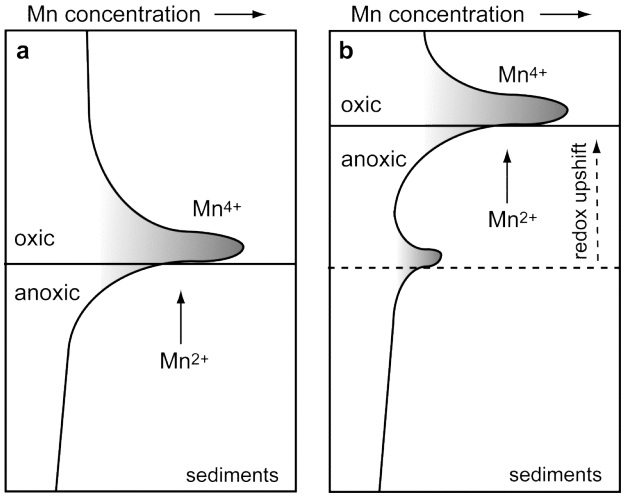

FIGURE 4.11. An illustration of solid phase manganese distribution in sediments when the redox boundary migrates, modified after Gobeil et al. (1997) and Burdige (2006). (**a**) the initial Mn profile, (**b**) after a redox upshift.

low concentrations of Mn and the absence of sharp peaks may be resulted from the instantaneous changes from oxic to anoxic conditions in the Kiel Bight depending on the salt-water inflows or water mixing during the storms. As a result the periods of oxygenation can be not enough long for accumulation of Mn as oxide, whereas the deoxygenetion of sediments leads to the diffusion of Mn to the water column.

Besides manganese, vanadium, molybdenum, uranium and cadmium are redox-sensitive elements. Their distribution is affected by diagenesis, and therefore they are frequently used for reconstruction of the paleoenvironment (Pedersen et al., 1989; Rosenthal et al., 1995; Morford and Emerson, 1999; McManus et al., 2006; Brumsack, 2006; Crusius and Thomson, 2000). Vanadium, U and Mo originate mostly from an early diagenetic processes and enter the sediment via diffusion from the water column because of their different solubility in oxic water as compared to reducing pore water (opposite to the behaviour of Mn). Other elements, such as cadmium and copper are involved in biological cycling and they are concentrated before deposition (Sundby et al., 2004; Brumsack, 2006).

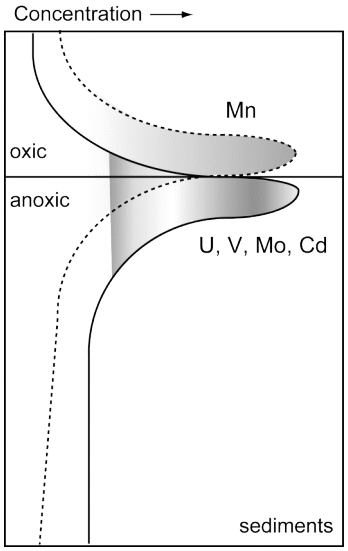

FIGURE 4.12. An illustration of redistribution of solid phase redox-sensitive metals at redox boundary (after Thomson, 1993; Gobeil et al., 1997; Crusius and Thomson, 2000)

Uranium

Uranium forms peak concentrations in the reducing environment immediately below the oxygen penetration front (Crusius and Thomson, 2000) and below the Mn spike (Klinkhammer and Palmer, 1991; Crusius et al., 1996; Fig. 4.12). In core PF1738 the elevated concentrations of

uranium are recognised at 6-8 cm. They are slightly shifted downward as compared to the peaks of Mn, but a significant correlation between Mn and U is observed (Appendix 2.7). The record of uranium in Kiel Fjord sediments is comparable to other records from suboxic hemipelagic sediments (Klinkhammer and Palmer, 1991). Generally, the increase of uranium in sediments is associated with bottom water oxygen depletion, higher rates of organic carbon rain or a combination of both factors (McManus et al., 2005). The similarity of C_{org} and U records in core PF1738 suggests that the amount of uranium is associated to the greater degree with organic carbon. In turn, organic carbon levels are determined by its preservation, which depends on the oxygenation of the near-bottom water and the sediments.

Molybdenum

Unlike uranium, Mo displays an increase in the two upper centimeter in parallel to Mn. Under oxic bottom water conditions, Mo may be captured in the near surface sediment layer by Mn-oxihydroxides and concentrates there (Sundby et al., 2004; Tribovillard et al., 2006). Then, at the depth of 7.75 cm it displays a sharp peak (though with relatively low magnitude). Mo is known to accumulate in extremely reduced sediments below the horizon where sulphides are generated. No substantial accumulation of Mo was found at suboxic conditions (Crusius et al., 1996; Tribovillard et al, 2006). The authigenic enrichment of Mo continues long after burial and several centimetres into the sediment, but at particular sites, there is a small separation between U and Mo enrichment patterns (McManus et al., 2005), in that Mo enrichment generally occurs deeper than that of U. Therefore, the spike at 7.75 cm may indicate strongly reduced conditions with presence of hydrogen sulphide, whereas the shallow peak at 2 cm is caused by Mn oxide co-precipitation.

On the other hand, Adelson et al. (2001) attributed the upward increase of Mo content in cores from the seasonally anoxic Chesapeake Bay to a rise of recent coastal anoxia. When bottom waters are anoxic, MoO_4^{2-} concentrates at the sediment-water interface, and thiomolybdates is fixed in sediments. As such, a subsurface change in Mo content in the outer Kiel Fjord might be interpreted in two different ways: as a marker for favourable oxic conditions at present time or for seasonal oxygen depletion caused by the lack of salt-water inflow from North Sea in the 1990s (Matthäus, 1990).

Vanadium and cadmium

Vanadium, which in PF1738 has no discernible deviations in concentration, is considered to precipitate as oxides/hydroxides in the presence of dissolved sulphide or to adsorb on

particle surfaces (Calvert and Pedersen, 1993). In our case, a clear correlation between V and Cd content suggests similarities in their sources and post-depositional behaviour. In turn, cadmium reduction occurs under suboxic conditions (Gobeil et al., 1997). Thus cadmium enrichment is commonly found a little shallower in the sediments than that of U. In anoxic sulphide bearing sediments, cadmium is known to immobilise as CdS, but Rosenthal et al. (1995) and Crusius et al. (1996) also proposed precipitation of cadmium sulphide in suboxic sediments in the presence of traces of free sulphide. In the outer Kiel Fjord core, cadmium does not show a perceptible peak, even though an increase in concentrations is observed at 7 cm depth. This feature may signify the absence of sulphide formation in the core shallower than 7 cm. A cadmium peak often overlaps with copper, zinc and lead accumulation, which also precipitate together with free dissolved sulphide (Rosenthal et al., 1995; Tribovillard et al., 2006). Indeed, the records of Cd and Pb are of similar character, with elevated element content between 5 and 7 cm. However to attribute the high levels of Zn and Cu in the layer 2.5-5 cm to anoxic conditions seems not plausible while other metals, e. g. Cd and Pb, do not support them. Therefore, their increased concentrations possibly had an anthropogenic source in the 1970s-1980s. The overall depletion of Zn, Cu, Cd and Pb in the uppermost oxic sediments is seemingly controlled by the migration from pore water solution to the near-bottom water as a result of active decomposition of organic matter.

From the considerations above, three sections can be distinguished in the core: the layer from surface to 2 cm is characterised by oxic conditions designated by a Mn peak. It is underlain by a suboxic layer down to 8 cm as evidence by the Mo spike. Below 8 cm, the conditions are apparently fully anoxic with presence of H_2S that is reflected in enhanced levels of trace metals and organic matter. This conclusion is in agreement with synchronous peaks of metals concentrations normalised to the Al content at 8 cm.

4.5.3.3 U:Mo ratio and salt water inflows

The variability of redox elements in the core may give us an impression of the redox conditions that prevailed in the sediments or in the water column at time of deposition or afterwards. McManus et al. (2006) investigating the relationships between U and Mo autigenesis and carbon burial, proposed that the U:Mo ratio is sensitive indicator for bottom water oxygen concentrations because both metals are differently sensitive to chemical parameters (e. g. presence of sulphides in pore water) coupled with oxygenation. The U:Mo ratio is higher at elevated oxygen content in bottom water. Values lower than 1 correspond to

anoxic waters. It is then plausible to suggest, that variations of U:Mo throughout the core may reflect the concentrations of oxygen in overlying water column during the deposition, at least the general tendency of the oxygen situation. In Kiel Fjord, the sedimentary U:Mo ratio shows a steady increase from surface to about 3.5 cm and a subsequent decrease downcore with a minimum at 8 cm (Fig. 4.13). The U:Mo profile negatively resembles the Mo record.

Oxygenation of bottom waters in the Baltic Sea mainly depends on the renewal of waters through the Skagerrak and Kattegat. In Kiel Bight, salt-water inflows are important for maintaining the general stratification and the ventilation of near-bottom waters. The salt water inflows occur randomly during the winter season at intervals from one to several years forced by variability of the wind pattern (Lass and Matthäus, 1996). This pattern was different in the mid-seventies when only weak or no major inflows were observed.

The periods without strong inflows are indicated by a salinity decrease in bottom waters in the Baltic Sea, together with steady increase of hydrogen sulphide concentrations. Thus, the salinity variation reflects deep-water renewal processes. The long term oceanographic

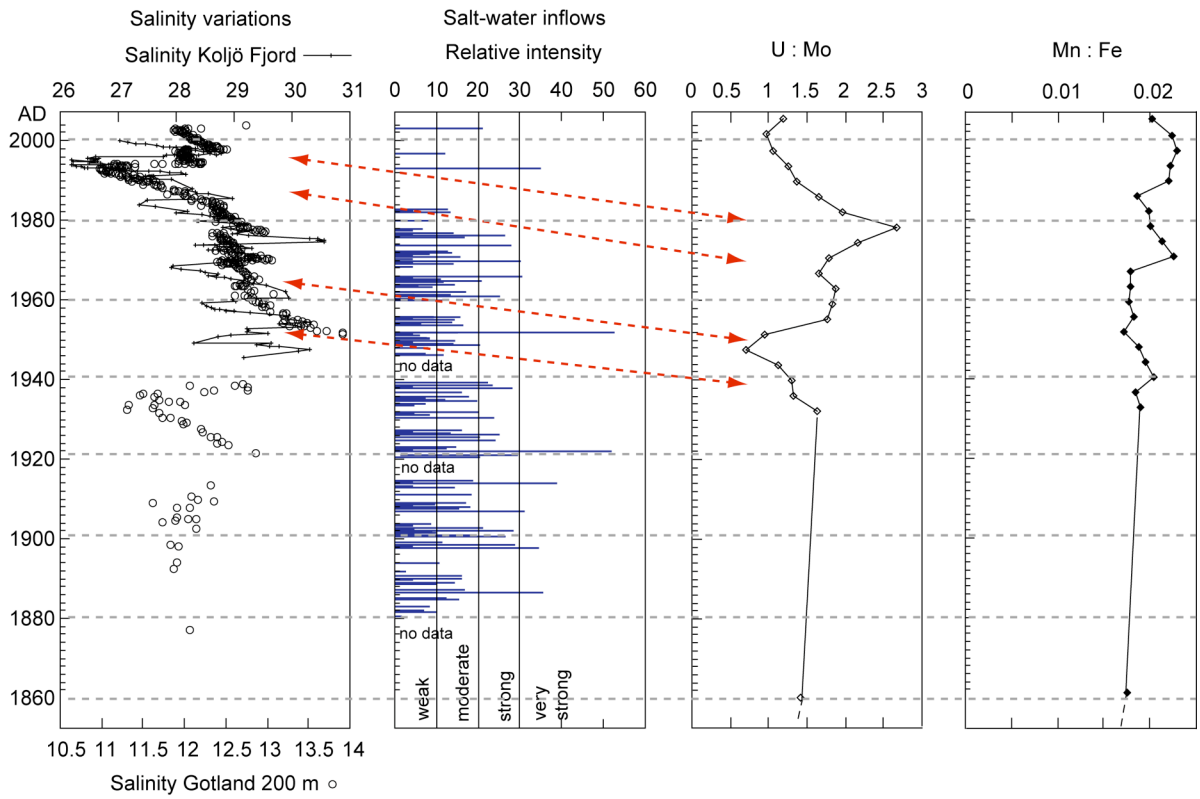

FIGURE 4.12. The variations in U:Mo and Mn:Fe ratios in core PF1738, multidecadal changes in salinity of Baltic Sea water from records in Koljö Fjord (Filipsson and Nordberg, 2004) and Gotland Basin (Matthäus, 1990; Nausch et al., 2003, 2005), and major Baltic inflows between 1880 and 2005. Major Baltic inflows are shown in their relative intensity (Matthäus and Frank, 1992; Fischer and Matthäus, 1996).

observations in Koljö Fjord (Filipsson and Nordberg, 2004) and Gotland Basin (Matthäus, 1990; Nausch et al., 2003, 2005), both on the way of inflowing North Sea water, together with frequency and intensity of inflows (Matthäus, 2006) make it possible to reconstruct the prevailing oxygen conditions. Comparison of downcore variations of the U:Mo ratio from Kiel Fjord core with salinity variability and inflows frequency through the time shows a general similarity of these records. The peaks of the U:Mo ratio are shifted downward relative to the time of salt water inflows. This shift in depth is explainable by the fact, that anoxic conditions in sediments do not necessarily mean that the water above the sediments was anoxic (Calvert and Pedersen, 1993). The water may still have been saturated with oxygen, but did not penetrate deeper in the sediments leading to the establishment of suboxia or anoxia in subsurface sediment layers. The shift in depth depends on the depth of oxygen penetration, which in turn is determined by oxygenation of near bottom water and sediment properties (at site are favorable). The observed U:Mo variations imply that near-bottom waters at the study site of the outer Kiel Fjord have never been fully anoxic. Otherwise the peaks of U:Mo ratio in the surface sediments would coincide with periods of low inflows. This conclusion is consistent with the record of the pigment ratio indicating strong degradation of chlorophyll *a* throughout the whole core. This can only have occurred under oxic conditions in the upper sediments.

Likewise, Neumann et al. (1997) used the Mn:Fe ratio in sediments of Gotland Basin to infer the major salt water inflows and relate them to oceanographic observations. In their study, the Mn:Fe ratio varied from 0.5 to 3, and good correlation was found between strong North Sea water inflows with values of 2-3. In our case, the Mn:Fe ratio ranged from 0.015 to 0.025 is very low and any correlation with the salt inflow record is not significant (Fig. 4.13). The low concentrations of manganese are possibly explained by its mobilization out of the core to the water column.

If the hypothesis on predominant oxic conditions in bottom water of the outer Kiel Fjord is right, then a constant replenishment of oxygen in the sediments would explain the absence of consistent peaks of uranium due to remobilization when oxygen penetrates to a region where authigenic U has accumulated (McManus et al., 2005; Tribovillard et al., 2006). The other trace elements such as V, Mo, Cd, Cu and Zn, also might be affected by re-oxidation process but to a lesser extend than uranium (Morford et al., 2001).

4.5.3.4 Vertical distribution of trace elements

The steady upward decrease of trace metals in the core looks quite unusual, though some examples of a similar behavior of redox sensitive metals are known (Chaillou et al., 2002; Crusius et al., 1996; Sundby et al., 2004). Two explanations of this distribution can be proposed. Firstly, changes in sediment properties may strongly affect the concentrations of metals. A gradual increase of the portion of the fine fraction reflects a greater accumulation of authigenic metals. The observed reduction of the sedimentation rate below 10 cm may also influence the fluxes of organic matter and metals. Secondly, the periodic oxygen exposure may lead to remobilization of metals. It is conceivable that downward diffusion could then increase their concentration in the sediment below the level of initial precipitation. This mechanism cannot explain the gradual downward increase of concentrations in the core. However, core PF1738 is quite short and probably does not cover all the most recent diagenetic processes. Indeed, the metal concentrations in core do not reach any stable levels that could be considered as background. Furthermore, Sundby et al. (2004) proposed that such a distribution of metals could be controlled by slow kinetics. That means, if the rate of metals precipitation is slow compared with diffusion, authigenic metal can accumulate in a broad sediment layer below those where precipitation initially started. These explanations might also be applicable together.

The increase of organic carbon, biogenic silica and pigments with depth in the core infer a higher primary production in pre-industrial time. The induced levels of metals as micronutrients (Fe, Cu, Cd, Zn), which are supplied to the sediments with organic matter and are incorporated in the sediments after organic matter decomposition, also propose an increase of primary production at that time. As the sediments did not suffer strong oxygen depletion causing a partial preservation of organic compounds, it may be concluded that in 1600-1700 AD the primary production was even higher than at present time under anthropogenically induced eutrophication.

4.5 Conclusions

By comparing the chemical composition of the dated sediments and the known environmental history of the Kiel Fjord, the effects of anthropogenic activity were minor. The most striking aspect of the data discussed is that the concentrations of trace elements as well as organic entities gradually increase throughout the 20 cm long core. Except for titanium, barium and aluminium, the vertical trend is distinguishable for all elements and compounds.

The most probable explanation for this is a dilution effect due to higher sedimentation rates in 20th century and coarsening of sediments in recent time.

Coastal protection measures and harbour construction in the inner fjord since the beginning of 20th century together with increased storminess in the region apparently caused the coarsening of sediments while the fine fraction was more efficiently captured in the depositional inner fjord. In turn, coarsening promotes lowered concentrations of trace metals as well as organic carbon, pigments and biogenic silica. Nevertheless, variations in organic carbon and nitrogen in the core reflect the increased eutrophication in the fjord in the 1940s due to sewage loading with consequent remediation after a treatment plant came into operation in 1972.

Among the trace metals, which are supposed to be anthropogenically introduced in Kiel Fjord, copper and zinc show distinct increase between the 1960s and the 1990s. Lead, tin and cadmium concentrations steadily raise downward. The overall low levels of metals and organic matter in the core in comparison with surface sediments from Kiel Fjord imply that metal pollution and high organic matter accumulation in Kiel Fjord are localised in the inner fjord and does not extend to the outer fjord.

In the core, only manganese and molybdenum exhibit distinct peak concentrations, whereas other redox sensitive metals continuously decrease with depth without distinct variations. According to this, the sediment column is subdivided into three zones according to oxygenation: from water-sediment surface to 2 cm the sediments are oxic, from 2 to 8 cm a suboxic layer expand, and below 8 cm the sediments are fully anoxic.

The main result of this study is that the outer Kiel Fjord appears not to have suffered strong oxygen depletion of bottom waters caused by organic matter decomposition and irregular salt water inflows as it is common for the deeps elsewhere in Kiel Bight. Nonetheless, the ventilation history is mirrored in the U:Mo ratio, which demonstrates that this proxy can be suitable tool under more oxygen depleted settings. In any case, the initial assumption that the outer Kiel Fjord exposed to sever anoxia turned out to be wrong. Periodical oxygenation of near bottom water resulted in remobilisation of elements and their diffusion and changes in sediment composition together induced the downward decreasing trend in redox sensitive metals.

Apparently the natural changes and environmental variability in the outer Kiel Fjord modify and mask anthropogenically induced disturbances. The decrease of organic matter and metals content should not be misinterpreted as being a result of a better sewage treatment.

Conclusions

This study revealed that the type of sediments and depositional regime mainly control the distribution of organic matter and trace elements in Kiel and Flensburg Fjords. The other factors are primary production and the oxygenation of near-bottom water and sediments, which is more important for accumulation of organic substances (organic carbon, pigments) and redox-sensitive metals. The anthropogenic influence follows these factors and interferes with them.

Kiel and Flensburg Fjords have a distinct morphological structure: an outer marine part and an enclosed inner part. This implies original differences in the natural conditions between both parts. In the inner fjords, higher productivity due to nutrient input and periodical anoxic conditions favour the accumulation of substances associated with fine-grained sediments.

The grain size distribution in surface sediments and upward coarsening of sediments in a core from the outer Kiel Fjord infer that the construction of piers, dykes and harbours promotes the accumulation of silt-sized material in the inner fjords. The inner fjords are partially affected by anthropogenic nutrient input from sewage and metal load from shipyards and harbours. In the outer fjords, the main role is played by natural variations. However, even weak anthropogenic disturbances always co-act with natural factors and may lead to stable environmental changes. These changes cannot be overcome by a simple elimination of the impact, as it was shown for Flensburg Fjord.

The levels of organic carbon, pigments and biogenic silica, which reflect the primary productivity, are not higher than in other fjords of the western Baltic Sea. They show that the conditions in Kiel and Flensburg fjords are mesotrophic-slightly eutrophic. The only exception is the innermost Flensburg Fjord, which suffers a high eutrophication.

Trace metals are mostly associated with organic matter and they are enriched the fine sediments of the inner fjords, where the anthropogenic load of metals is also concentrated. Overall, the metal concentrations are typical for those elsewhere in Kiel Bight, except for tin. The significant tin enrichments of the surface sediments are attributed to the harbours and shipyards as a result of using of tin containing antifouling paints. The lead concentrations are related to combustion of lead containing gasoline. They are higher than pre-industrial levels

but the recent decrease of lead concentrations during last thirty years is recorded in sediments from Flensburg Fjord. Elevated concentrations of copper and zinc were discovered only in the innermost fjords in the vicinity of shipyards. Friedrichsort Sound and Gelting Bay differ significantly from the other areas. In that, they are hydro-dynamically active shallow zones, distinguished by extremely low concentration of organic matter and trace metals.

The variations of sedimentary organic matter and metals through time are another aspect of this study. In that, the investigation of sediments from Kiel Fjord during the year revealed that seasonal variations in organic matter supply are quite distinct and are related to the seasonal cycle of phytoplankton production. The sedimentary concentrations of organic compounds increase in spring with a gradient from the inner to the outer fjord reflecting the development of the spring bloom.

The study of eutrophication and metal pollution in Flensburg Fjord on decadal scale showed that the remediation of the system is slow after the cessation of enhanced nutrient input. The concentrations of metals, which come from sewage, shipyards and harbours, did not change significantly, but the levels of organic matter in the system have even increased. Although the annual cycle of oxic-anoxic conditions favours the loss of nitrogen from the sediments and the water column due to denitrification, the system still sustains high levels of organic carbon and biogenic silica. This is due to high primary production levels promoted by nutrients from resuspension and redeposition of sediments at shallow depths.

The study of a core from the outer Kiel Fjord shows changes in accumulation of organic carbon and trace elements in this area on multidecadal scale – during the last 400 years. Here, in comparison to other areas of the Baltic Sea, no consistent upward enrichment in organic matter and trace metals was found. In general, an unexpected upward coarsening of sediments together with elevated sedimentation rates during the 20^{th} century is responsible for this. The variations in sedimentation rates are referred to changes in erosion and runoff intensity. The upward decrease of organic matter concentrations in the core seems to reflect the higher primary productivity at pre-industrial time. The increase of organic matter supply the 1940-1970s due to high nutrient load before the construction of central sewage plant is, however, discernible.

The enrichment of core sediments in copper, zinc, cadmium and tin is masked by changes in sediment composition. But nevertheless, it is perceptible for the last 40 years related to the shipbuilding industry. The record of redox-sensitive elements elucidates that no drastic changes in oxygen regime in the outer Kiel Fjord had occurred. The U: Mo ratio in the

sediments as a proxy of water column oxygenation showed in comparison with a record of salt-water inflows that the near-bottom waters in the outer Kiel Fjord was not completely anoxic during the last 150 years. However, the inner fjords had suffered strong anoxia in the past and during the last years.

Kiel and Flensburg Fjords are of particular interest by the fact that each of them presents two environments due to their morphological settings. The further monitoring of the fjords allows to understand the combined effects of natural and anthropogenic factors that is a main point in the environmental studies of the coastal areas. The investigation of cores from the depositional areas of fjords may provide insight in the functioning of the inner fjords as a sink of organic matter and trace metals. The study of fluxes and budgets of nitrogen and carbon as well as metals in sediments and in the water column may illuminate the role of annual anoxic events in the distribution and accumulation of organic matter and metals. Further detailed investigations and monitoring will allow to forecast the development of the environmental conditions in the fjords.

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Appendix

Appendix 1. Sampling stations

Appendix 1.1

Location and depth of sampling stations in Kiel Fjord

Station	Datum	Latitude (N)	Longitude (E)	Depth, m
P0220-35.2	09.07.1996	10º00.19´	54º47.04´	26.3
P0220-37.2	10.07.1996	10º15.98´	54º27.66´	18.6
PF15-01	09.12.2005	54°20.207´	10°10.119´	11.3
PF15-02	09.12.2005	54°20.266´	10°10.043´	13.2
PF15-03	09.12.2005	54°20.437´	10°10.486´	4.6
PF15-04	09.12.2005	54°20.415´	10°10.423´	8.7
PF15-05	09.12.2005	54°20.336´	10°10.342´	13.2
PF15-06	09.12.2005	54°20.324´	10°10.157´	13.1
PF15-07	09.12.2005	54°20.530´	10°10.473´	4.6
PF15-08	09.12.2005	54°20.541´	10°10.328´	9.0
PF15-09	09.12.2005	54°20.563´	10°10.293´	12.5
PF15-10	09.12.2005	54°20.557´	10°10.144´	13.1
PF15-11	09.12.2005	54°20.725´	10°10.435´	5.0
PF15-12	09.12.2005	54°20.719´	10°10.319´	11.4
PF15-13	09.12.2005	54°20.713´	10°10.160´	13.4
PF15-14	09.12.2005	54°20.888´	10°10.458´	5.0
PF15-15	09.12.2005	54°20.895´	10°10.360´	11.2
PF15-16	08.12.2005	54°20.931´	10°10.202´	13.4
PF15-17	08.12.2005	54°24.339´	10°12.948´	4.5
PF15-18	08.12.2005	54°24.325´	10°12.870´	8.0
PF15-19	08.12.2005	54°24.308´	10°12.699´	12.2
PF15-20	08.12.2005	54°27.323´	10°27.516´	18.1
PF15-21	09.12.2005	54°21.411´	10°09.087´	10.4
PF15-22	10.02.2006	54°19.781´	10°10.414´	8.0
PF15-23	10.02.2006	54°19.833´	10°10.251´	7.2
PF15-24	10.02.2006	54°19.900´	10°09.966´	11.0
PF15-25	10.02.2006	54°19.981´	10°09.753´	13.3
PF15-26	17.02.2006	54°21.048´	10°10.576´	7.6
PF15-27	17.02.2006	54°21.072´	10°10.501´	11.6
PF15-28	17.02.2006	54°21.116´	10°10.295´	13.3
PF15-29	10.02.2006	54°21.702´	10°09.020´	11.4
PF15-30	10.02.2006	54°21.575´	10°09.121´	13.2
PF15-31	10.02.2006	54°21.481´	10°09.155´	12.6
PF15-32	10.02.2006	54°21.371´	10°09.291´	13.2
PF15-33	10.02.2006	54°21.216´	10°09.388´	13.2
PF15-34	17.02.2006	54°21.820´	10°10.401´	14.0
PF15-35	10.02.2006	54°20.793´	10°09.599´	12.5
PF15-36	10.02.2006	54°19.408´	10°08.961´	16.0
PF15-37	17.02.2006	54°23.185´	10°11.546´	16.9
PF15-38	17.02.2006	54°25.233´	10°12.704´	16.8
PF15-39	10.02.2006	54°20.012´	10°09.356´	12.8
PF15-40	10.02.2006	54°23.176´	10°11.246´	13.5
PF15-41	10.02.2006	54°23.177´	10°10.837´	12.6

PF15-42	10.02.2006	54°23.270′	10°10.837′	9.5
PF15-43	10.02.2006	54°23.344′	10°10.856′	6.2
PF15-44	17.02.2006	54°21.692′	10°10.609′	5.7
PF15-45	17.02.2006	54°21.740′	10°10.496′	12.6
PF15-46	17.02.2006	54°21.813′	10°10.127′	14.3
PF15-47	17.02.2006	54°23.528′	10°12.464′	8.8
PF15-48	17.02.2006	54°23.591′	10°12.288′	14.9
PF15-49	17.02.2006	54°23.591′	10°12.429′	10.5
PF15-50	17.02.2006	54°23.667′	10°12.383′	13.0
PF15-51	10.02.2006	54°19.771′	10°09.752′	15.3
PF15-52	10.02.2006	54°19.519′	10°09.314′	15.2
PF15-53	28.03.2006	54°20.801′	10°09.933′	14.8
PF15-54	28.03.2006	54°21.208′	10°09.907′	13.8
PF15-55	28.03.2006	54°22.306′	10°09.944′	14.1
PF15-56	28.03.2006	54°22.620′	10°10.128′	14.2
PF15-57	28.03.2006	54°22.615′	10°11.557′	10.9
PF15-58	04.05.2006	54°25.586′	10°11.843′	7.4
PF15-59	28.03.2006	54°25.982′	10°11.664′	17.5
PF15-60	04.05.2006	54°30.315′	10°17.532′	16.2
PF15-61	04.05.2006	54°31.105′	10°19.063′	12.5
PF15-62	04.05.2006	54°23.942′	10°12.388′	12.4
PF15-63	04.05.2006	54°23.963′	10°12.277′	16.3
PF15-64	04.05.2006	54°23.837′	10°11.990′	17.3
PF15-65	04.05.2006	54°23.940′	10°12.762′	16.2
PF15-66	04.05.2006	54°24.155′	10°12.239′	15.3
PF15-67	04.05.2006	54°24.137′	10°12.256′	16.6
PF15-68	04.05.2006	54°24.157′	10°12.001′	17.1
PF15-69	04.05.2006	54°24.147′	10°11.740′	15.4
PF15-70	04.05.2006	54°23.176′	10°12.293′	10.2
PF15-71	04.05.2006	54°23.180′	10°11.991′	13.5
PF15-72	05.05.2006	54°22.612′	10°11.241′	15.3
PF15-73	05.05.2006	54°22.586′	10°10.865′	16.0
PF15-74	05.05.2006	54°22.214′	10°10.420′	15.0
PF15-75	05.05.2006	54°22.216′	10°11.464′	9.6
PF15-76	05.05.2006	54°22.224′	10°11.400′	11.6
PF15-77	05.05.2006	54°22.351′	10°11.317′	13.6
PF15-78	05.05.2006	54°22.329′	10°10.667′	15.3
PF15-79	05.05.2006	54°22.053′	10°11.522′	7.0
PF15-80	05.05.2006	54°22.054′	10°10.688′	13.3
PF15-81	05.05.2006	54°22.068′	10°10.222′	14.5
PF15-82	05.05.2006	54°21.958′	10°10.983′	10.8
PF15-83	05.05.2006	54°21.076′	10°09.265′	12.1
PF15-84	05.05.2006	54°20.966′	10°09.205′	6.9
PF15-85	05.05.2006	54°20.971′	10°09.416′	12.4
PF15-86	05.05.2006	54°20.917′	10°09.896′	14.5
PF15-87	05.05.2006	54°20.377′	10°09.754′	14.1
PF15-88	05.05.2006	54°20.354′	10°09.575′	10.7
PF15-89	05.05.2006	54°19.480′	10°09.444′	12.0
PF15-90	05.05.2006	54°19.432′	10°09.347′	12.2

APPENDIX 1.2

Location and depth of sampling stations in Flensburg Fjord

Station	Datum	Latitude (N)	Longitude (E)	Depth, m
PF16-01	08.06.2006	54°47.717′	9°26.142′	8.5
PF16-02	08.06.2006	54°48.105′	9°25.818′	6.3
PF16-03	08.06.2006	54°48.608′	9°26.322′	6.5
PF16-04	08.06.2006	54°49:497′	9°27.270′	15.1
PF16-05	08.06.2006	54°49.783′	9°26.204′	14.6
PF16-06	08.06.2006	54°49.989′	9°28.822′	5.1
PF16-07	08.06.2006	54°50.319′	9°30.021′	15.4
PF16-08	08.06.2006	54°51.194′	9°32.711′	11.8
PF16-09	08.06.2006	54°51.603′	9°33.896′	2.8
PF16-10	08.06.2006	54°50.949′	9°35.858′	5.8
PF16-11	08.06.2006	54°52.445′	9°35.909′	8.3
PF16-12	08.06.2006	54°52.683′	9°34.325′	12.6
PF16-13	08.06.2006	54°53.095′	9°35.444′	8.9
PF16-14	08.06.2006	54°52.933′	9°36.753′	10.5
PF16-15	08.06.2006	54°52.185′	9°36.842′	13.6
PF16-16	07.06.2006	54°50.190′	9°40.886′	19.4
PF16-17	07.06.2006	54°48.400′	9°45.639′	8.1
PF16-18	07.06.2006	54°49.149′	9°45.367′	22.3
PF16-19	07.06.2006	54°50.196′	9°36.839′	9.6
PF16-20	07.06.2006	54°45.767′	9°51.551′	5.6
PF16-21	07.06.2006	54°46.915′	9°51.263′	8.5
PF16-22	07.06.2006	54°49.947′	9°50.230′	30.5
PF16-23	07.06.2006	54°48.414′	9°47.937′	19.1
PF16-24	07.06.2006	54°47.276′	9°48.864′	8.8
PF16-25	07.06.2006	54°46.693′	9°52.843′	8.1
PF16-26	07.06.2006	54°48.281′	9°53.493′	7.5
PF16-27	07.06.2006	54°47.086′	9°59.976′	26.0
PF16-28	07.06.2006	54°50.037′	9°53.369′	28.1
PF16-29	07.06.2006	54°48.548′	9°56.306′	24.7
PF16-30	07.06.2006	54°44.280′	10°6.087′	25.8
PF16-31	07.06.2006	54°42.495′	10°7.345′	21.5
PF16-32	08.06.2006	54°50.459′	9°36.608′	16.0

Appendix 2. Geochemical data

Appendix 2.1

Concentrations of organic compounds and trace metals in the surface sediments of Kiel Fjord together with characteristics of near-bottom water during sampling. – indicates the absence of data

Stations	Sand, %	t, °C	S, psu	O_2, µmol/l	TC, %	TN, %	C_{org}, %	C:N	$CaCO_3$, %	SiO_2, %	Chl *a*, µg g^{-1}	Phaeo, µg g^{-1}	Chlorine, µg g^{-1}	Phaeo: Chl *a*	Cu, µg g^{-1}	Zn, µg g^{-1}	Sn, µg g^{-1}	Pb, µg g^{-1}
PF15-01	48.8	8.0	22.2	475	2.46	0.15	1.74	13.8	5.97	0.71	4.6	27.5	37.3	6.0	28.8	90	0.75	34.1
PF15-02	18.2	8.5	23.2	297	3.15	0.11	1.25	13.0	15.84	1.11	3.7	21.1	29.0	5.8	44.2	148	1.44	62.5
PF15-03	10.0	8.2	21.8	394	6.41	0.45	5.42	14.0	8.25	2.57	24.5	130.0	181.9	5.3	143	434	1.84	153
PF15-04	14.9	8.1	22.3	343	6.96	0.35	4.43	14.7	21.06	2.84	12.8	82.4	109.6	6.4	138	388	1.66	150
PF15-05	6.5	9.1	23.2	267	6.04	0.42	5.25	14.6	6.59	2.57	23.3	111.5	161.0	4.8	128	353	2.31	136
PF15-06	8.0	9.1	23.2	308	4.62	0.38	3.79	11.7	6.92	2.86	36.4	136.6	213.8	3.8	45.7	145	3.24	49.3
PF15-07	12.2	8.0	22.2	427	4.62	0.29	3.30	13.2	11.04	2.46	22.4	100.8	148.5	4.5	59.6	207	0.87	78.5
PF15-08	6.3	8.1	22.0	484	4.30	0.31	3.33	12.5	8.11	2.72	15.4	91.8	124.5	6.0	79.1	211	1.86	86.7
PF15-09	14.9	8.6	22.9	291	5.96	0.52	4.87	10.9	9.07	4.27	42.5	155.8	246.1	3.7	98.3	264	2.22	101
PF15-10	1.3	8.8	23.0	313	5.74	0.47	4.85	11.9	7.39	4.28	39.7	140.7	225.0	3.5	92.5	280	1.56	111
PF15-11	16.7	7.9	21.9	333	3.58	0.21	2.43	13.3	9.56	2.16	21.2	82.4	127.5	3.9	44.7	144	1.29	65.1
PF15-12	0.6	7.9	22.4	331	5.62	0.48	4.59	11.2	8.62	4.35	30.1	130.0	193.8	4.3	89.1	236	2.03	108
PF15-13	0.2	8.5	23.0	406	6.10	0.59	5.35	10.6	6.27	5.41	50.0	181.1	287.3	3.6	75.3	221	1.82	85.5
PF15-14	16.7	7.9	22.2	438	4.74	0.42	4.03	11.1	5.93	3.51	35.6	178.7	254.3	5.0	89.2	262	1.74	105
PF15-15	1.1	8.5	22.5	391	6.06	0.53	5.04	11.0	8.52	5.52	35.0	143.8	218.0	4.1	97.3	277	2.21	135
PF15-16	3.4	8.2	23.0	219	6.18	0.48	4.69	11.3	12.39	4.11	44.7	143.4	238.3	3.2	77.8	228	2.57	86.7
PF15-17	49.1	6.9	22.0	262	3.20	0.22	2.08	10.9	9.33	2.00	38.3	111.2	192.5	2.9	26.0	80.6	0.53	20.3
PF15-18	51.1	7.7	22.4	269	1.50	0.10	0.86	10.3	5.36	1.09	16.8	33.1	68.7	2.0	10.7	46.6	0.45	13.1
PF15-19	10.5	8.5	22.8	300	3.33	0.24	2.27	11.1	8.85	2.87	23.9	68.9	119.6	2.9	30.1	95.4	0.97	30.1
PF15-20	6.3	-	-	522	4.35	0.50	3.72	8.7	5.25	3.28	23.0	88.7	137.6	3.9	34.7	131	1.42	46.3
PF15-21	29.4	7.5	22.0	476	3.63	0.24	2.58	12.5	8.69	2.58	16.9	84.9	120.8	5.0	44.4	140	1.02	53.8
PF15-22	1.7	2.1	15.1	462	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PF15-23	1.7	2.2	15.9	447	8.70	0.82	7.81	11.1	7.42	7.96	47.4	280.0	379.1	5.9	109	341	9.65	104
PF15-24	2.4	1.9	15.7	473	5.72	0.49	4.83	11.5	7.38	4.63	24.8	155.4	207.3	6.3	-	-	-	-
PF15-25	4.7	2.1	17.3	357	4.93	2.15	4.20	2.3	6.09	3.31	25.0	115.9	168.3	4.6	70.0	195	9.53	91.5
PF15-26	20.8	2.3	17.0	458	5.72	0.37	4.08	12.9	13.65	3.50	29.1	149.2	210.1	5.1	-	-	-	-
PF15-27	1.9	2.8	17.3	405	6.59	0.55	5.81	12.4	6.49	6.62	32.9	177.6	246.4	5.4	88.9	253	7.74	135
PF15-28	1.0	2.4	17.6	416	6.91	0.63	6.03	11.1	7.31	5.69	41.3	181.5	267.9	4.4	-	-	-	-
PF15-29	1.2	2.0	16.2	475	5.92	0.46	5.29	13.5	5.28	4.12	27.2	150.0	206.8	5.5	77.8	338	7.01	127
PF15-30	1.1	2.0	16.9	420	5.96	0.53	5.33	11.7	5.19	3.81	29.4	141.7	203.2	4.8	-	-	-	-
PF15-31	1.1	2.0	16.2	419	5.69	0.47	5.19	12.8	4.17	4.64	30.6	125.3	189.3	4.1	-	-	-	-
PF15-32	0.5	2.0	17.9	398	6.34	0.60	5.73	11.2	5.04	5.65	36.2	157.4	233.2	4.3	69.6	206	6.43	85.8
PF15-33	0.6	2.1	17.6	384	6.29	0.55	5.80	12.3	4.06	6.40	39.1	160.0	242.0	4.1	-	-	-	-

Stations	Sand, %	t, °C	S, psu	O_2, µmol/l	TC, %	TN, %	C_{org}, %	C:N	$CaCO_3$, %	SiO_2, %	Chl *a*, µg g^{-1}	Phaeo, µg g^{-1}	Chlorine, µg g^{-1}	Phaeo: Chl *a*	Cu, µg g^{-1}	Zn, µg g^{-1}	Sn, µg g^{-1}	Pb, µg g^{-1}
PF15-34	28.7	2.3	17.8	458	2.65	0.21	2.69	14.9	0.00	1.03	8.9	47.0	65.6	5.3	34.2	98.7	4.39	41.6
PF15-35	1.5	2.0	16.5	373	5.88	0.54	5.44	11.7	3.70	5.21	35.2	148.0	221.6	4.2	74.7	222	9.80	99.6
PF15-36	4.4	2.3	17.2	493	6.40	0.51	5.71	13.0	5.68	4.15	28.5	140.3	199.9	4.9	162	330	16.0	135
PF15-37	61.8	2.1	18.1	398	0.67	0.06	0.58	11.2	0.81	0.55	4.5	19.8	29.2	4.4	13.9	45.3	3.13	20.5
PF15-38	23.8	2.0	17.4	426	3.86	0.32	3.14	11.3	6.01	1.31	24.6	63.6	115.3	2.6	24.9	88.6	6.80	32.2
PF15-39	0.6	2.0	16.1	510	6.80	0.58	6.06	12.1	6.18	5.21	36.5	168.5	244.9	4.6	106	280	13.1	129
PF15-40	0.8	2.3	17	414	5.16	0.47	4.23	10.4	7.74	4.60	38.0	130.9	210.5	3.4	-	-	-	-
PF15-41	0.8	2.5	17.2	475	5.15	0.50	4.45	10.5	5.82	3.90	27.5	115.9	173.5	4.2	73.4	186	8.10	71.4
PF15-42	2.9	1.9	16.6	484	5.49	0.50	4.93	11.4	4.68	5.98	24.1	111.0	161.4	4.6	-	-	-	-
PF15-43	10.8	1.9	16.5	494	3.97	0.32	3.37	12.1	4.94	2.51	22.6	91.7	139.0	4.1	49.3	103	5.27	38.6
PF15-44	8.3	2.2	16.9	472	7.21	0.60	5.07	9.9	17.83	5.83	33.5	207.8	277.7	6.2	-	-	-	-
PF15-45	0.9	2.4	17.8	439	6.58	0.64	5.86	10.7	6.01	7.24	39.8	159.4	242.8	4.0	-	-	-	-
PF15-46	19.0	2.2	17.9	458	4.38	0.33	4.38	15.6	0.07	2.63	6.0	36.4	48.9	6.1	-	-	-	-
PF15-47	20.4	2.2	17	414	3.46	0.32	2.57	9.5	7.40	4.50	22.9	142.2	190.0	6.2	31.45	111	4.59	41.7
PF15-48	3.2	2.3	17.8	415	5.43	0.53	4.37	9.6	8.83	4.18	57.0	173.7	293.3	3.0	-	-	-	-
PF15-49	35.5	2.0	17.3	458	4.22	0.27	2.03	8.9	18.20	1.39	14.0	70.1	99.3	5.0	-	-	-	-
PF15-50	1.1	2.2	17	393	5.64	0.46	4.30	10.8	11.12	3.96	50.0	167.1	271.9	3.3	48.7	149	5.10	54.3
PF15-51	1.5	2.7	18.7	323	7.34	0.63	6.60	12.3	6.13	6.72	41.2	187.8	274.1	4.6	-	-	-	-
PF15-52	17.8	2.2	17	365	4.62	0.39	4.58	13.7	0.37	3.68	17.9	80.2	117.6	4.5	-	-	-	-
PF15-53	3.0	2.3	17.1	-	5.31	0.42	4.74	13.1	4.69	2.73	19.5	74.8	115.7	3.8	-	-	-	-
PF15-54	2.1	2.8	17.0	340	6.89	0.61	6.73	13.0	1.28	4.45	36.4	116.3	192.6	3.2	73.6	280	18.4	97.5
PF15-55	5.3	2.7	16.9	385	5.92	0.50	5.22	12.2	5.86	4.12	34.6	75.7	148.3	2.2	-	-	-	-
PF15-56	38.9	2.4	16.9	409	2.56	0.14	1.65	13.7	-	0.52	3.7	29.6	37.3	8.0	28.1	80.1	4.60	48.1
PF15-57	4.5	3.0	16.6	432	5.18	0.51	4.46	10.2	6.01	4.08	59.8	141.0	266.5	2.4	59.9	183	7.60	103
PF15-58	88.9	-	-	-	0.16	0.02	0.10	5.6	0.52	0.26	2.0	2.8	7.3	1.4	-	-	-	-
PF15-59	5.0	3.0	16.7	-	6.16	0.66	4.79	8.47	11.41	6.54	170.0	251.2	608.0	1.5	33.6	126	3.85	42.1
PF15-60	94.0	-	-	-	0.16	0.03	0.15	4.92	0.15	0.24	1..6	3.7	7.4	2.3	2.54	11.2	0.51	8.43
PF15-61	87.2	-	-	-	0.14	0.03	0.10	4.11	0.26	0.50	2.5	2.7	8.2	1.1	1.79	11.3	0.24	6.81
PF15-62	3.1	7	20.2	644	4.94	0.50	3.86	9.08	9.05	5.09	103.6	156.8	376.3	1.5	37.0	113	3.77	42.4
PF15-63	16.9	5.7	22	305	4.25	0.36	3.65	11.77	5.00	1.77	36. 6	76.8	154.3	2.1	-	-	-	-
PF15-64	14.6	5.4	21.9	353	2.94	0.24	2.36	11.56	4.82	2.00	18.8	54.1	94.1	2.9	-	-	-	-
PF15-65	12.7	6.6	21.9	306	2.83	0.29	1.99	8.13	6.98	2.30	31.5	68.8	135.7	2.2	-	-	-	-

Stations	Sand, %	t, °C	S, psu	O_2, µmol/l	TC, %	TN, %	C_{org}, %	C:N	$CaCO_3$, %	SiO_2, %	Chl *a*, µg g^{-1}	Phaeo, µg g^{-1}	Chlorine, µg g^{-1}	Phaeo: Chl *a*	Cu, µg g^{-1}	Zn, µg g^{-1}	Sn, µg g^{-1}	Pb, µg g^{-1}
PF15-66	14.0	5.9	20.6	297	3.68	0.31	2.95	11.10	6.12	1.97	47.4	91.5	191.8	1.9	23.7	86.2	3.13	32.6
PF15-67	26.1	5.5	21.9	1128	4.31	0.29	2.04	8.2	18.87	1.27	5.5	27.1	38.9	5.0	-	-	-	-
PF15-68	1.6	6.6	20.5	515	5.43	0.55	4.28	9.0	9.58	6.49	85.9	186.5	368.6	2.2	-	-	-	-
PF15-69	18.4	6.4	21.6	523	2.98	0.24	1.88	9.1	9.15	1.82	30.4	69.1	133.7	2.3	17.3	64.8	1.74	22.9
PF15-70	0.7	6.7	20.3	697	4.92	0.49	3.89	9.3	8.59	4.88	69.1	138.7	285.2	2.0	-	-	-	-
PF15-71	1.9	6.4	21	483	5.31	0.50	4.41	10.2	7.47	5.07	77.0	188.1	351.2	2.4	-	-	-	-
PF15-72	14.1	6.3	18.2	444	4.75	0.33	1.39	4.9	27.98	2.83	9.2	55.8	75.6	6.1	-	-	-	-
PF15-73	20.3	5.4	18.2	228	4.14	0.25	3.40	15.8	6.17	0.76	4.6	30.7	40.8	6.7	56.7	101	5.06	50.8
PF15-74	26.5	5.5	18.2	450	5.95	0.24	3.33	16.0	21.81	1.80	3.5	22.5	30.1	6.5	-	-	-	-
PF15-75	0.9	6.3	17.3	389	5.71	0.58	5.20	10.5	4.27	6.03	59.8	163.7	290.6	2.7	-	-	-	-
PF15-76	0.2	6.3	17.3	486	5.88	0.60	5.30	10.4	4.81	5.48	61.6	156.5	287.2	2.5	-	-	-	-
PF15-77	0.4	5.5	17.7	428	5.06	0.44	4.77	12.8	2.45	2.50	19.9	83.4	125.6	4.2	50.5	181	8.51	92.0
PF15-78	37.7	5.8	18.2	533	5.94	0.14	4.55	38.6	11.62	0.77	3.3	16.4	23.5	5.0	-	-	-	-
PF15-79	8.8	7.7	15.9	572	5.41	0.56	4.28	8.9	9.40	5.61	91.0	186.4	379.2	2.0	58.8	236	7.75	2169
PF15-80	13.8	6.1	18.2	524	4.31	0.28	3.73	15.4	4.83	1.79	4.9	34.4	45.1	7.0	-	-	-	-
PF15-81	7.3	6.1	18.2	517	6.70	0.51	6.10	13.9	5.02	4.08	15.6	61.3	94.5	3.9	33.6	101	3.47	41.0
PF15-82	0.3	6.6	17.3	616	5.91	0.59	5.29	10.5	5.16	6.74	86.8	169.7	353.6	2.0	-	-	-	-
PF15-83	0.7	7.2	17.3	534	5.92	0.60	5.53	10.7	3.27	5.16	44.5	131.6	225.8	3.0	72.0	207	8.17	90.3
PF15-84	1.1	7.8	15.9	650	6.06	0.49	4.98	11.9	9.00	4.40	75.4	160.4	320.2	2.1	62.7	218	7.26	260
PF15-85	0.5	6.0	17.7	866	6.67	0.66	5.58	9.9	9.04	5.14	100.4	183.1	395.9	1.8	-	-	-	-
PF15-86	0.3	6.9	18.2	532	6.70	0.62	5.74	10.7	8.02	3.60	47.0	136.1	235.8	2.9	-	-	-	-
PF15-87	35.8	5.7	18.2	763	2.83	0.21	2.66	15.1	1.42	1.80	11.6	40.1	64.9	3.5	-	-	-	-
PF15-88	0.4	5.6	15.5	884	6.60	0.62	5.58	10.5	8.46	5.41	61.8	170.1	301.3	2.8	84.3	232	10.5	107
PF15-89	12.1	6.6	17.7	853	4.09	0.32	3.85	14.3	1.98	2.03	19.0	74.2	114.7	3.9	96.4	232	18.2	106
PF15-90	0.5	6.9	18.2	806	6.11	0.55	5.34	11.3	6.45	5.17	72.2	161.6	314.6	2.2	-	-	-	-

Appendix 2.2

Concentrations of organic compounds and trace metals in the surface sediments of Flensburg Fjord together with characteristics of near-bottom water during sampling. – indicates the ansence of data

Stations	Sand, %	t, °C	S, psu	O_2, µmol/l	TC, %	TN, %	C_{org}, %	C:N	$CaCO_3$, %	SiO_2, %	Chl *a*, µg g^{-1}	Phaeo, µg g^{-1}	Chlorine, µg g^{-1}	Phaeo: Chl *a*	Cu, µg g^{-1}	Zn, µg g^{-1}	Sn, µg g^{-1}	Pb, µg g^{-1}
PF16-01	5.3	11.0	19.3	475	11.16	0.95	8.97	11.04	18.32	7.36	199.8	353.7	777.1	1.8	151	438	16.5	123.6
PF16-02	11.4	10.2	19.8	297	12.52	0.91	10.96	14.10	12.99	7.58	73.9	307.9	464.6	4.2	194	437	18.1	158.1
PF16-03	15.8	8.8	20.7	394	5.93	0.48	11.52	27.88	-	3.50	51.4	170.0	279.2	3.3	135	176	8.8	62.4
PF16-04	1.7	7.7	23.0	343	10.37	1.16	5.52	5.56	40.41	7.33	113.3	398.3	638.8	3.5	123	379	11.0	96.8
PF16-05	0.5	7.6	22.6	267	9.95	1.16	11.27	11.34	-	5.43	130.0	370.4	646.2	2.8	-	-	-	-
PF16-06	0.5	7.6	23.0	308	9.61	1.11	9.65	10.15	-	7.54	88.8	362.0	550.7	4.1	-	-	-	-
PF16-07	0.6	10.2	20.7	427	8.63	1.09	8.53	9.11	0.86	10.25	188.9	513.5	913.6	2.7	76.3	283	4.7	50.8
PF16-08	12.5	9.5	21.2	484	7.25	0.58	6.85	13.71	3.35	2.78	43.3	134.8	226.5	3.1	33.8	140	3.8	36.1
PF16-09	62.7	-	-	291	0.51	0.05	0.36	7.77	1.28	0.75	7.7	17.9	34.3	2.3	3.2	22.6	0.4	7.0
PF16-10	59.1	-	-	313	3.39	0.30	0.33	1.28	25.49	1.00	28.2	64.0	123.9	2.3	-	-	-	-
PF16-11	23.5	8.7	21.3	333	6.14	-	1.96	-	6.65	2.01	43.2	84.4	176.0	2.0	9.9	50.3	1.1	12.8
PF16-12	0.2	7.7	23.1	331	4.25	0.72	5.34	8.70	4.06	3.58	87.4	191.0	376.2	2.2	-	-	-	-
PF16-13	6.1	9.5	22.3	406	3.58	0.48	3.76	9.07	2.56	4.05	32.4	119.6	188.4	3.7	-	-	-	-
PF16-14	9.0	7.6	23.1	438	4.71	0.38	3.28	10.00	11.35	2.04	22.8	91.9	140.4	4.0	23.1	108	2.4	26.6
PF16-15	0.9	7.6	24.3	391	4.57	0.53	3.35	7.31	5.10	3.05	50.1	135.4	241.6	2.7	-	-	-	-
PF16-16	0.3	11.3	20.2	219	0.56	0.52	3.96	8.95	0.61	3.60	26.0	109.6	164.8	4.2	31.6	137	3.1	46.6
PF16-17	94.2	-	-	262	3.63	0.08	0.48	7.10	25.68	0.25	12.9	22.6	50.1	1.8	2.3	12.6	0.5	6.3
PF16-18	15.2	7.6	24.6	269	1.63	0.40	0.54	1.59	5.29	2.83	22.3	81.0	128.4	3.6	-	-	-	-
PF16-19	30.3	-	-	300	0.42	0.15	1.00	7.56	1.78	1.28	22.0	48.8	95.6	2.2	10.1	52.9	1.3	14.8
PF16-20	99.0	13.7	18.3	522	1.13	0.06	0.21	4.35	4.96	0.25	4.1	6.6	15.5	1.6	2.5	10.4	0.3	6.4
PF16-21	80.8	-	-	476	5.34	0.07	0.54	8.51	6.25	1.05	8.8	17.8	36.7	2.0	4.4	19.5	0.6	8.2
PF16-22	3.9	7.7	-	462	8.41	0.61	4.59	8.72	58.96	4.64	55.6	155.7	273.7	2.8	31.1	141	3.1	46.1
PF16-23	42.2	-	-	447	0.40	0.79	1.33	1.96	1.34	1.26	9.9	32.6	53.9	3.3	8.9	43.4	1.1	18.0
PF16-24	93.6	-	-	473	5.01	0.07	0.24	4.23	37.62	0.50	9.7	12.9	33.7	1.3	2.9	34.5	0.5	7.03
PF16-25	87.6	-	-	357	1.19	0.42	0.49	1.37	5.85	1.74	19.3	24.4	65.5	1.3	-	-	-	-
PF16-26	68.8	11.7	18.9	458	4.44	0.11	0.48	5.23	5.10	0.77	14.1	22.6	52.7	1.6	-	-	-	-
PF16-27	8.6	7.6	25.0	405	5.67	0.54	3.83	8.36	11.61	3.51	42.1	107.0	196.3	2.5	25.7	116.9	2.6	35.4
PF16-28	11.8	7.2	25.4	416	5.66	0.61	4.28	8.18	6.25	3.29	47.0	126.1	225.7	2.7	27.0	113.8	2.5	32.3
PF16-29	24.7	7.9	25.0	475	5.25	0.65	4.91	8.77	3.71	5.08	38.7	124.5	206.6	3.2	-	-	-	-
PF16-30	0.6	7.9	25.1	420	0.46	0.60	4.81	9.33	0.55	4.83	64.8	124.3	261.8	1.9	-	-	-	-
PF16-31	84.5	-	-	419	4.84	0.07	0.39	6.87	5.76	1.03	4.5	12.3	22.1	2.7	4.0	22.5	0.6	11.1
PF16-32	0.6	8.1	23.9	398	11.16	0.55	4.14	8.78	18.32	3.42	64.1	151.8	287.7	2.4	-	-	-	-

Appendix 2.3

Concentrations of organic compounds and trace metals in the surface sediments of Flensburg Fjord in 1972/1973 according to GKFF (1973a)

Station N, 1972/73	Station N, 2006	C_{org}, %	TN, %	Cu, µg g^{-1}	Zn, µg g^{-1}	Pb, µg g^{-1}
0	PF16-01	12	0.8	200	810	200
2	PF16-02	5.5	0.5	110	360	160
3	PF16-03	5.1	0.6	120	330	170
4	PF16-04	3.1	0.3	45	140	54
5	PF16-05	4.9	0.5	89	290	110
6	PF16-06	3.9	0.6	69	210	100
7	PF16-07	7.1	0.8	96	260	120
8	PF16-08	5.1	0.8	67	190	88
11	PF16-11	1.4	0.3	23	98	23
12	PF16-13	3.5	0.5	32	160	45
12a	PF16-15	3.5	0.4	29	170	49
18	PF16-10	2.8	0.3	23	120	30
19	PF16-16	2.9	0.4	27	170	42
20	PF16-17	3.7	0.5	32	170	63
21	PF16-18	3.8	0.5	34	200	64
23	PF16-20	0.2	0.1	2.3	12	2.0
24	PF16-21	3.7	0.4	29	180	55
25	PF16-22	3.9	0.5	29	150	56
37	PF16-27	3.0	0.4	20	130	40

Appendix 2.4

Concentrations of organic compounds, trace and minor metals in core PF1738

Slice, cm	Depth, cm	TC, %	TN, %	C_{org}, %	C:N	$CaCO_3$, %	SiO_2, %	Chl *a*, μg g^{-1}	Phaeo, μg g^{-1}	Chlorine, μg g^{-1}	Phaeo: Chl *a*	Al, μg g^{-1}	Ti, μg g^{-1}	Ba, μg g^{-1}	Mn, μg g^{-1}	Fe, μg g^{-1}	U, μg g^{-1}	Mo, μg g^{-1}	V, μg g^{-1}	Cd, μg g^{-1}	Cu, μg g^{-1}	Zn, μg g^{-1}	Pb, μg g^{-1}	Sn, μg g^{-1}
0-0.5	0.25	3.05	0.27	1.75	7.54	10.86	1.63	0.70	3.45	4.86	4.9	34.4	4808	379	432	21.4	2.83	2.36	69.2	0.92	45.4	145	46.9	4.58
0.5-1	0.75	3.17	0.19	1.29	8.06	15.71	1.85	3.38	19.47	26.05	5.8	37.6	4806	393	518	23.2	2.76	2.87	66.5	0.90	33.3	132	46.1	4.04
1-1.5	1.25	3.74	0.21	1.42	7.76	19.40	2.12	3.27	18.42	24.82	5.6	34.0	4566	381	565	24.9	2.79	2.63	71.4	0.95	42.9	147	49.9	4.41
1.5-2	1.75	4.14	0.26	1.62	7.32	21.04	2.60	3.46	19.67	26.42	5.7	42.0	4175	371	594	26.8	2.78	2.19	74.2	1.08	61.2	161	55.5	4.90
2-2.5	2.25	3.92	0.24	1.69	8.10	18.54	2.41	3.65	20.99	28.19	5.7	36.1	4222	385	551	25.2	2.59	1.88	73.1	0.98	42.0	136	55.9	4.57
2.5-3	2.75	3.81	0.18	1.49	9.48	19.35	2.07	2.52	17.77	22.62	7.1	32.7	4337	379	481	26.2	2.64	1.59	77.0	1.11	101	213	59.3	4.13
3-3.5	3.25	3.49	0.21	1.60	9.05	15.74	1.88	4.47	19.67	28.51	4.4	35.6	4403	390	446	22.7	2.35	1.20	67.0	1.04	37.6	131	52.3	4.04
3.5-4	3.75	3.64	0.24	1.77	8.50	15.55	2.60	3.32	19.61	26.10	5.9	38.1	4117	409	471	23.7	2.86	1.07	66.6	1.04	97.1	212	53.8	4.44
4-4.5	4.25	3.59	0.28	1.91	7.91	14.02	1.90	4.25	23.90	32.34	5.6	42.1	4287	418	559	26.4	2.60	1.21	72.3	1.13	43.5	149	55.1	5.16
4.5-5	4.75	3.79	0.27	2.03	8.79	14.67	2.83	3.99	22.11	29.96	5.5	32.0	4392	412	503	22.4	2.43	1.35	64.9	0.94	190	135	48.6	4.85
5-5.5	5.25	3.52	0.28	2.16	8.97	11.32	2.89	4.36	25.58	34.21	5.9	35.6	4430	405	468	26.4	2.52	1.52	74.5	1.15	45.8	164	64.0	5.13
5.5-6	5.75	3.86	0.28	2.08	8.61	14.83	3.12	4.00	21.74	29.64	5.4	43.3	4367	401	456	25.7	2.60	1.38	74.8	1.08	71.3	179	59.8	5.07
6-6.5	6.25	3.58	0.36	2.07	6.75	12.60	3.28	4.21	23.26	31.62	5.5	43.1	4406	410	439	25.2	2.80	1.53	76.3	1.11	42.6	154	61.8	4.94
6.5-7	6.75	3.01	0.23	1.60	8.10	11.77	3.84	4.45	20.64	29.48	4.6	41.8	4483	418	404	22.3	2.92	1.66	68.5	1.05	47.8	149	56.7	4.67
7-7.5	7.25	3.20	0.25	1.78	8.20	11.83	3.48	5.21	24.67	35.05	4.7	38.9	4404	423	411	24.2	2.83	3.02	74.3	1.24	43.1	166	66.1	5.45
7.5-8	7.75	2.72	0.23	1.37	6.89	11.20	3.09	4.07	19.35	27.43	4.7	26.7	4442	387	372	20.0	2.96	4.16	62.4	0.90	35.4	122	48.2	4.34
8-8.5	8.25	3.04	0.22	1.47	7.89	13.09	3.68	4.55	20.16	29.21	4.4	34.1	4684	381	435	22.5	2.96	2.61	63.7	0.95	34.0	126	52.6	4.49
8.5-9	8.75	2.89	0.18	1.34	8.63	12.89	3.60	3.47	17.48	24.30	5.0	36.5	4585	393	418	20.7	2.88	2.23	60.9	0.90	32.2	121	47.5	4.46
9-9.5	9.25	3.32	0.27	1.80	7.88	12.65	3.11	4.42	23.01	31.76	5.2	34.5	4406	379	431	23.6	2.64	1.98	65.7	1.08	38.7	167	63.0	5.81
9.5-10	9.75	3.30	0.23	1.68	8.57	13.57	3.93	3.85	21.15	28.72	5.5	37.9	4248	389	415	22.2	2.79	1.71	61.0	1.08	36.8	153	61.4	5.42
10-12	11.00	3.90	0.28	2.10	8.75	14.97	2.58	4.77	24.03	33.54	5.0	39.1	4170	391	416	24.0	2.71	1.88	67.0	1.17	44.4	173	70.8	6.33
12-14	13.00	3.93	0.31	2.16	8.14	14.74	3.67	4.74	24.82	34.25	5.2	40.9	3975	381	400	24.5	2.87	2.66	70.0	1.17	39.7	175	72.2	5.97
14-16	15.00	4.00	0.35	2.48	8.38	12.71	3.63	6.05	32.99	45.08	5.5	41.5	4111	423	402	26.6	3.10	2.83	76.8	1.32	51.9	219	95.9	7.14
16-18	17.00	4.22	0.49	3.50	8.30	6.05	4.20	7.14	40.48	54.82	5.7	43.8	4311	431	410	30.3	3.55	4.84	84.9	1.49	57.5	273	115	8.34
18-20	19.00	4.37	0.38	2.82	8.64	12.88	4.38	7.50	44.06	59.15	5.9	35.9	4023	391	426	30.8	3.56	4.76	74.9	1.31	61.0	227	97.7	8.05

Appendix 2.5

Correlation matrix of organic compounds, metals, sand fraction and foraminiferal relative abundances in surface sediments of Kiel Fjord. Significant correlations ($p<0.05$, $n=40$) are shown with bold font

	Sand, %	SiO_2, %	$C_{org.}$ %	TN, %	C:N ratio	Chl *a*, μg g^{-1}	Cu, μg g^{-1}	Zn, μg g^{-1}	Sn, μg g^{-1}	Pb, μg g^{-1}	Pop den. ind/10cm^3	Abnorm tests, %	A:E index	Am bec, %	El ex ex, %	El ex cl, %	El gert, %	El wil, %	El alb, %	El inc, %	El gunt, %	A cas, %	R dent, %
Sand, %	**1.000**																						
SiO_2, %	**-0.736**	**1.000**																					
$C_{org.}$ %	**-0.797**	**0.825**	**1.000**																				
TN, %	**-0.498**	**0.472**	**0.511**	**1.000**																			
C:N	0.226	**-0.351**	-0.075	**-0.662**	**1.000**																		
Chl *a*, μg g^{-1}	**-0.378**	**0.605**	**0.402**	**0.280**	**-0.372**	**1.000**																	
Cu., μg g^{-1}	**-0.580**	**0.458**	**0.737**	**0.312**	0.128	0.031	**1.000**																
Zn, μg g^{-1}	**-0.614**	**0.499**	**0.782**	**0.319**	0.131	0.071	**0.946**	**1.000**															
Sn, μg g^{-1}	**-0.384**	**0.414**	**0.584**	**0.424**	-0.080	0.121	**0.318**	**0.286**	**1.000**														
Pb, μg g^{-1}	**-0.635**	**0.508**	**0.754**	**0.350**	0.127	0.042	**0.928**	**0.950**	**0.318**	**1.000**													
Pop den. ind/10cm^3	-0.226	0.190	0.213	0.231	-0.252	0.263	-0.122	-0.056	**0.341**	-0.043	**1.000**												
Abnorm tests. %	0.147	0.125	0.077	0.027	-0.067	0.108	-0.054	0.051	0.140	-0.023	0.039	**1.000**											
A:E index	-0.244	**0.341**	**0.349**	0.165	-0.067	0.104	0.078	0.150	**0.332**	0.125	0.029	0.163	**1.000**										
Am bec, %	**-0.296**	**0.406**	**0.337**	0.263	-0.098	-0.098	**0.330**	**0.310**	**0.295**	**0.347**	-0.042	**0.307**	**0.442**	**1.000**									
El ex ex, %	0.151	**-0.406**	-0.228	-0.207	0.156	-0.148	-0.018	-0.029	-0.165	-0.096	0.148	-0.148	**-0.394**	**-0.521**	**1.000**								
El ex cl, %	-0.257	**0.303**	0.157	0.098	-0.170	**0.622**	-0.185	-0.125	-0.043	-0.089	0.171	-0.103	-0.029	**-0.338**	-0.269	**1.000**							
El gert, %	-0.034	-0.033	0.111	0.114	0.043	-0.117	0.165	0.171	0.150	0.109	-0.185	0.177	0.062	-0.095	0.255	-0.296	**1.000**						
El wil, %	0.014	-0.058	0.039	-0.046	0.181	-0.116	0.312	0.311	-0.112	0.284	-0.129	0.025	-0.093	-0.210	0.296	-0.043	0.196	**1.000**					
El alb, %	**0.359**	**-0.280**	**-0.416**	-0.255	-0.173	-0.061	**-0.364**	**-0.365**	**-0.351**	**-0.372**	**-0.293**	0.026	-0.178	-0.246	0.027	0.216	-0.093	-0.106	**1.000**				
El inc, %	0.073	-0.046	-0.178	-0.112	-0.093	0.070	**-0.340**	**-0.339**	-0.075	-0.277	-0.135	-0.085	-0.032	-0.257	-0.223	**0.534**	0.020	-0.108	**0.419**	**1.000**			
El gunt, %	-0.141	0.221	0.107	0.117	-0.261	0.608	-0.199	-0.130	0.039	-0.186	0.032	0.054	0.078	-0.394	-0.128	**0.713**	-0.048	-0.043	0.285	**0.539**	**1.000**		
A cas, %	0.254	-0.271	-0.152	-0.151	**0.566**	-0.172	-0.175	-0.199	-0.001	-0.131	-0.119	-0.082	-0.028	-0.020	-0.103	0.183	0.014	-0.026	-0.106	0.156	-0.043	**1.000**	
R dent, %	-0.090	0.056	0.042	0.033	-0.103	0.175	-0.034	-0.028	0.113	0.092	0.063	0.033	-0.033	-0.100	-0.133	0.314	-0.011	-0.026	0.148	0.215	-0.043	-0.026	**1.000**

Am bec = *Ammonia beccarii*; El ex ex = *Elphidium excavatum excavatum*; El ex cl = *E. excavatum clavatum*; El gert = *E. gerthi*; El wil = *E. williamsoni*; El alb = *E. albiumbilicatum*; El gunt = *E. gunteri*; A cas = *Ammotium cassis*; R dent = *Reophax dentaliniformis*.

Appendix 2.6

Correlation matrix of organic compounds, metals and sand fraction in surface sediments of Flensburg Fjord. Significant correlations ($p<0.05$, $n=40$) are shown with bold font

	Sand, %	TC, %	C_{org}, %	TN, %	C:N	$CaCO_3$, %	SiO_2, %	Chl *a*, µg g^{-1}	Phaeo, µg g^{-1}	Chlorine, µg g^{-1}	Phaeo: Chl a	Cu, µg g^{-1}	Zn, µg g^{-1}	Sn, µg g^{-1}	Pb, µg g^{-1}
Sand, %	**1.000**														
TC, %	**-0.748**	**1.000**													
C_{org}, %	**-0.725**	**0.812**	**1.000**												
TN, %	**-0.791**	**0.951**	**0.736**	**1.000**											
C:N	-0.388	0.281	**0.745**	0.155	**1.000**										
$CaCO_3$, %	-0.101	0.385	-0.226	**0.424**	**-0.709**	**1.000**									
SiO_2, %	**-0.732**	**0.836**	**0.797**	**0.891**	0.267	0.134	**1.000**								
Chl *a*, µg g^{-1}	**-0.591**	**0.734**	**0.698**	**0.791**	0.206	0.120	**0.905**	**1.000**							
Phaeo, µg g^{-1}	**-0.677**	**0.813**	**0.776**	**0.879**	0.261	0.130	**0.980**	**0.932**	**1.000**						
Chlorine, µg g^{-1}	**-0.649**	**0.791**	**0.754**	**0.854**	0.240	0.128	**0.962**	**0.979**	**0.986**	**1.000**					
Phaeo: Chl *a*	**0.702**	**-0.509**	-0.465	-0.514	-0.353	-0.114	-0.389	-0.099	-0.326	-0.227	**1.000**				
Cu, µg g^{-1}	**-0.559**	**0.824**	**0.889**	**0.712**	**0.571**	-0.031	**0.780**	**0.693**	**0.773**	**0.750**	-0.340	**1.000**			
Zn, µg g^{-1}	**-0.674**	**0.894**	**0.828**	**0.847**	0.333	0.183	**0.906**	**0.840**	**0.897**	**0.886**	-0.339	**0.929**	**1.000**		
Sn, µg g^{-1}	**-0.538**	**0.832**	**0.823**	**0.698**	0.457	0.087	**0.749**	**0.693**	**0.732**	**0.727**	-0.279	**0.974**	**0.945**	**1.000**	
Pb, µg g^{-1}	**-0.615**	**0.868**	**0.824**	**0.757**	0.400	0.146	**0.802**	**0.687**	**0.762**	**0.741**	-0.371	**0.957**	**0.961**	**0.983**	**1.000**

Appendix 2.7

Correlation matrix of organic cmpounds, trace and minor metals and sediment size fractions in core PF738 from the outer Kiel Fjord. Significant correlations ($p<0.05$, $n=25$) are shown with bold font

	Ti, µg g^{-1}	V, µg g^{-1}	Cu, µg g^{-1}	Zn, µg g^{-1}	Mo, µg g^{-1}	Cd, µg g^{-1}	Sn, µg g^{-1}	Ba, µg g^{-1}	Pb, µg g^{-1}	U, µg g^{-1}	Al, µg g^{-1}	Fe, µg g^{-1}	Mn, µg g^{-1}	TC, %	TN, %	C_{org}, %	SiO_2, %	Chl *a*, µg g^{-1}	Phaeo, µg g^{-1}	Chlorine, µg g^{-1}	< 2 µm, %	< 20 µm, %
Ti, µg g^{-1}	**1.000**																					
V, µg g^{-1}	-0.309	**1.000**																				
Cu, µg g^{-1}	-0.180	0.063	**1.000**																			
Zn, µg g^{-1}	**-0.554**	**0.708**	0.199	**1.000**																		
Mo, µg g^{-1}	-0.047	0.266	-0.243	0.382	**1.000**																	
Cd, µg g^{-1}	**-0.607**	**0.734**	-0.029	**0.848**	**0.404**	**1.000**																
Sn, µg g^{-1}	**-0.550**	**0.509**	-0.031	**0.753**	**0.598**	**0.873**	**1.000**															
Ba, µg g^{-1}	-0.127	0.389	0.205	0.371	0.048	**0.511**	0.371	**1.000**														
Pb, µg g^{-1}	**-0.551**	**0.655**	-0.047	**0.849**	**0.588**	**0.937**	**0.951**	**0.429**	**1.000**													
U, µg g^{-1}	-0.211	0.338	-0.195	**0.604**	**0.840**	**0.553**	**0.711**	0.229	**0.719**	**1.000**												
Al, µg g^{-1}	-0.335	**0.514**	-0.172	**0.402**	-0.112	**0.554**	0.398	**0.476**	**0.434**	0.203	**1.000**											
Fe, µg g^{-1}	**-0.521**	**0.852**	0.083	**0.774**	0.347	**0.794**	**0.695**	0.263	**0.762**	**0.459**	**0.472**	**1.000**										
Mn, µg g^{-1}	0.059	0.154	0.223	-0.199	-0.345	-0.292	-0.366	-0.228	-0.374	**-0.410**	0.044	0.223	**1.000**									
TC, %	**-0.707**	**0.673**	0.336	**0.681**	0.130	**0.637**	**0.599**	0.090	**0.630**	0.231	**0.415**	**0.840**	0.315	**1.000**								
TN, %	**-0.439**	**0.674**	0.056	**0.707**	**0.494**	**0.811**	**0.862**	**0.487**	**0.854**	**0.623**	**0.487**	**0.706**	-0.259	**0.596**	**1.000**							
C_{org}, %	**-0.502**	**0.666**	0.156	**0.791**	**0.449**	**0.867**	**0.906**	**0.512**	**0.909**	**0.582**	**0.454**	**0.753**	-0.275	**0.672**	**0.955**	**1.000**						
SiO_2, %	-0.356	0.095	-0.086	0.372	**0.480**	**0.514**	**0.631**	0.324	**0.613**	**0.661**	0.260	0.242	**-0.611**	0.106	**0.495**	**0.503**	**1.000**					
Chl *a*, , µg g^{-1}	**-0.516**	0.383	-0.074	**0.540**	**0.552**	**0.769**	**0.810**	**0.487**	**0.820**	**0.598**	0.324	**0.600**	-0.358	**0.449**	**0.674**	**0.727**	0.711	**1.000**				
Phaeo, µg g^{-1}	**-0.585**	**0.514**	0.035	**0.677**	**0.550**	**0.817**	**0.854**	**0.465**	**0.874**	**0.626**	0.338	**0.761**	-0.219	**0.609**	**0.736**	**0.802**	0.650	**0.955**	**1.000**			
Chlorine, µg g^{-1}	**-0.571**	**0.484**	0.005	**0.647**	**0.557**	**0.812**	**0.851**	**0.475**	**0.869**	**0.626**	0.337	**0.725**	-0.260	**0.571**	**0.728**	**0.791**	0.672	**0.976**	0.997	**1.000**		
< 2 µm, %	-0.068	-0.325	-0.186	-0.142	0.308	0.039	0.168	0.052	0.087	0.299	-0.101	-0.275	**-0.435**	-0.244	0.020	-0.037	0.340	0.247	0.109	0.147	**1.000**	
< 20 µm, %	-0.158	-0.279	-0.375	0.064	**0.437**	0.267	**0.462**	0.038	0.374	**0.450**	-0.028	-0.147	**-0.729**	-0.225	0.181	0.170	**0.710**	**0.480**	0.339	0.380	**0.676**	**1.000**

Appendix 3. Foraminiferal data

Appendix 3.1

Foraminiferal census data (percentages) of the living assemblages 63-2000 μm, Kiel Fjord

Stations	*Ammonia beccarii*	*Ammoium cassis*	*Elphidium albiumbilicatum*	*Elphidium e. clavatum*	*Elphidium e. excavatum*	*Elphidium incertum*	*Reophax dentaliniformis regularis*	*Elphiidium gerthi*	*Elphidium williamsoni*	*Elphidium guntheri*	Counted specimens	Population density. ind.10cm^{-3}	Test abnormalities. %	Species with abnormal tests*
P0220-37.2		90.0					10.0				10	3.1	no	
P0220-35.2		6.3	2.1	73.7		6.3		1.0			95	29.7	no	
PF15-01											0	-	-	
PF15-02	60.9				39.1						23	10.5	13.0	am, el ex ex
PF15-03	57.8				38.8			3.4			147	272.7	12.0	am, el ex ex
PF15-04	22.6			5.5	66.4			4.8	0.7		146	67.1	1.4	am, el ex ex
PF15-05	51.6		5.4	4.1	41.8						122	125.9	5.7	am, el ex ex
PF15-06	34.7			9.0	56.3						245	1568.0	3.8	am, el ex ex
PF15-07	25.3		2.2		72.2						79	21.0	3.8	am, el ex ex
PF15-08	27.7		2.2		56.9	4.6		10.0			130	135.4	3.1	am, el ex ex
PF15-09	48.6			2.4	49.0						255	868.1	4.7	am, el ex ex
PF15-10	51.5		3.3	28.7	18.1						171	342.0	2.4	am, el ex ex
PF15-11	57.1		3.3		36.7						49	8.2	6.0	am, el ex ex
PF15-12	72.5		2.2		25.1	1.2		0.6			346	424.5	1.4	el ex ex
PF15-13	84.1			11.6	2.9	1.4					138	447.9	2.2	am, el ex cl
PF15-14	55.3				37.4			7.3			179	703.9	3.9	am, el ex ex
PF15-15	58.0			13.0	21.0	8.0					138	581.1	1.4	am, el ex ex
PF15-16	59.9		2.2	12.6	25.3	1.5					269	1484.1	2.6	am
PF15-17	80.2		3.3		15.1			2.4			126	44.2	19.8	am
PF15-18	32.6		13.0		52.2			2.2			92	39.1	4.3	am
PF15-19	68.1		3.6	6.2	21.8	6.2		0.3			385	810.5	7.0	am, el ex ex, el inc, el ex cl, el al
PF15-20	21.4		9.7	44.7	5.8	17.5				1.0	103	238.8	3.9	am, el ex ex

PF15-21	46.5		3.5	7.0	36.8	3.5		1.8		114	536.5	2.6	am, el ex ex, el alb
PF15-22	53.4			7.9	37.6			1.1		189	1314.8	17.5	am, el ex ex
PF15-23	72.5			2.8	20.2			4.6		109	684.4	14.7	am, el ex ex
PF15-24	79.3			3.0	13.6			4.0		198	1413.0	11.1	am, el ex ex
PF15-25	71.0			1.0	24.5			3.5		200	1405.6	6.5	am, el ex ex, el ger
PF15-26	12.0			6.7	61.3	10.7	1.3	8.0		75	84.6	5.3	am, el ex cl, el ex ex
PF15-27	79.9		0.7	5.8	12.9			0.7		139	1263.2	4.3	am
PF15-28	68.1			6.7	22.1	3.1				163	3798.5	2.5	am
PF15-29	72.0			12.2	13.3	1.8		0.7		271	2043.6	12.9	am, el ex ex, el inc
PF15-30	46.0		1.0	15.0	30.0	3.0		3.0	1.0	100	956.6	3.0	am, el ger
PF15-31	43.5		0.8	21.0	27.4	0.8		6.5		124	561.9	3.2	am, el ex ex, el ger
PF15-32	62.8		0.7	16.0	17.4	2.4		0.7		288	995.2	4.2	am, el ex ex
PF15-33	62.4		0.0	15.1	18.8	1.4		2.3		218	1074.3	5.5	am, el ex cl, el ex ex
PF15-34	43.2		0.5		51.8	3.2		1.4		220	721.3	4.5	am, el ex ex
PF15-35	56.3		1.0	12.5	26.0	4.2				96	451.8	4.2	am
PF15-36	79.5				20.5					117	260.0	1.7	am, el exc ex
PF15-37	47.1		5.9		36.1	10.9				119	280.0	4.2	am, el ex ex
PF15-38	3.0			12.5	84.5					168	4895.1	4.2	el ex ex
PF15-39	79.4		0.5	3.4	13.7	2.0		1.0		204	2199.8	11.3	am, el ex ex
PF15-40	55.5		0.7	25.5	13.9	4.4				274	550.1	5.1	am, el ex ex, el inc
PF15-41	47.8		0.5	14.0	37.1			0.5		186	551.2		
PF15-42	51.4	0.7	3.4	12.8	29.7	1.4		0.7		148	341.9	6.8	am, el ex ex
PF15-43	34.7		2.0	1.3	45.3	8.0		8.7		150	81.1	3.3	am, el ex ex
PF15-45	70.2			6.0	22.4	1.1		0.3		352	1448.6	5.1	am
PF15-46	44.9			10.8	38.0	6.3				158	239.0	3.2	am, el exc ex
PF15-47	80.3		0.5	7.1	9.8	2.2				183	1255.4	8.7	am, el ex ex
PF15-48	62.9	0.8	0.8	4.4	27.9	1.6		1.6		251	1249.9	6.0	am, el ex ex, el ger
PF15-49	58.3		1.2	10.4	28.2	0.6		1.2		163	191.8	6.7	am
PF15-50	71.8			6.6	21.2			0.4		241	2298.9	1.2	am
PF15-51	50.8		0.3	8.8	33.1	7.0				329	2117.9	2.1	am, el ex ex, el inc
PF15-52	76.6			0.8	18.9	1.1		2.6		265	749.7	5.7	am, el ex ex, el ger
PF15-52	76.6			0.8	18.9	1.1		2.6		265	749.7	5.7	am, el ex ex, el ger

PF15-53	35.1			3.1	60.8	1.0				288	332.0	5.2	am, el exc ex
PF15-54	54.2			0.0	2.4	2.4		7.2	0.4	249	1010.2	10.4	am, el ex ex, el inc, el ger
PF15-55	52.1		1.0	10.0	25.1	4.7	0.9	5.7		211	446.5	6.6	am, el ex ex, el ger
PF15-56	48.8	1.2		22.8	19.1	6.2		1.9		162	122.0	3.1	am, el ex cl
PF15-57	37.8		4.4	32.8	15.7	7.6	0.3	1.5		344	1151.4	7.0	am, el ex cl, el inc, el ger
PF15-58										1			
PF15-59	3.8		2.2	54.3	32.3	6.5			1.1	186	1454.3	5.4	el ex ex, el ex cl
PF15-60	3.1		1.0	9.3	53.6	32.0		1.0		97	36.8	3.1	el inc
PF15-61	9.8		7.1	21.9	39.9	20.2		0.5	0.5	183	60.9	3.3	am, el inc, el ex ex, el ex cl
PF15-90	68.8			10.6	13.5	6.5	0.6			170	347.1	5.3	am, el inc
Mean	52.0	19.8	2.6	13.2	31.2	5.5	2.6	2.8	0.6	0.9	174	806.6	5.7	
Lutze`s samples**:													
342 (PF15-36)		15.4			80.8	3.8					26	**50.0**	
341 (PF15-35)			12.5		68.8	18.8					16	**22.5**	
340 (PF15-34)			3.5	7.0	57.9	14.0	15.8	1.8			57	**11.3**	
239 (PF15-38)		10.4	3.8	46.2	24.5	13.2		0.9			106	**11.0**	
Mean		0.9	6.6	26.6	58.0	12.5	15.8	1.3			51	23.7	

*am indicates the specie *Ammonia beccari*. el ex ex – *Elphidium excavatum excavatum*. el ex cl – *E. excavatum clavatum*. el inc – *E. incertum*. el alb – *E. albiiumbilicatum*. el ger – *E. gerthi.*

** The **bold** numbers indicate data taken from the Lutze`s manuscript (Lutze. 1965)

Appendix 3. 2

The living and dead percentages of foraminifera in years 1963 (Lutze. 1965) and 2006, Kiel Fjord

Sample	1963*			2006		
	Living ind. %	Dead ind. %	Living/ Dead ratio	Living ind. %	Dead ind. %	Living/ Dead ratio
342 (PF15-36)	15	85	0.2	47	53	0.9
341 (PF15-35)	15	85	0.2	24	76	0.3
340 (PF15-34)	0	100	0.0	40	60	0.7
238 (PF15-37)	20	80	0.3	38	62	0.6
239 (PF15-38)	10	90	0.1	76	24	3.2
mean	12	88	0.2	45	55	1.1

* The living and dead foraminifera percentages in 1963 are taken from Lutze (1965)

Appendix 3.3
Foraminifera species from Kiel Fjord

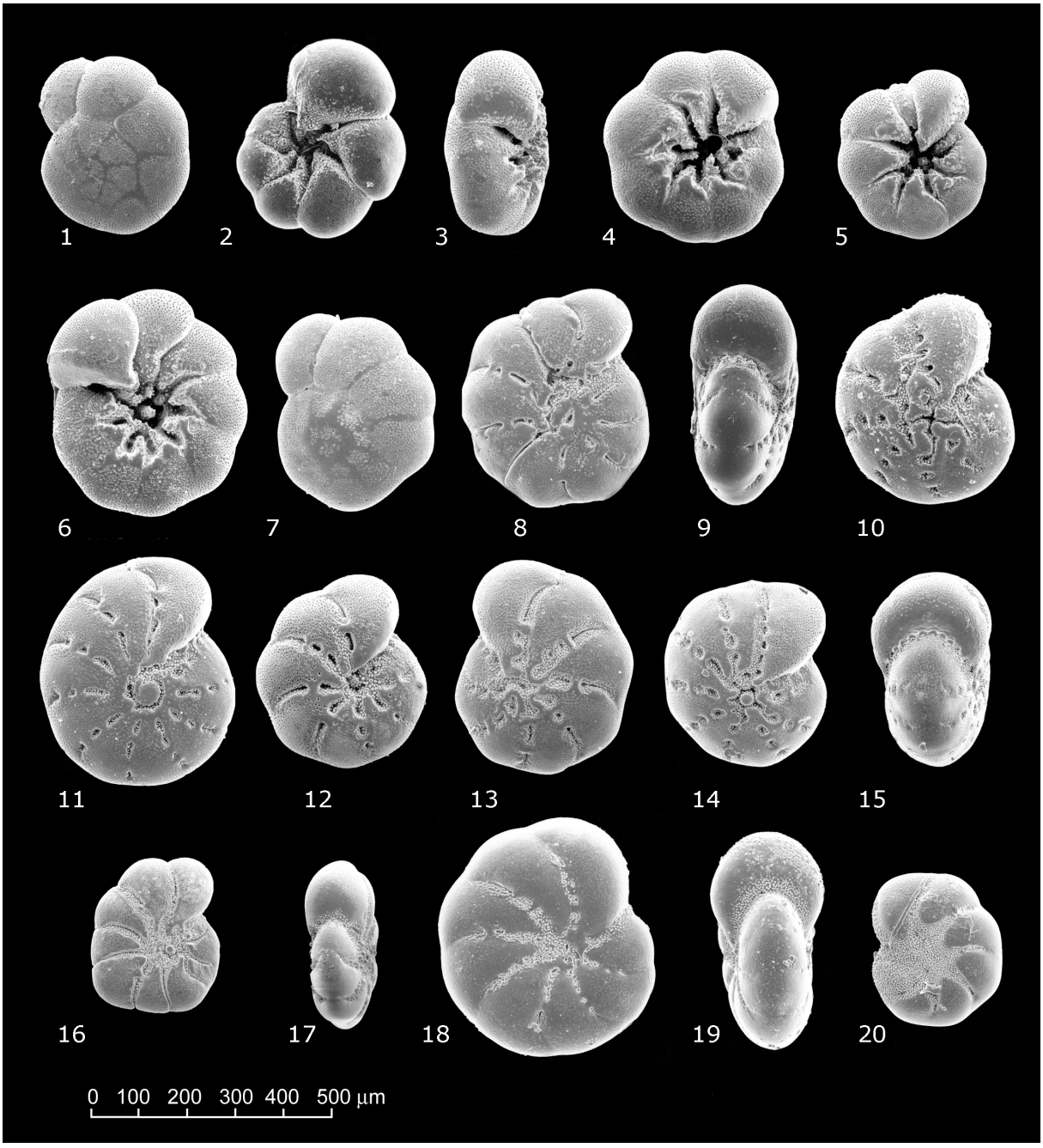

PLATE 1. **1-7.** *Ammonia beccarii*. Poorly ornamented spiral sides (1.7). Aperture view (3). Umbilical view (2. 4-6). **8-13.** *Elphidium excavatum excavatum.* Spiral view (8.11-13). Aperture view (9). **14-15.** *Elphidium excavatum clavatum.* spiral and aperture view. **16-17.** *Elphidium gerthi.* spiral and aperture view. **18-19.** *Elphidium incertum.* spiral and aperture view. **20.** *Elphidium albiumbilicatum*. spiral view.

Appendix 4

Activities of ^{210}Pb and ^{137}Cs in core PF1738

Slice	Mean depth, cm	Density, g cm^{-3}	$^{210}Pb_{exc}$, Bq g^{-1}	Error $^{210}Pb_{exc}$, Bq g^{-1}	2 σ, %	$^{210}Pb_{sup}$, Bq g^{-1}	Error act. $^{210}Pb_{sup}$, Bq g^{-1}	2 σ, %	^{137}Cs, Bq g^{-1}	Error ^{137}Cs, Bq g^{-1}	2 σ, %
0.0-0.5	0.25	1.785	56.78	14.48	17.9	23.95	2.06	8.6	18.86	1.71	9.0
0.5-1.0	0.75	1.304	71.82	19.23	20.6	21.39	2.43	11.4	20.28	2.19	10.8
1.0-1.5	1.25	1.374	56.81	16.65	21.8	19.41	2.18	11.2	20.76	2.00	9.6
1.5-2.0	1.75	1.451	57.64	16.65	21.0	21.61	2.21	10.2	24.94	2.05	8.2
2.0-2.5	2.25	1.462	60.62	16.28	20.5	18.81	2.14	11.4	26.39	2.01	7.6
2.5-3.0	2.75	1.430	63.02	16.60	19.9	20.39	2.23	11.0	26.51	2.09	7.9
3.0-3.5	3.25	1.620	45.12	13.83	19.7	25.06	2.06	8.2	25.61	1.76	6.9
3.5-4.0	3.75	1.641	41.75	12.63	20.7	19.16	1.79	9.4	22.43	1.66	7.4
4.0-4.5	4.25	1.349	46.3	15.44	22.4	22.77	2.14	9.4	24.97	1.99	7.8
4.5-5.0	4.75	1.672	27.28	13.10	24.7	25.83	1.99	7.7	24.49	1.74	7.1
5.0-6.0	5.5	1.385	33.01	15.23	26.7	24.10	2.17	9.0	32.11	2.10	6.5
6.0-7.0	6.5	1.613	34.49	14.53	25.4	22.74	2.09	9.2	26.06	1.96	7.5
7.0-8.0	7.5	1.328	26.69	15.64	30.5	24.62	2.25	9.1	19.17	1.87	9.7
8.0-9.0	8.5	1.429	16.19	15.00	33.4	28.73	2.37	8.3	21.57	1.88	8.7
9.0-10	9.5	1.425	12.92	15.28	34.2	31.77	2.40	7.5	19.50	1.86	9.5

Appendix 5 Grain-size data

Appendix 5.1

Sand (>63 µm), silt (2-63 µm) and clay (< 2 µm) content, core PF1738, outer Kiel Fjord

Depth, cm	>63 µm, %	2-63 µm, %	< 2 µm, %
0-0.5	84.6	14.9	0.50
0.5-1.0	84.6	14.9	0.50
1.0-1.5	84.6	14.9	0.50
1.5-2.0	83.1	16.1	0.8
2.0-2.5	83.1	16.1	0.8
2.5-3.0	83.1	16.1	0.8
3.0-3.5	84.4	15.1	0.5
3.5-4.0	84.4	15.1	0.5
4.0-4.5	82.5	16.8	0.7
4.5-5.0	82.5	16.8	0.7
5.0-5.5	85.3	14.3	0.4
5.5-6.0	85.3	14.3	0.4
6.0-6.5	81.0	18.4	0.6
6.5-7.0	81.0	18.4	0.6
7.0-7.5	75.7	33.5	0.8
7.5-8.0	75.7	33.5	0.8
8.0-8.5	35.4	53.2	11.4
8.5-9.0	35.0	53.7	11.3
9.0-9.5	29.1	57.6	13.3
9.5-10.0	27.8	62.3	10.0
10.0-10.5	24.0	64.3	11.7
10.5-11.0	49.1	40.9	10.0
11.0-11.5	26.5	62.1	11.5
11.5-12.0	47.5	44.7	7.8
12.0-12.5	37.8	52.7	9.5
12.5-13.0	33.3	56.4	10.3
13.0-13.5	31.0	57.7	11.2
13.5-14.0	27.5	60.7	11.8
14.0-14.5	13.4	71.1	15.5
14.5-15.0	18.6	64.8	16.5
15.0-15.5	23.6	60.8	15.6
15.5-16.0	19.3	64.9	15.8
16.0-16.5	20.2	65.4	14.4
16.5-17.0	29.0	56.2	14.8
17.0-17.5	22.1	61.9	16.0
17.5-18.0	10.3	71.1	18.6
18.0-18.5	12.1	68.3	19.6
18.5-19.0	10.6	71.5	17.9
19.0-19.5	21.1	63.7	15.1
19.5-20.0	15.6	69.0	15.4
20.0-20.5	14.6	67.4	18.0
20.5-21.0	22.6	62.0	15.5
21.0-21.5	15.2	66.4	18.4
21.5-22.0	20.6	64.2	15.2
22.0-22.5	18.7	64.2	17.2
22.5-23.0	13.1	68.1	18.9
23.0-23.5	13.8	68.7	17.6
23.5-24.0	54.9	37.3	7.8
24.0-24.5	47.9	43.4	8.7
24.5-25.0	50.2	42.0	7.9

APPENDIX 5.2

Silt fraction of core PF1838 in mass-%. Sedigraph output data

cm/µm	63.1	59.6	56.2	53.1	50.1	47.3	44.7	42.2	39.8	37.6	35.5	33.5	31.6	29.9	28.2	26.6	25.1	23.7	22.4	21.1	20.0	18.8	17.8	16.8	15.9	15.0	14.1	13.3	12.6	11.9	11.2
0.0-1.5	1.0	2.5	3.3	4.1	4.9	5.5	5.8	5.7	5.5	5.0	4.5	3.8	3.2	2.7	2.3	2.0	1.7	1.5	1.3	1.0	0.8	0.6	0.5	0.5	0.5	0.7	0.8	0.8	0.8	0.8	0.8
1.5-3.0	0.8	2.2	2.9	3.8	4.8	5.6	6.1	6.3	6.2	5.8	5.2	4.5	3.8	3.2	2.6	2.2	1.8	1.5	1.2	1.0	0.9	0.8	0.7	0.7	0.7	0.6	0.6	0.5	0.5	0.5	0.4
3.0-4.0	1.0	2.4	3.2	4.1	5.0	5.8	6.2	6.3	6.0	5.5	4.9	4.2	3.5	2.9	2.4	1.9	1.5	1.3	1.1	1.0	1.0	1.0	1.0	0.9	0.8	0.7	0.6	0.6	0.6	0.5	0.4
4.0-5.0	0.8	1.8	2.3	3.0	3.9	4.9	5.6	6.0	6.0	5.7	5.2	4.6	3.9	3.2	2.5	2.0	1.6	1.3	1.2	1.1	1.0	0.9	0.9	0.8	0.8	0.7	0.6	0.6	0.6	0.6	0.5
5.0-6.0	0.8	1.9	2.4	3.1	3.7	4.3	4.7	4.9	4.9	4.7	4.4	4.0	3.5	3.0	2.6	2.3	2.0	1.8	1.7	1.5	1.4	1.3	1.2	1.1	1.0	0.9	0.9	0.8	0.8	0.8	0.7
6.0-7.0	0.5	1.4	1.9	2.4	3.0	3.4	3.7	3.9	3.8	3.7	3.5	3.2	3.0	2.8	2.5	2.3	2.1	1.9	1.7	1.5	1.5	1.5	1.5	1.6	1.5	1.4	1.2	1.0	0.8	0.8	0.8
7.0-8.0	0.1	0.3	0.4	0.5	0.7	0.9	1.1	1.3	1.5	1.6	1.7	1.8	1.8	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	2.0	2.1	2.2	2.2	2.3	2.3	2.3	2.4	2.4	2.4
8.0-8.5	0.0	0.1	0.2	0.3	0.4	0.6	0.7	0.9	1.0	1.1	1.2	1.2	1.2	1.3	1.3	1.4	1.5	1.6	1.6	1.7	1.7	1.7	1.8	1.8	1.9	2.1	2.2	2.4	2.5	2.7	2.7
8.5-9.0	0.1	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.4	1.4	1.4	1.4	1.5	1.5	1.6	1.7	1.9	2.0	2.1	2.2	2.2	2.3	2.3	2.3	2.3	2.3
9.0-9.5	0.1	0.2	0.2	0.3	0.5	0.7	0.8	1.0	1.2	1.3	1.4	1.5	1.5	1.6	1.6	1.7	1.8	1.8	1.8	1.9	1.9	2.0	2.1	2.2	2.4	2.5	2.5	2.5	2.5	2.5	2.5
9.5-10.0	0.1	0.1	0.2	0.4	0.6	0.7	0.9	1.1	1.3	1.4	1.5	1.6	1.6	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.8	1.9	2.1	2.3	2.6	2.9	3.4	3.8	4.2
10.0-10.5	0.0	0.1	0.3	0.4	0.6	0.8	1.0	1.2	1.4	1.5	1.6	1.7	1.8	1.8	1.8	1.8	1.8	1.9	1.9	1.9	2.0	2.0	2.2	2.3	2.6	2.8	2.9	3.0	3.0	2.9	2.8
10.5-11.0	0.2	0.4	0.5	0.6	0.7	0.9	1.1	1.2	1.4	1.6	1.7	1.8	1.8	1.8	1.8	1.7	1.7	1.7	1.8	1.9	2.0	2.1	2.2	2.2	2.2	2.2	2.2	2.2	2.1	1.9	1.8
11.0-11.5	0.1	0.2	0.3	0.4	0.6	0.8	1.0	1.1	1.3	1.4	1.4	1.4	1.4	1.3	1.3	1.3	1.4	1.4	1.5	1.6	1.7	1.8	2.0	2.2	2.4	2.7	3.1	3.4	3.7	3.9	4.0
11.5-12.0	0.3	0.8	1.1	1.5	1.9	2.3	2.7	2.9	3.1	3.2	3.1	3.0	2.8	2.6	2.4	2.2	2.0	1.9	1.8	1.7	1.6	1.6	1.6	1.6	1.7	1.7	1.7	1.7	1.7	1.6	1.6
12.0-12.5	0.2	0.5	0.6	0.9	1.1	1.4	1.7	1.9	2.1	2.2	2.3	2.3	2.3	2.3	2.2	2.0	2.0	1.9	1.9	1.8	1.8	1.8	1.8	1.9	2.1	2.3	2.4	2.6	2.6	2.6	2.6
12.5-13.0	0.1	0.3	0.3	0.5	0.6	0.8	1.0	1.3	1.5	1.6	1.8	1.8	1.8	1.8	1.8	1.7	1.7	1.7	1.7	1.8	1.8	1.9	2.0	2.0	2.2	2.4	2.6	2.8	3.1	3.3	3.3
13.0-13.5	0.1	0.3	0.4	0.5	0.7	0.9	1.0	1.2	1.4	1.5	1.6	1.6	1.7	1.7	1.8	1.7	1.8	1.8	1.8	1.8	1.8	1.8	1.9	2.0	2.1	2.2	2.4	2.5	2.6	2.7	2.7
13.5-14.0	0.0	0.1	0.2	0.3	0.5	0.7	0.9	1.1	1.3	1.5	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.7	1.8	2.0	2.2	2.3	2.5	2.6	2.6	2.6	2.6	2.5
14.0-14.5	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.2	1.3	1.3	1.3	1.3	1.4	1.5	1.6	1.7	1.8	2.0	2.2	2.4	2.6	2.7	2.9	2.9	2.9	2.9
14.5-15.0	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.9	0.9	0.9	0.9	1.0	1.0	1.0	1.1	1.2	1.3	1.5	1.7	1.9	2.1	2.3	2.5	2.6	2.7	2.9	2.9	3.0
15.0-15.5	0.1	0.2	0.2	0.3	0.4	0.4	0.5	0.6	0.6	0.7	0.7	0.8	0.9	1.0	1.1	1.1	1.2	1.2	1.3	1.3	1.4	1.5	1.7	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.1
15.5-16.0	0.1	0.2	0.2	0.3	0.4	0.5	0.7	0.8	0.9	0.9	1.0	1.0	1.0	1.0	0.9	1.0	1.0	1.0	1.1	1.1	1.2	1.3	1.4	1.5	1.7	2.0	2.3	2.6	2.9	3.2	3.4
16.0-16.5	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.0	1.1	1.1	1.2	1.2	1.2	1.2	1.2	1.3	1.3	1.3	1.4	1.4	1.6	1.8	2.0	2.3	2.6	3.0	3.4	3.8
16.5-17.0	0.0	0.1	0.2	0.2	0.3	0.5	0.6	0.8	0.9	1.0	1.2	1.2	1.3	1.2	1.2	1.1	1.1	1.2	1.3	1.4	1.5	1.6	1.8	1.9	2.1	2.3	2.4	2.5	2.6	2.6	2.6
17.0-17.5	0.1	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.7	0.8	0.9	1.0	1.1	1.2	1.2	1.3	1.3	1.3	1.3	1.4	1.4	1.5	1.6	1.7	1.9	2.1	2.4	2.6	2.8	2.9	3.0
17.5-18.0	0.1	0.2	0.2	0.3	0.4	0.4	0.5	0.6	0.6	0.6	0.7	0.7	0.8	0.8	0.9	0.9	0.9	1.0	1.0	1.0	1.1	1.2	1.3	1.5	1.8	2.1	2.5	2.8	3.1	3.4	3.6
18.0-18.5	0.0	0.1	0.1	0.1	0.2	0.2	0.3	0.4	0.5	0.6	0.6	0.7	0.8	0.8	0.8	0.8	0.8	0.9	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.7	2.0	2.3	2.7	3.1	3.6
18.5-19.0	0.1	0.2	0.2	0.3	0.3	0.4	0.5	0.6	0.6	0.7	0.7	0.7	0.7	0.8	0.8	0.9	1.0	1.1	1.1	1.2	1.2	1.2	1.3	1.4	1.5	1.7	1.9	2.1	2.4	2.7	3.1
19.0-19.5	0.0	0.1	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.1	1.1	1.2	1.2	1.3	1.3	1.4	1.5	1.7	1.9	2.2	2.6	3.1
19.5-20.0	0.1	0.2	0.2	0.4	0.5	0.6	0.7	0.7	0.8	0.8	0.8	0.8	0.8	0.8	0.9	0.9	1.0	1.1	1.2	1.3	1.4	1.6	1.8	2.0	2.2	2.5	2.8	3.2	3.6	3.9	4.1
20.0-20.5	0.1	0.2	0.3	0.3	0.4	0.5	0.6	0.7	0.7	0.7	0.8	0.9	0.9	0.9	1.0	1.0	1.0	1.0	1.1	1.1	1.2	1.3	1.5	1.6	1.7	1.8	1.9	2.1	2.2	2.3	2.5
20.5-21.0	0.0	0.1	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.9	1.0	1.0	1.1	1.1	1.1	1.1	1.1	1.1	1.2	1.2	1.3	1.4	1.6	1.7	1.8	2.0	2.1	2.3	2.4	2.5	2.7
21.0-21.5	0.0	0.1	0.1	0.2	0.2	0.3	0.4	0.5	0.5	0.6	0.7	0.9	1.0	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.2	1.3	1.5	1.6	1.8	2.0	2.2	2.5	2.8	3.1
21.5-22.0	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.8	0.8	0.9	1.0	1.0	1.0	1.1	1.1	1.1	1.1	1.1	1.2	1.3	1.4	1.6	1.7	1.8	1.8	1.9	2.1	2.3	2.5	2.8	3.0
22.0-22.5	0.0	0.0	0.0	0.1	0.1	0.2	0.2	0.3	0.4	0.5	0.6	0.6	0.6	0.7	0.7	0.7	0.8	0.9	0.9	1.0	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.8	2.0	2.3	2.8
22.5-23.0	0.1	0.2	0.2	0.3	0.3	0.4	0.4	0.4	0.4	0.5	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.9	0.9	1.0	1.1	1.2	1.4	1.6	1.8	2.0	2.3	2.6	3.0	3.3	3.5
23.0-23.5	0.0	0.1	0.2	0.3	0.4	0.6	0.8	0.9	1.1	1.1	1.2	1.2	1.2	1.2	1.1	1.1	1.1	1.1	1.1	1.2	1.3	1.4	1.6	1.8	1.9	2.1	2.2	2.3	2.4	2.4	2.3
23.5-24.0	0.1	0.3	0.4	0.6	0.7	0.9	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.8	1.8	1.7	1.7	1.6	1.6	1.6	1.6	1.8	1.9	2.0	2.1	2.2	2.2	2.2	2.2	2.1
24.0-24.5	0.1	0.3	0.4	0.5	0.7	0.8	1.0	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.8	1.9	1.9	1.8	1.8	1.7	1.7	1.7	1.8	1.9	1.9	2.0	2.1	2.2	2.3	2.4	2.5
24.5-25.0	0.1	0.3	0.5	0.7	0.9	1.1	1.4	1.6	1.7	1.8	1.8	1.8	1.7	1.7	1.7	1.7	1.6	1.6	1.6	1.6	1.6	1.7	1.7	1.8	1.9	2.0	2.0	2.1	2.1	2.1	2.1

→

cm / µm	10.6	10.0	9.44	8.91	8.41	7.94	7.50	7.08	6.68	6.31	5.96	5.62	5.31	5.01	4.73	4.47	4.22	3.98	3.76	3.55	3.35	3.16	2.99	2.82	2.66	2.51	2.37	2.24	2.11	2.00
0.0-1.5	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.2	0.3	0.4	0.5	0.6	0.6	0.6	0.6	0.5	0.5	0.5	0.4	0.4	0.4	0.3	0.2	0.0	0.0	0.1	0.2	0.4	0.5
1.5-3.0	0.4	0.4	0.4	0.3	0.3	0.3	0.3	0.2	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.3	0.4	0.4	0.4	0.4	0.4	0.3	0.2	0.2	0.1	0.0	0.0	0.0	0.1	0.2
3.0-4.0	0.3	0.3	0.4	0.4	0.5	0.4	0.4	0.3	0.3	0.3	0.3	0.3	0.2	0.3	0.3	0.3	0.3	0.3	0.2	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.2
4.0-5.0	0.5	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.5	0.5	0.4	0.4	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.2
5.0-6.0	0.7	0.7	0.7	0.8	0.8	0.8	0.7	0.6	0.5	0.4	0.4	0.4	0.4	0.5	0.5	0.6	0.6	0.6	0.6	0.6	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.3
6.0-7.0	0.9	1.0	1.1	1.1	1.0	0.9	0.8	0.7	0.6	0.6	0.5	0.4	0.4	0.5	0.5	0.6	0.6	0.6	0.6	0.5	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.3
7.0-8.0	2.3	2.2	2.1	1.9	1.8	1.6	1.5	1.4	1.3	1.2	1.2	1.1	1.1	1.0	1.0	1.0	1.0	0.9	0.9	0.9	0.8	0.8	0.7	0.7	0.7	0.7	0.7	0.6	0.6	0.6
8.0-8.5	2.8	2.8	2.7	2.5	2.3	2.1	1.9	1.7	1.5	1.3	1.2	1.1	1.0	0.9	0.9	1.0	1.0	1.0	1.0	1.0	0.9	0.9	0.8	0.8	0.8	0.8	0.7	0.7	0.7	0.7
8.5-9.0	2.2	2.2	2.1	1.9	1.8	1.7	1.6	1.5	1.5	1.5	1.4	1.4	1.3	1.2	1.2	1.2	1.2	1.2	1.1	1.1	1.0	1.0	0.9	0.9	0.8	0.8	0.7	0.7	0.7	0.7
9.0-9.5	2.5	2.4	2.2	2.0	1.8	1.5	1.3	1.2	1.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.9	0.9	0.8	0.7	0.7	0.7	0.7	0.7	0.6	0.5	0.5	0.5	0.5
9.5-10.0	4.4	4.4	4.1	3.6	2.9	2.2	1.5	1.1	0.8	0.6	0.5	0.5	0.5	0.4	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.3
10.0-10.5	2.7	2.5	2.2	2.0	1.7	1.5	1.3	1.1	1.0	0.9	0.9	0.9	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.7	0.7	0.7	0.7	0.6	0.6	0.5	0.5	0.5	0.5	0.5
10.5-11.0	1.7	1.6	1.5	1.5	1.5	1.4	1.3	1.3	1.2	1.2	1.1	1.1	1.0	1.0	0.9	0.9	0.8	0.8	0.8	0.8	0.8	0.9	0.9	0.8	0.8	0.7	0.7	0.7	0.7	0.7
11.0-11.5	3.9	3.7	3.3	2.8	2.2	1.7	1.3	1.0	0.8	0.7	0.6	0.6	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.5
11.5-12.0	1.6	1.5	1.4	1.3	1.1	1.0	0.8	0.8	0.7	0.7	0.7	0.7	0.7	0.8	0.8	0.8	0.8	0.8	0.8	0.7	0.7	0.7	0.6	0.6	0.5	0.4	0.4	0.4	0.4	0.5
12.0-12.5	2.5	2.3	2.1	1.9	1.6	1.3	1.1	0.9	0.8	0.7	0.7	0.7	0.6	0.6	0.6	0.6	0.7	0.7	0.7	0.6	0.6	0.6	0.5	0.5	0.5	0.5	0.4	0.4	0.4	0.5
12.5-13.0	3.3	3.1	2.8	2.5	2.1	1.7	1.4	1.1	0.9	0.8	0.7	0.7	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.5	0.5	0.5
13.0-13.5	2.7	2.6	2.4	2.2	2.0	1.8	1.5	1.3	1.2	1.1	1.0	0.9	0.9	0.8	0.8	0.8	0.8	0.8	0.8	0.9	0.8	0.8	0.8	0.7	0.7	0.6	0.6	0.5	0.5	0.5
13.5-14.0	2.5	2.4	2.3	2.1	2.0	1.8	1.6	1.4	1.2	1.1	1.0	1.0	1.0	1.0	1.1	1.1	1.1	1.0	0.9	0.9	0.9	0.8	0.8	0.8	0.8	0.7	0.6	0.6	0.6	0.6
14.0-14.5	2.8	2.6	2.4	2.2	2.1	1.9	1.7	1.5	1.3	1.2	1.1	1.0	0.9	0.9	0.9	1.0	1.0	1.0	1.0	1.0	0.9	0.8	0.8	0.7	0.7	0.6	0.6	0.6	0.6	0.6
14.5-15.0	3.0	2.9	2.7	2.5	2.2	1.9	1.7	1.5	1.4	1.3	1.2	1.2	1.1	1.1	1.0	1.0	1.0	1.0	0.9	0.9	0.9	0.8	0.8	0.8	0.7	0.7	0.7	0.7	0.7	0.7
15.0-15.5	3.1	2.9	2.7	2.4	2.2	1.9	1.7	1.6	1.4	1.3	1.2	1.2	1.1	1.1	1.1	1.1	1.1	1.1	1.0	1.0	1.0	1.0	1.0	0.9	0.9	0.8	0.7	0.7	0.7	0.6
15.5-16.0	3.5	3.5	3.3	3.0	2.6	2.2	1.8	1.6	1.3	1.2	1.1	1.0	1.0	0.9	0.9	1.0	1.0	1.0	1.0	1.0	0.9	0.9	0.9	0.8	0.8	0.8	0.7	0.7	0.7	0.7
16.0-16.5	4.0	4.0	3.9	3.5	3.0	2.5	1.9	1.5	1.2	0.9	0.8	0.7	0.6	0.6	0.7	0.7	0.7	0.8	0.8	0.8	0.8	0.7	0.7	0.7	0.7	0.7	0.7	0.6	0.6	0.6
16.5-17.0	2.6	2.6	2.4	2.3	2.0	1.8	1.6	1.5	1.4	1.3	1.3	1.2	1.2	1.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.9	0.9	0.8	0.8	0.7	0.7	0.7	0.7
17.0-17.5	3.0	2.9	2.8	2.5	2.3	2.0	1.7	1.5	1.3	1.2	1.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.9	0.9	0.9	0.8	0.8	0.8	0.7	0.7	0.7	0.7
17.5-18.0	3.8	3.8	3.6	3.2	2.7	2.2	1.8	1.4	1.2	1.1	1.0	1.0	0.9	0.9	0.9	1.0	1.0	1.1	1.1	1.0	1.0	0.9	0.8	0.7	0.7	0.7	0.7	0.7	0.7	0.7
18.0-18.5	4.1	4.4	4.5	4.4	3.9	3.3	2.6	2.0	1.5	1.1	0.8	0.7	0.6	0.6	0.7	0.7	0.7	0.8	0.8	0.7	0.7	0.7	0.7	0.7	0.6	0.6	0.6	0.6	0.6	0.6
18.5-19.0	3.4	3.7	3.8	3.8	3.6	3.2	2.7	2.2	1.8	1.4	1.2	1.0	0.9	0.9	0.9	0.9	0.9	0.9	1.0	1.0	0.9	0.9	0.9	0.8	0.8	0.7	0.6	0.6	0.6	0.6
19.0-19.5	3.6	4.3	4.8	5.1	4.9	4.4	3.6	2.7	1.8	1.2	0.8	0.6	0.5	0.5	0.4	0.4	0.5	0.5	0.5	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.5
19.5-20.0	4.1	3.8	3.4	2.9	2.4	1.9	1.6	1.3	1.1	1.0	0.9	0.8	0.7	0.7	0.7	0.7	0.8	0.8	0.7	0.7	0.7	0.7	0.7	0.7	0.8	0.8	0.7	0.7	0.6	0.6
20.0-20.5	2.5	2.5	2.5	2.4	2.3	2.2	2.0	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.1	1.1	1.0	0.9	0.9	0.9	0.9	0.9	0.9
20.5-21.0	2.8	2.8	2.8	2.7	2.5	2.3	2.1	1.9	1.7	1.5	1.3	1.2	1.2	1.1	1.1	1.1	1.2	1.1	1.1	1.1	1.0	1.0	1.0	0.9	0.9	0.9	0.8	0.8	0.8	0.7
21.0-21.5	3.3	3.5	3.5	3.4	3.1	2.7	2.3	1.9	1.6	1.3	1.2	1.1	1.0	0.9	0.9	0.9	0.9	0.9	1.0	1.0	0.9	0.9	0.8	0.8	0.7	0.7	0.7	0.7	0.7	0.7
21.5-22.0	3.1	3.1	3.0	2.8	2.5	2.3	2.0	1.8	1.6	1.4	1.3	1.2	1.1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.9	0.9	0.8	0.8	0.8	0.8	0.8	0.7	0.7
22.0-22.5	3.3	3.9	4.4	4.7	4.8	4.5	3.9	3.2	2.4	1.8	1.3	1.0	0.8	0.7	0.6	0.6	0.6	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
22.5-23.0	3.7	3.7	3.6	3.3	2.9	2.5	2.1	1.8	1.5	1.3	1.1	1.0	1.0	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.8	0.8	0.8	0.8	0.8	0.8	0.7	0.7
23.0-23.5	2.3	2.2	2.1	2.0	1.9	1.9	1.8	1.7	1.6	1.6	1.5	1.4	1.2	1.2	1.1	1.2	1.2	1.3	1.2	1.2	1.1	1.0	1.0	1.0	1.0	1.0	0.9	0.8	0.8	0.7
23.5-24.0	2.1	2.0	2.0	1.9	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.2	1.1	1.0	1.0	1.0	1.0	1.0	1.0	0.9	0.9	0.8	0.8	0.8	0.7	0.7	0.6	0.6	0.5
24.0-24.5	2.5	2.5	2.4	2.2	2.1	1.9	1.7	1.6	1.4	1.3	1.2	1.1	1.0	0.9	0.9	0.9	0.9	0.9	0.9	0.8	0.8	0.8	0.7	0.7	0.7	0.6	0.6	0.6	0.5	0.5
24.5-25.0	2.1	2.1	2.0	2.0	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.1	1.0	1.0	1.0	1.0	1.1	1.1	1.0	1.0	0.9	0.8	0.8	0.7	0.7	0.7	0.6	0.6	0.5

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Academic background

Since 2005	PhD student
	IFM-GEOMAR at University of Kiel
	St.Petersburg State University, Faculty of Geography and Geoecology
2002-2004	MSc in Hydrometeorology (State University St. Petersburg)
	MSc in Applied Polar and Marine Sciences (University Bremen)
	St.Petersburg State University, Russian-German Master Program POMOR for Applied Polar and Marine Sciences (in cooperation with Universities of Northern Germany)
	Master thesis: Assessment of ecological effects of oil and gas production development in the Kara Sea. Including case study of oil pollution effects on recent benthic foraminifera in Persian Gulf
1998-2002	BSc in Geoecology and Nature management (State University St. Petersburg, Faculty of Geography and Geoecology).
	Bachelor thesis: Ecological effects of dumped chemical weapons on benthic organisms in the Baltic Sea

Grants and scholarships

2007-2008	Research Fellowship of Otto Schmidt Laboratory for Polar and Marine Science at Arctic and Antarctic Research Institute, St.-Petersburg, Russia
2005-2006	DAAD scholarship for scientific research in Germany, IFM-Geomar, Kiel.
2002-2003	Scholarship of President of the Russian Federation.

Research background

May-June 2007	Guest scientist at IFM-GEOMAR, Kiel, Germany. Geochemical and foraminiferal studies in Kiel Bight
2006 October	Participant of advanced course “Foraminifera – ecology and biodiversity”, University of Bergen, the Espeland Marine Biological Station

2004 -2005	Research assistant of the Laboratory of Environmental Modeling. St.Petersburg State University, Faculty of Geography and Geoecology
March 2004	Guest scientist, IFM-GEOMAR, Kiel, Germany.
2003 September	Educational fieldwork (geobotanical, geological and climatic observations) Ny-Alesund, Spitsbergen
2002 July, 2001 July	Research expedition Mapping of heavy metal pollution, St.Petersburg State University, non-ferrous smelter "Severonikel", Murmansk region

Publications

Nikulina, A., Polovodova, I., and Schönfeld, J. (2008) Foraminiferal response to environmental changes in Kiel Fjord, SW Baltic Sea. eEarth 3, 37-49.

Nikulina, A., and Dullo, W.-Ch. Eutrophication and metal pollution in Flensburg Fjord: A reassessment after 30 years; submitted to Marine Pollution Bulletin.

Polovodova, I., Nikulina, A., Schönfeld, J, and Dullo, W.-Ch. Recent benthic foraminifera in the Flensburg Fjord: Distribution and response to environmental change; accepted to Journal of Micropaleontology.

Conference contribution

Schweizer, M., Nikulina, A., Polovodova, I., Schönfeld, J. (2008) Molecular indication of an Ammonia species (Foraminifera, Rotaliida) from the Kiel Fjord (Germany). The Micropaleontologial Society's Foraminifera and Nannofossil Groups, Joint Spring Meeting 2008 (Tübingen, Germany); poster

Nikulina, A., Polovodova, I., Schönfeld, J., Dullo, W-Ch. (2007) Living benthic foraminifera distribution in Flensburg Fjord (western Baltic Sea). The Micropaleontologial Society's Foraminifera and Nannofossil Groups, Joint Spring Meeting 2007(Angers, France); poster

Nikulina A., Polovodova I., Schönfeld J., Belozersky G., Dullo W-Ch. (2007) Response of living benthic foraminifera to environmental geochemistry in the Kiel Bight, south-western Baltic Sea: preliminary results. EGU General Assembly (Vienna, Austria); poster

Nikulina A., Polovodova I. (2007) Benthic foraminifera as an indicator of trace metals pollution in the Baltic Sea. Conference "From geology to biospherology: present issues and future perspectives" (Kiev, Ukraine); poster

Nikulina A., Polovodova I., Belozersky G., Dullo W.-C. (2006) Benthic foraminifera response to sediment geochemistry in the Kiel Fjord. 4th International Conference "Ecological and hydrometeorological problems of the large cities and industrial regions" (St.Petersburg, Russia); oral presentation

Schönfeld J., Nikoulina A., Numberger L., Polovodova I., Dullo W.-Chr. (2006) Long-term changes of benthic foraminiferal assemblages in the western Baltic Sea associated with Anthropocene environmental changes. Biology and Palaeobiology of Foraminifera and Coccolithophores, The Micropalaeontological Society's Foraminifera and Nannofossil Groups, Joint Spring Meeting 2006 (Liverpool, UK)

Belozerski G.N., Nikoulina A.L. (2005) Assessment of the present state of the Kara Sea ecosystem under coming oil and gas production. 3d Italian-Russian symposium "Water quality and water resource management" (St. Petersburg, Russia); oral presentation

Belozersky G., Nikoulina A. (2002) Estimation of the environmental effects of the dumping of the chemical weapons in the Baltic Sea region. 2nd international conference "Ecological and hydrometeorological problems of large cities and industrial regions" (St. Petersburg, Russia); oral presentation

Erklärung gem. §10 Absatz 2 der PO der mathematischen und naturwissenschaftlichen Fakultät

Hiermit erkläre ich, dass ich erstmalig an einem Promotionsverfahren teilnehme. Außerdem versichere ich, dass die vorliegende Dissertation nach Inhalt und Form, abgesehen von den von mir angegebenen Quellen und Hilfsmitteln, sowie der Beratung durch meine akademischen Lehrer, meine eigene Arbeit ist.

Kiel, im September 2008 …….