



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

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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 promote the enrichment of present day surface sediments in organic matter and metals in contrast 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.

Although 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 still high levels of 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.

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1. Introduction

The coastal areas of the Baltic Sea exhibit a high trophic status resulting from high level of discharge of organic and inorganic nutrients through rivers, as well as local coastal and diffusive sources (HELCOM, 1993). Moreover, the benthic–pelagic coupling favoured by the shallow–water depth of the Baltic enhances primary production (Zeitschel, 1980). Therefore, most Baltic coastal areas were classified as being mesotrophic and eutrophic (Nixon, 1995). As a consequence of this high level organic content, the fjords and bays often become anoxic since their topography restricts water exchange with the open Baltic Sea leading to a persistent water column stratification (Jørgensen and Richardson, 1996; Meyer-Reil and Köster, 2000). High production and stagnation of deeper bottom waters then leads to oxygen deficiency and to long-term hypoxia, or even anoxia in the fjords and bays, driving profound changes in the ecosystem structure (Bonsdorf et al., 2002).

The coast of Schleswig–Holstein along the southwestern Baltic Sea is characterised 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. Since the fjords and shallow bays possess a high filtering and buffering capacity (Schiewer and Gocke, 1996), they are often significantly eutrophied and polluted (Müller et al., 1980; Rheinheimer, 1998; Brüggmann and Lange, 1990; Gerlach, 1996; Leipe et al., 1998; Meyer-Reil and Köster, 2000).

The Flensburg Fjord eventually exhibits the lowest impact of anthropogenic activities. Nevertheless, severe anoxia and an extremely high primary production in the inner Flensburg Fjord raised concern of local authorities in the 1970s (GKFF, 1973a,b). In addition, high concentrations of heavy metals in bottom sediments were reported in the 1970s. 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 the Flensburg Fjord. After these measures were taken, the primary production in the fjord decreased, although oxygen depletion still occurred by time.

Our investigation focused on the fjord and to study whether the decrease in input of nutrient and other anthropogenic contaminants has reduced the eutrophication and pollution levels in the Flensburg Fjord over last three decades. Specifically, we measured organic carbon, total nitrogen, chlorophyll *a* and biogenic silica in the surface sediments in order to constrain both the pattern of surface productivity and the capacity of organic matter preservation in the modern sediments. The concentrations of heavy metals copper, zinc, lead and tin, commonly derived from anthropogenic sources, were also measured. The

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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, we attempted to predict the future development of the fjord by interpreting our data with the similar data set from the 1972 study.

2. Study area

The Flensburg Fjord is a narrow, 50 km-long bay of the north-western Kiel Bight between Germany and Denmark (Fig. 1). The inner fjord with water depths not exceeding 19 m is characterised by restricted water exchange with the Kiel Bight and the Baltic Sea over a sill of 10 m depth off Holnis Peninsula. The inner fjord terminates on the narrow, elongated Flensburg city harbour having 7–9 m water depth. The outer Flensburg Fjord comprises shallow-water bights and deep basins of 22–39 m depth (Fig. 1).

The bottom topography is shaped by currents and wave activities that drives erosion of cliffs and favours also erosion in the shallow-water areas, and deposit the eroded material in deeper waters of the outer fjord (Köster, 1958; Exon, 1971). The sediments of the outer fjord are dominated by silt, while in waters shallower than 8 m sand and muddy sand prevail (Exon, 1972; GKFF, 1973a). In contrast the sediments of the inner fjord are composed of dark, sandy mud and soft mud (Exon, 1971).

The hydrography of the Flensburg Fjord, expressed particularly in salinity distributions, is spatially determined by salt-water inflows from the Belt Sea (GKFF, 1973b). The more saline bottom water in the outer fjord in spring and in autumn forces its way across Holnis sill and renews the stagnant bottom waters of the inner fjord. After such an inflow, the pycnocline occurs at 8 to 9 m depth and greatly inhibits vertical water mixing between the water layers of the inner fjord. In the outer fjord this pycnocline is found between 16 and 20 m depth (Exon, 1972). During the periods between saline water inflows, density and wind-induced currents determine the rate of water renewal of the inner and outer fjords. Runoff of small rivers and creeks, atmospheric precipitation and sewage discharges input fresh water at a rate of around $470 \text{ km}^3 \text{ a}^{-1}$ to the Fjord (LANU, 2001). The annual salinity ranges between 15 and 20 psu in surface water, and 20–26 psu in bottom waters (Kändler, 1963; Exon, 1972; Bluhm, 1990).

2.1. Oxygen deficiency events

The combined effects of the bathymetry and the seasonal stratification of the bottom water result in an oxygen deficiency (Kändler, 1963; GKFF, 1973b). A short period of oxygen depletion with values less than $90 \mu\text{mol l}^{-1}$ has been noted in late May–July in the inner fjord and in the Flensburg harbour (Wahl, 1985). Severe long-term oxygen depletions (less than $4 \mu\text{mol l}^{-1}$ in bottom water), however, occur in August and September (Kändler, 1963; GKFF, 1973b; Wahl, 1984; Lorenzen et al., 1987; DDTFF, 1992; LANU, 2003). This late summer deoxygenation was accompanied by a decline of the benthic macrofauna (Bluhm, 1990). During winter and early spring, however, the oxygen conditions become favourable again for benthic organisms caused by enhanced wind-driven vertical mixing (Fig. 2).

Anthropogenic eutrophication in 1960–1980 is said to have had intensified the oxygen deterioration of the inner fjord (Anonymus, 1984). Therefore, large amounts of nutrients derived from uncontrolled sewage input induced an increase of primary production within the inner fjord, thus depleting the oxygen in near-bottom water due to organic matter-decaying microorganisms. After the installation of a purification system at the Flensburg sewage plant in 1967–1969, Rheinheimer (1970) found an improvement of the oxygen situation within the inner fjord. Nevertheless, in the 1980s severe periodical oxygen depletions, even including hydrogen sulphide formation, were reported from the inner fjord (Bluhm, 1990). In 1989, an experimental ventilation pump started operation in the inner Flensburg Fjord (Jaeger, 1990), which resulted in increased oxygen content in bottom waters after complete anoxia. This ventilation experiment did not intend to regenerate the inner fjord waters, since it lasted only for several months, however, it clearly demonstrated the efficiency of such ventilation techniques for the oxygenation of stagnant waters (D. Jaeger, written comm.). Seasonal oxygen depletions have been reported for the 1990s and the 2000s (DDTFF, 1993; LANU, 2001, 2003), despite significant reduction of sewage discharges.

2.2. Nutrient input and primary production

The main sources of nutrient input into Flensburg Fjord are the drainage from agricultural watershed and the communal sewages. For the most recent decades, input of phosphorous from all sources has decreased from 305 t a^{-1} in 1986 to 84 t a^{-1} in 1997. Since 40%

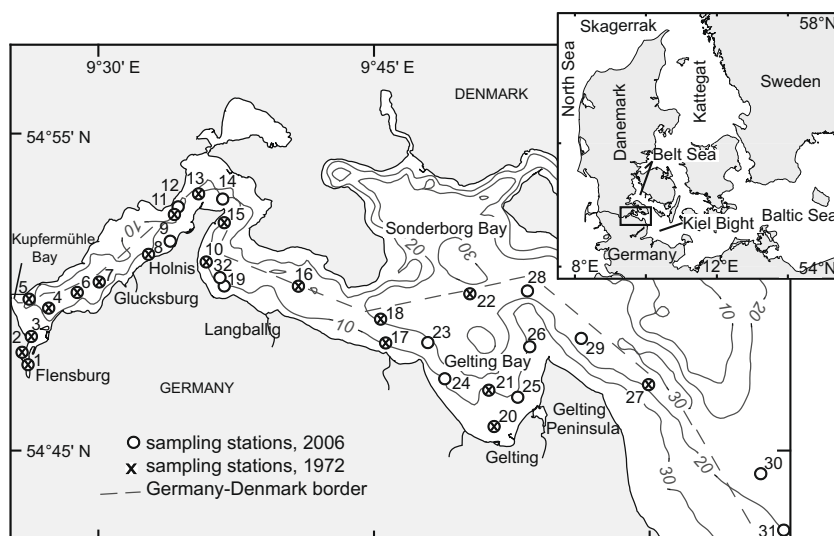


Fig. 1. Sampling stations in Flensburg Fjord. Depth counters in meters. Station prefix PF16- is omitted. Stations 1972 are given according to GKFF (1973a).

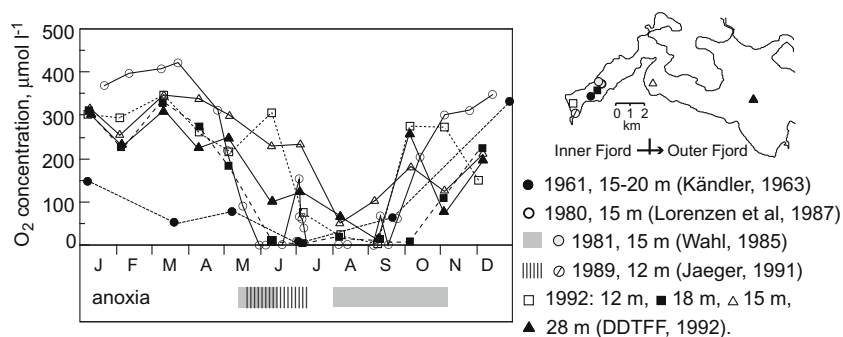


Fig. 2. Oxygen content in near-bottom water of the Flensburg Fjord: year, depth and location of measurement are given for every series. Shadow boxes depict the reported anoxia periods.

of the nitrogen comes into the Fjord from diffusive sources, the reduction of nitrogen from sewage alone was not so effective, it dropped from 2600 t a^{-1} in 1986 to 1600 t a^{-1} in 1997 (LANU, 2001). The largest part of nutrient input mainly affected the inner fjord.

The reduction in nutrient input apparently decreased primary production of more than 50% in the inner fjord from $630 \text{ gC m}^{-2} \text{ a}^{-1}$ in 1986–1989 to $260 \text{ gC m}^{-2} \text{ a}^{-1}$ in 1995–1997 (LANU, 2001), although considerable variations were observed between different years. The primary production remained consistently at $150 \text{ gC m}^{-2} \text{ a}^{-1}$ over this period in the outer fjord.

3. Material and methods

3.1. Samples collection

The sediment samples were collected in June 2006 with RB Polarfuchs (IFM-GEOMAR) at 32 stations in the German area of the Flensburg Fjord (Fig. 1, Supplementary material 1 and 3) applying 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 taken for analysis. A Van Veen grab was used for sandy sediments, and the samples were taken with scaled syringes. After returning from each cruise, the samples stored in plastic vials 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 during the same season as those from the 1972 study by Flensburg Fjord Commission (GKFF, 1973a). However, in the 1972 study the upper three centimeters 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.

3.2. Geochemical analysis

To assess the productivity and nutrient status of the Fjord, the organic carbon, total nitrogen, silica, and pigments were measured. Organic carbon, and nitrogen contents of the sediment were determined using a Carlo Erba NA-1500-CNS analyzer at IFM-GEOMAR with accuracy better than $\pm 1.5\%$. The organic carbon content was measured in decalcified sediments. Total carbon content was obtained from bulk sediments to calculate atomic ratio of C:N 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 the bulk sediment by sodium hydroxide at 85°C for about 45 min. The dissolved silica in the solution was determined by molybdate-blue spectrophotometry with a precision of $\pm 1\%$. Chlorine contents in sediments were measured with a Turner TD-700 Fluorometer after acetone extraction. The precision of this method was $\pm 10\%$.

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. The accuracy of analytical results estimated from replicate measurements of the international standard MAG-1 was better than $\pm 1.5\%$ (Garbe-Schönberg, 1993).

4. Results

4.1. Physical parameters

4.1.1. Hydrography

The bottom water temperature varied between 8°C in the open, eastern part of the Fjord and 11°C in the sheltered inner fjord and 14°C in the Gelting Bay in June 2006. Bottom water salinities increased from 18.3 psu in the Gelting Bay and 19.3 psu in the inner fjord, where freshwater input has a significant influence, to 25.4 psu in open bight waters. The surface water temperature in June fluctuated around 16°C throughout the entire fjord and only increased up to 22°C in the Gelting Bight. Surface water salinities ranged between 18 psu in the inner fjord, 16–18 psu in the Gelting Bight and 24 psu in the outer fjord (MAEWEST, 2007).

4.1.2. Oxygen

The dissolved oxygen content varied from 159 to $307 \mu\text{mol l}^{-1}$ throughout the Fjord. 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. The oxygen saturation in the outer fjord was 53–58% at 25–28 m water depth and up to 100% in well-mixed waters of the shallow Gelting Bay. Therefore favourable oxygen conditions were presented almost everywhere in the investigated stations.

At the inner fjord stations PF16-2; -3; -4 under a water oxygen saturation around 50% black sediments were recovered, in which H_2S was present and which were barren of any benthic organisms. The cores from these stations contained very dark sediments

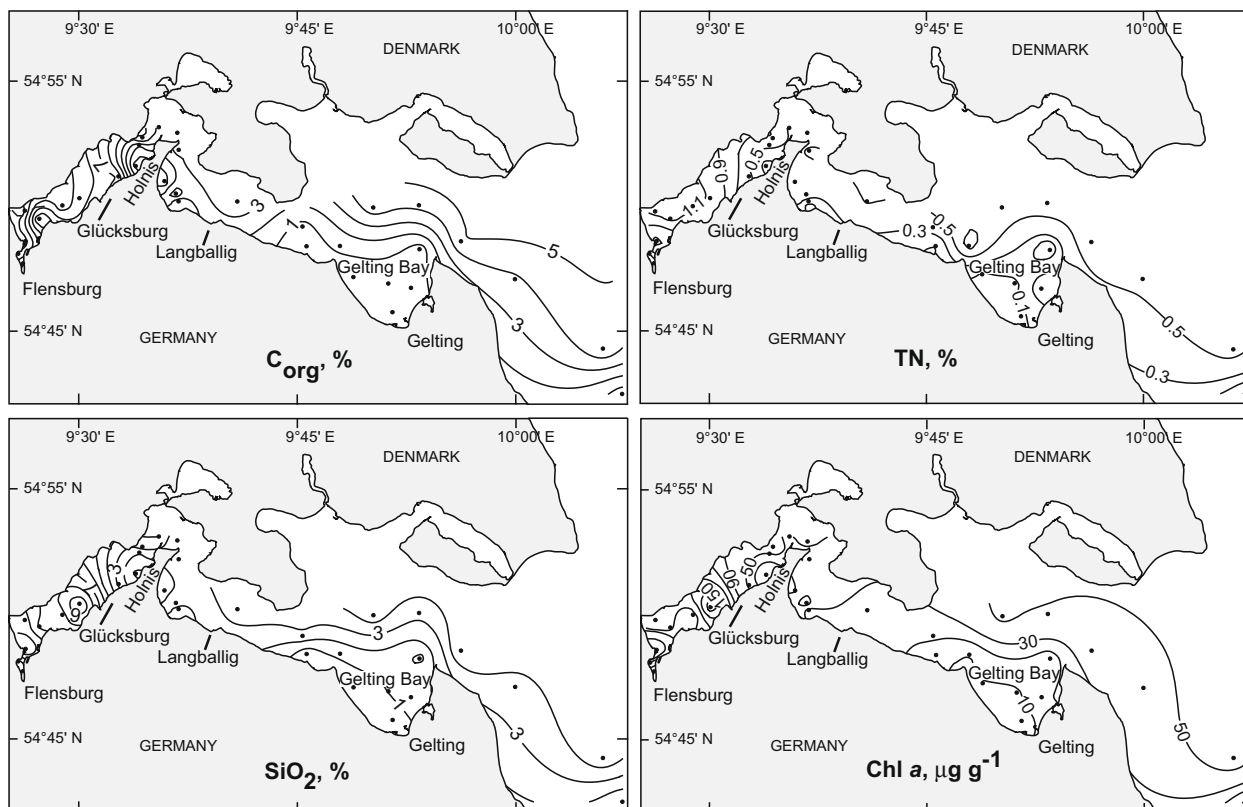


Fig. 3. Distribution of organic carbon, total nitrogen, biogenic silica and chlorophyll *a* in sediments of the Flensburg Fjord. Dots indicate sampling stations.

covered by few millimeters of light brown oxygenised sediments indicating the recent oxygenation of bottom waters.

4.1.3. Bottom sediments

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

4.2. Organic compounds

4.2.1. Organic carbon and total nitrogen

Organic carbon concentrations increased from the outer to the inner fjord (Fig. 3). The distribution of C_{org} is inversely correlated

to the sand content of the sediments ($r = -0.685$). At mean 4% of organic carbon for the whole Flensburg Fjord, the highest C_{org} concentrations around 11.5% were recorded in the Flensburg harbour, around the Flensburg sewage plant and in sediments of Kupfermühle Bay at the mouth of the Krusau river. Exceptionally low C_{org} values of 0.2–1.3% characterise the sandy sediments offshore Glücksburg (stations PF16–8 and -9) and the Gelting Bay.

Total nitrogen concentrations in the Flensburg Fjord sediments varied from 0.06% to 1.2% with the lowest values in the Gelting Bay and along the shore off Langballig, and with a distinct increase in the inner fjord (Fig. 3). The distribution pattern followed the distribution of organic carbon, total nitrogen correlates negatively with the sand volume ($r = -0.749$).

The C:N ratio of the sediments ranges from 14 in the inner part to 6.8 in the outer fjord. Surprisingly low values of C:N (4–5) were measured in the Gelting Bay, despite a substantial organic matter input from rivers and agricultural watershed.

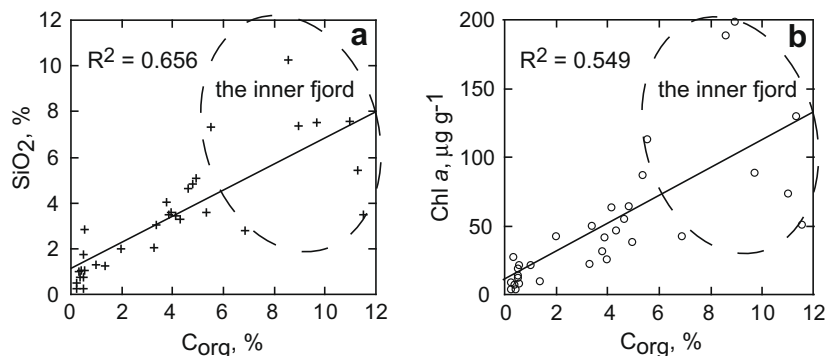


Fig. 4. Relationships between biogenic silica and organic carbon, chlorophyll *a* and organic carbon contents in sediments of the Flensburg Fjord.

Table 1

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

Trace metal	Mean ($\mu\text{g g}^{-1}$)	Range ($\mu\text{g g}^{-1}$)	Pearson correlation coefficient r with	
			Sand (%)	C_{org} (%)
Cu	45.1	2.3–194	−0.542	0.891
Zn	137	10.4–438	−0.655	0.831
Sn	4.15	0.3–18.1	−0.595	0.827
Pb	40.3	6.30–158	−0.522	0.826

4.3. Biogenic silica and pigments

Sediments of the 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, exhibiting minimal values in the Gelting Bay (Fig. 3). The chlorophyll a content ranged from 4.1 to $200 \mu\text{g g}^{-1}$ with a minimum in the Gelting Bay (Fig. 3) while concentrations more than $100 \mu\text{g g}^{-1}$ occurred only in the inner fjord. Biogenic silica correlates well with organic carbon (Fig. 4) and chlorophyll a content ($r = 0.862$). We observed highly variable chlorine concentrations in the sediments of the Flensburg Fjord ($150 \mu\text{g g}^{-1}$ – $910 \mu\text{g g}^{-1}$). The highest values occurred at some stations in the inner fjord, while the values of all other stations in the Fjord did not exceed $300 \mu\text{g g}^{-1}$. Gelting Bay exhibits the lowest concentrations of chlorine between 20 and $70 \mu\text{g g}^{-1}$.

The ratio of phaeopigments to chlorophyll a , which indicates the degree of chlorophyll a decay and the preservation of organic matter, ranged from 3.3 in the inner fjord to 1.3 in the Gelting

Bay. The average 2.7 indicates a high preservation potential of the sediments. However, at some stations of the inner fjord (PF16-2, -6, -14 and -16) having a sand portion less than 11%, pigment ratio exceeded 4.2 indicating a low preservation potential.

4.4. Heavy metals

Heavy metal concentrations in the sediments of the Flensburg Fjord vary considerably (Table 1, Fig. 5). All the metals measured show a significant correlation with organic carbon and the sand portion (Table 1), which means the inner fjord sediments exhibit elevated metal levels whereas sediments of the Gelting Bay contain low metal concentrations.

Unexpectedly, normalisation of heavy metal content with C_{org} did not reveal any changes in the distribution of the metals (Newman and Walting, 2007). Nevertheless, the metal content in the inner fjord sediments deviates from the C_{org} -regression model (e. g. Cu; Fig. 6). In the outer fjord the metal content is proportional to the organic matter and likely represents a natural situation whereas in the inner fjord the metals correlate less to C_{org} . In particular zinc and tin contents are uncorrelatedly high.

The high concentrations of metals are seen only at few stations (Fig. 5). For example, Cu concentrations higher than $50 \mu\text{g g}^{-1}$ were encountered only at 25% of the stations and all of these were located in the inner fjord. Only 20% of the stations had Zn concentrations above $200 \mu\text{g g}^{-1}$ and lead concentrations above $60 \mu\text{g g}^{-1}$. Tin contents above $5 \mu\text{g g}^{-1}$ were found at four stations in the inner fjord, while most of the outer fjord stations had values not exceeding $2 \mu\text{g g}^{-1}$.

The data on the bottom water properties during the sampling period and the concentrations of the measured variables of the sediments are completely presented in Supplementary material 2.

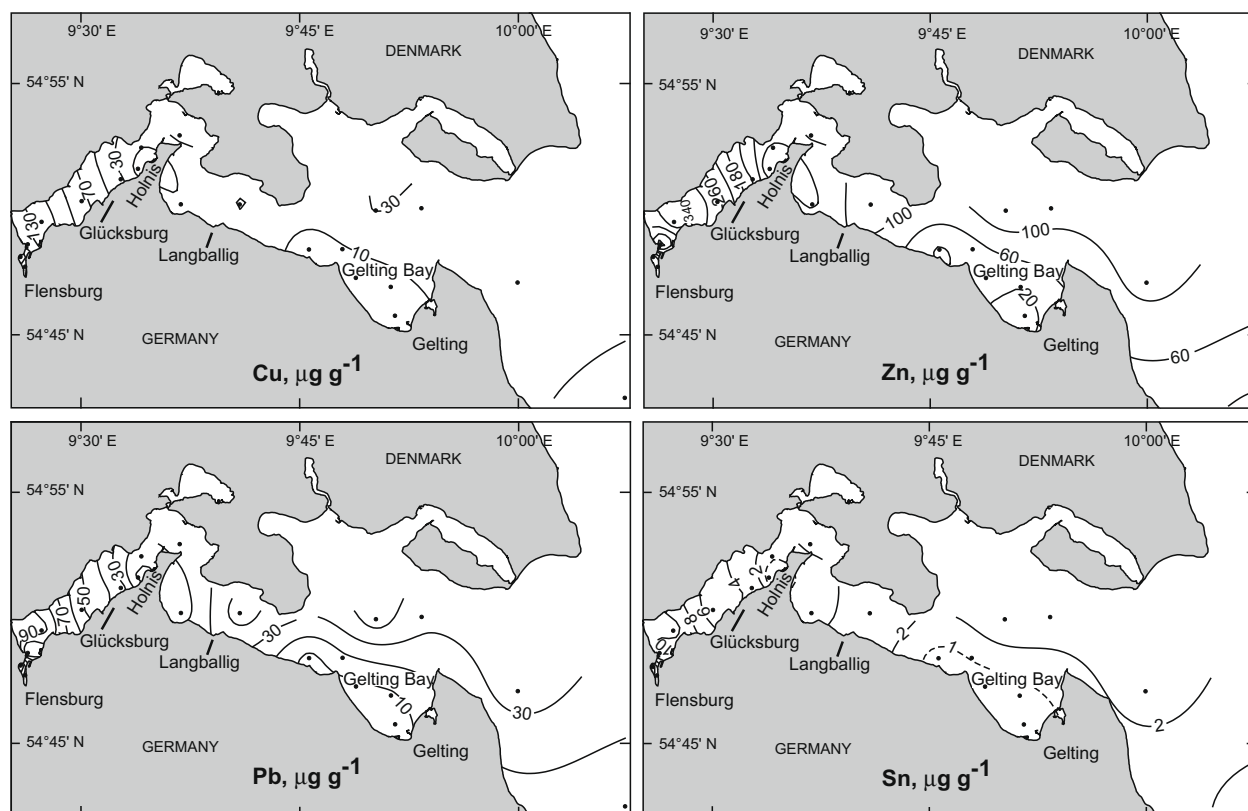


Fig. 5. Distribution of copper, zinc, lead and tin in sediments of the Flensburg Fjord. Dots indicate sampling stations.

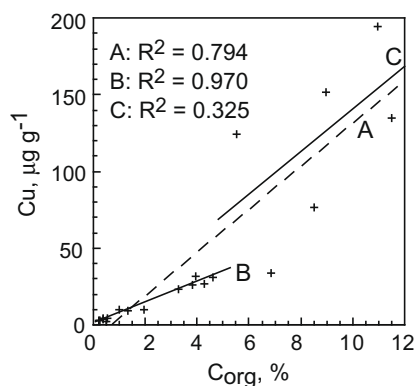


Fig. 6. Relationships between organic matter and copper content in the entire Flensburg Fjord (A), in the outer fjord (B) and in the inner fjord (C).

5. Discussion

5.1. Present state

The difference between surface and bottom water salinities measured in June 2006 points to the existence of a halocline throughout almost entire fjord, except in the Gelting Bay, which is too shallow. The salinity in 2006 was higher in contrast to the long-term summer average (Krug, 1963; GKFF, 1973b). These two facts imply that an inflow of oxygenated and saline water from the North Sea had occurred, probably starting in April 2006 (MAE-WEST, 2007). The thin oxidized top layer of the 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 recognised as a consequence of short oxygen depletion after the formation of the halocline and water stratification. Similar summer oxygen depletions, accompanied by the distortion and even absence of benthic organisms in the sediments, were described by Wahl (1985) and Bluhm (1990) in the inner fjord. Nevertheless, winter studies showed the recovery of normally structured benthic communities (Bluhm, 1990).

The distribution of the sediments depends on the water dynamics in the Fjord. In the inner fjord and central outer fjord muddy sediments have been deposited whereas in the dominantly erosive regime in the Gelting Bay and off Holnis Peninsula mostly sandy sediments occur.

5.1.1. Organic matter distribution and sources

The observed distribution of organic compounds in the Flensburg Fjord reflects the hydrographical boundary conditions of the inner and outer fjords. In additions our sampling in late spring de-

picted the phytoplankton spring bloom. The sediments of the inner fjord, characterised by its restricted current regime, are enriched in organic matter compared to the outer fjord and in particular to the Gelting Bay (Table 2). Low levels of organic matter in the eastern Gelting Bay are apparently linked to the prevailing sandy sediments and the strong wave erosion, whereas in the southern and the southwestern parts, they are caused by a lack of water mixture and low nutrient content (Exon, 1971, 1972). Moreover the enrichment of organic matter in the inner fjord mainly points to a higher productivity in comparison to the outer fjord (LANU, 2001). Nevertheless, organic matter levels in the sediments are still in the same range as the organic carbon values of bottom sediments elsewhere in the Kiel Bight (Exon, 1972; Balzer, 1984; Gerlach, 1996; Leipe et al., 1998).

Total nitrogen concentrations along with organic carbon are also high but in 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 indicate the high rates of accumulation of organic matter due to both high primary production and a high burial potential of sediments.

Biogenic silica contents as a measure of 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. However, these values of biogenic opal correspond to those found in similar settings of eutrophied bays of the Baltic Sea (Conley and Johnstone, 1995; Carman and Aigars, 1997; Kaupplila et al., 2005; Vaalgamaa and Conley, 2008).

The spring bloom of phytoplankton usually occurs around the beginning of March to April (Hickel, 1967; Smetacek, 1980; Wasmund and Uhlig, 2003) in the Kiel Bight while the maximum of primary production in the Flensburg Fjord was observed in May (LANU, 2001). The high levels of biogenic silica in the inner Flensburg Fjord in June 2006 are apparently linked to both phytoplankton bloom deposition, and the restricted water exchange in this area. The topographical and hydrographical restriction of the inner fjord and the shallow-water depth inhibit silica export from this area. Silica is being recycled and therefore made available for diatom production (Ragueneau 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 the Flensburg Fjord sediments indicate a non-detrital but diatom origin of Chl *a* (Kristiansen et al., 2000). Both silica and chlorophyll *a* were incorporated in the bottom sediments within a month from production indicated by their high portion within the sediments.

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

Table 2

Spatial aspect of organic matter and heavy metal distributions in the Flensburg Fjord. Welch's test for H_0 hypothesis Mean inner Fjord \leq Mean outer Fjord.

Variable	Mean inner Fjord	Mean outer Fjord	t-Value	df	p-Value one-sided
C_{org} (%)	7.1	2.2	4.244	14	0.0004 ^a
TN (%)	0.79	0.38	3.683	17	0.0009 ^a
SiO_2 (%)	5.2	2.3	3.383	15	0.0020 ^a
Chlorine ($\mu g g^{-1}$)	439	134	3.936	12	0.0010 ^a
Chl <i>a</i> ($\mu g g^{-1}$)	88.3	28.4	3.473	12	0.0023 ^a
Cu ($\mu g g^{-1}$)	91.0	14.4	3.962	11	0.0011 ^a
Zn ($\mu g g^{-1}$)	241	67.7	3.710	12	0.0015 ^a
Pb ($\mu g g^{-1}$)	68.5	21.6	3.541	11	0.0042 ^a
Sn ($\mu g g^{-1}$)	8.05	1.55	3.149	12	0.0023 ^a

^a Indicates 10% significance.

Fjord (Fig. 4) indicating allochthonous organic matter input (Carman and Aigars, 1997). Indeed, the regression of biogenic silica and chlorophyll *a* on organic carbon (Fig. 4) showed that in the inner fjord an additional source of organic carbon must exist as river discharges, sewage outlets or drainage from agricultural area. The same is reflected by high C:N ratios of 10–14 indicating organic carbon of terrestrial origin (Calvert and Pedersen, 1992). The portion of the allochthonous organic matter apparently decreases in the outer fjord, where the C:N ratios vary between 7 and 8 and have almost 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 bloom (Graf, 1994).

The concentrations of total pigments and chlorophyll *a* in the Flensburg Fjord are as high as in other sediments of the Baltic Sea, except 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 the Flensburg Fjord their elevated values apparently indicate periodic suboxic conditions. These suboxic conditions support the preservation of pigments since the grazing macrofauna is periodically reduced under oxygen depletion (Bianchi et al., 2000). The good oxygenation and the light conditions in the Gelting Bay keep chlorophyll *a* concentrations low due to the activity of microbes and herbivores (Leavitt, 1993).

The ratios of the phaeopigments: chlorophyll *a* for the entire Fjord surface sediments indicate the existence of a recent spring bloom. But in the inner part, the high values are comparable to those which depict the winter conditions with a decayed Chl *a*, or resuspension under oxic conditions (Bianchi et al., 2002). However, the low pigment ratios in the Gelting Bay under periodically oxic conditions are enigmatic. The only explanation can be a general low level of pigments due to the high hydrodynamic activity and also a lower productivity due to the absence of nutrient recycling from bottom sediments (Exon, 1972). The latter might be responsible for the low total concentration of pigments in the sediments of this area (Leavitt, 1993; Reuss et al., 2005).

5.1.2. Heavy metals pollution

The heavy metal concentrations in the sediments of the Flensburg Fjord exhibit a distinct distribution; they decrease from the inner to the outer part. Since there are no large specific point sources of heavy metals in the fjord that is seen from the normalisation of metal concentrations with C_{org} content, the geographic and the hydrographic settings of the Fjord seem to be the main constraints of metal distribution. In the inner stagnant and restricted fjord, the highest levels of all measured metals occur, whereas the metal contents are significantly lower in the dynamic, outer fjord, where sandy sediments dominate (Fig. 5, Table 2). However, the regression model (Fig. 6) shows that the regional sources of contamination particularly by zinc and tin, which are sewage water, harbours and shipyards of Flensburg and Glücksburg cities, apparently affect the inner fjord. The absence of correlation between high levels of C_{org} and metals in the inner fjord reveals that here the simultaneous accumulation of metals bound with organic matter and metals from direct anthropogenic pollution occur.

In the inner fjord the metal contents reach very high values, which are clearly higher than the “background” determined for coastal sediments in the western Baltic Sea (HELCOM, 1993). Sediments provide a temporally integrated indication of the state of an ecosystem and its pollution. The mean sedimentation rate derived from a core from the outer, deep Gelting Bay was determined to be 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 the most recent conditions. The heavy metal concentrations and distributional patterns of 2006 correspond well to the findings of the State Department for the Environment of Bun-

desland 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 the Kiel Bight (Leipe et al., 1998; Haarich et al., 2003; Pohl et al., 2005). Comparing our results with the pre-1880 concentrations from the core derived from the Gelting Bay (Müller et al., 1980), a sixfold enrichment of sediments in Zn and an eightfold 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).

The distribution of lead is almost not affected by sewage outlets, and harbours, or fine sediment distribution, but mostly by the input from the atmosphere (Brüggemann, 1996), and has therefore a more uniform pattern. Copper contents show some increase above background level (HELCOM, 1993) in the inner fjord, but remains low in the outer fjord and the Gelting Bay. Tin concentrations in the outer fjord sediments are comparable to those from the western Baltic (Cato and Kjellin, 2005), whereas in the inner fjord, they are much higher and even exceed the levels of the Kiel Fjord (Nikulina et al., 2007). 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.

5.2. Reassessment of the Flensburg Fjord

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 entire fjord (Table 3) although some discrepancies were observed at particular stations. The distribution pattern remains the same and is in good agreement to those described eventually in different parts of the Fjord (Exon, 1971; Lorenzen et al., 1987). The median values for C_{org} and TN are very similar. However, the variability of 2006 data was significantly higher (Fig. 7). This is probably due to the top-most 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 compared to 1972 is revealed in the inner part of the fjord (Fig. 7, Supplementary material 3).

The reason for such changes might be an increase of primary production in this area, enhanced accumulation and input of organic matter, which cannot be completely decomposed in bottom sediments. Moreover, the preservation of organic carbon in sediments under dysoxic–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 encountered (Kändler, 1963; Kremling et al., 1979; 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

Table 3

Temporal aspect of organic matter and heavy metal distributions in the Flensburg Fjord. Dependent *t*-test for H_0 hypothesis Mean 1972 = Mean 2006.

Variable	Mean 1972	Mean 2006	<i>t</i> -value	df	<i>p</i> -Value two-sided
C_{org} (%)	4.2	5.1	−1.258	18	0.3235
TN (%)	0.49	0.61	−1.521	18	0.0929
Cu ($\mu\text{g g}^{-1}$)	61.6	63.2	−0.151	12	0.8822
Zn ($\mu\text{g g}^{-1}$)	231	180	1.266	12	0.2297
Pb ($\mu\text{g g}^{-1}$)	82.5	53.1	2.536	12	0.0261 ^a

^a Indicates 10% significance.

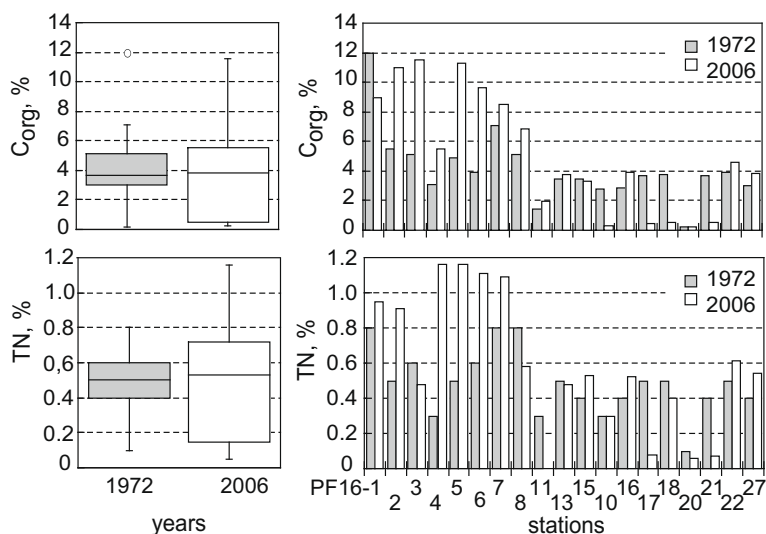


Fig. 7. Organic carbon and total nitrogen in Flensburg Fjord sediments in 1972 (GKFF, 1973a) and 2006 (this study).

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 Pedersen, 1992; Cowie and Hedges, 1992; Henrichs, 1995). Thus, eventually, the primary production is still high enough to favour the accumulation of organic carbon even though the external input of nutrients in

the Fjord significantly decreased over the last decades (DDTFF, 1993; LANU, 2001). It was reported that the primary production in the inner fjord decreased in the 1990s comparing with the 1970s, however did not reach the levels of the outer fjord (LANU, 2001). An internal forcing may explain the stability of primary production over the last decades. The settled nutrients may become available again for plankton growth after storm events topping up externally added nutrients in the restricted inner fjord (DDTFF,

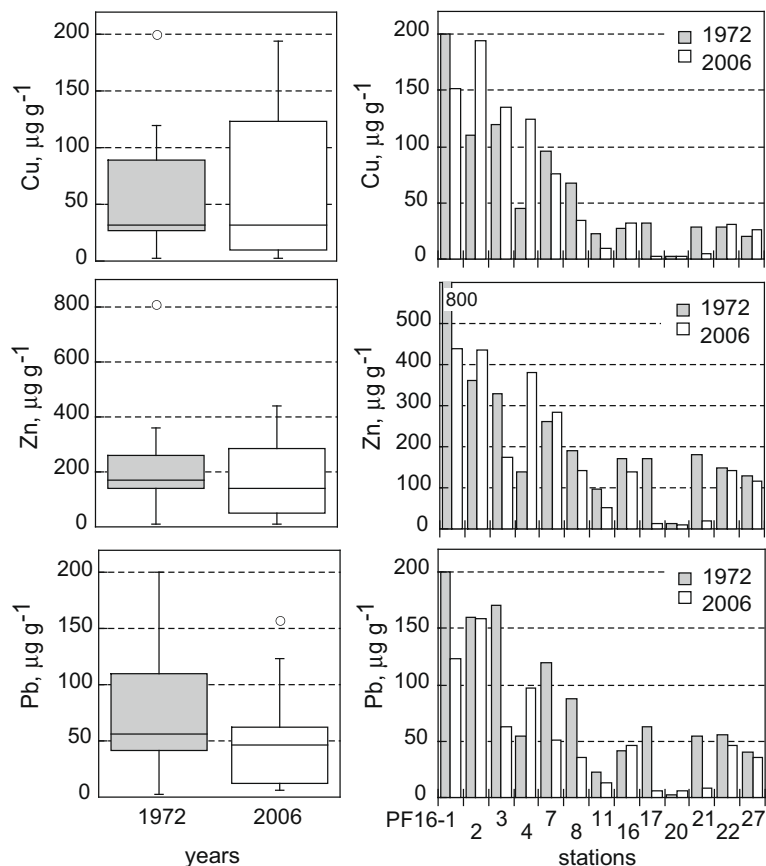


Fig. 8. Heavy metal concentrations in Flensburg Fjord sediments in 1972 (GKFF, 1973a) and 2006 (this study).

1993; Meyer-Reil and Köster, 2000; Kaupila et al., 2005). The 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 of the surface layer of sediments also induces the mobilization and the release of phosphates bound to the 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, 2001), which suggests an internal source of nutrients. Further, the high C:N ratios in the inner fjord supposes that the organic matter contains some compounds (e.g. lignin) which anaerobic microorganisms cannot metabolize quickly (Cowie and Hedges, 1992; Calvert and Pedersen, 1992; Canfield, 1994). Hence, this terrestrial organic carbon has a higher potential to be preserved in marine sediments and contributes to the generally high content of organic carbon.

5.2.2. Heavy metal trends

The comparison of the mean metal concentrations as well as the *t*-tests on significant differences between 1972 and 2006 showed that only the lead concentrations had changed significantly (Table 3). Copper and zinc contents did not show any changes through time (Table 3).

Although the medians of 1972 and 2006 are very close for Cu and Zn, we observed strong variations of metal content at isolated stations (Fig. 8, Supplementary material 3), which were probably due to the patchiness of sediments. The distributional 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. Thus the high concentrations of metals in the inner fjord in 1972 had the same causes as at present time. The lowest metal concentrations occur in the Gelting Bay due to high water dynamics similar to 1972. However, the common enrichment of metals in the sediments of the Baltic Sea leads to enhanced levels of metal concentrations today if we compare either 2006 or 1972 concentrations to those from 1880 as being preserved in the nearby core (Müller et al., 1980).

The changes in lead concentrations are noticeable in Flensburg Fjord for the last three decades in contrast to the overall steady distributions of metals in the Baltic Sea (Pohl et al., 2005). A similar decrease of lead was observed in the sediments of Northern American lakes twenty years after the significant reduction of lead levels in the atmosphere (Callender and Van Metre, 1997). Atmospheric transport and surface runoff together with boating, shipping, and industrial activities are considered as the main sources of lead into the Baltic (Nriagu, 1978; Brüggemann, 1996). As such, the decrease of lead in sediments of the enclosed fjord is apparently associated with ban of lead additives into gasoline.

6. Conclusions

The distribution of both organic compounds and heavy metals in the Flensburg Fjord are mostly constrained by natural conditions, such as geographical and hydrographical settings and the related water exchange. High concentrations of organic matter in the Flensburg Fjord sediments did not significantly change since protection measures were applied and the sewage discharge was reduced firstly at the beginning of 1980s and secondly in the 1990s. Apparently, the high levels of intensive nutrient discharges into the inner fjord until the end of 1970s are still a source for the ongoing primary production and organic matter formation in the inner fjord. Obviously the inner fjord in contrast to the outer fjord is a depositional area with a very high rate of recycling and remin-

eralisation of organic matter, but not a sealed sink. In the outer fjord no significant changes were encountered and nutrient concentrations are comparable to those of the Kiel Bight.

We suggest that under the efficiently decreased anthropogenic nutrient input, natural cycles of oxic and anoxic conditions overall may 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 to a reduced organic input into the sediments and consequently to 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 the outer Flensburg Fjord, where the water exchange processes play the main role.

High levels of copper, zinc, lead, and tin at distinct stations were observed in 1972 and 2006 even though no prominent point sources could be identified. The restricted water exchange and the prevailing muddy sediments makes the inner part of the fjord a depositional area favouring for metal enrichment and for the 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 the 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 be reduced in the near future. Even the reduction of metal concentrations in the discharges from the sewage systems and the shipyards will not give a successful result on a short-time perspective.

The development of anoxia on a seasonal scale in the Flensburg Fjord due to water stagnation and high productivity may provide a helpful scenario to better understand the development and consequences of anoxia in the Baltic deeps through time. Even for the interpretation of regional and oceanwide stagnation periods during the Miocene or the Cretaceous, new insights are gained by this study. Furthermore, the seasonal changes of oxic and anoxic conditions in semi-enclosed basins may provide new ideas on small-scaled hydrocarbon accumulation, since new targets in “strange settings” have been discovered recently.

Though the reasons for the onset of anoxia and eutrophication may be a temperature rise due to high CO₂ content (Wilson and Norris, 2001) or nutrients input due to sea levels change (Jenkyns, 1980; Filippelli et al., 2003) the processes involved are similar on 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 the sediments and in the water column. Meanwhile, the demand of nitrate for phytoplankton growth is partially compensated by N₂ fixation in near-surface waters at the absence of external inputs. In greater depths, the return of nutrient derived 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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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.marpolbul.2009.01.017.

References

- Anonymus, 1984. Die Sanierung der Flensburger Förde: eine europäische Aufgabe? Dokumentation zur deutsch-dänischen Grenzregion Nr. 4. Institut für regionale Forschung und Information, Flensburg.
- Balzer, W., 1984. Organic matter degradation and biogenic element cycling in a nearshore sediment (Kiel Bight). *Limnology and Oceanography* 29, 1231–1236.
- Beucher, C., Treguer, P., Corvaisier, R., Hapette, A.M., Elkins, M., 2004. Production and dissolution of biosilica, and changing microphytoplankton dominance in the Bay of Brest (France). *Marine Ecology Progress Series* 267, 57–69.
- Bianchi, T.S., Johansson, B., Elmgren, R., 2000. Breakdown of phytoplankton pigments in Baltic sediments: effects of anoxia and loss of deposit-feeding macrofauna. *Journal of Experimental Marine Biology and Ecology* 251, 161–183.
- Bianchi, T.S., Rolff, C., Widbom, B., Elmgren, R., 2002. Phytoplankton pigments in Baltic Sea seston and sediments: seasonal variability, fluxes, and transformations. *Estuarine, Coastal and Shelf Science* 55, 369–383.
- Blum, H., 1990. Analyse zyklischer Wiederbesiedlungsvorgänge am Beispiel sublitoraler Makrobenthosgemeinschaften in der Flensburger Förde. Ph.D. thesis. Institut für Meereskunde an der Christian-Albrechts-Universität, Kiel.
- Bonsdorf, E., Rönnberg, C., Aarnio, K., 2002. Some ecological properties in relation to eutrophication in the Baltic Sea. *Hydrobiologia* 475 (476), 371–377.
- Brüggemann, L., 1996. Quellen und regionale Verteilung von Schwermetallen im Wasser und Sediment. In: Lozan, J.L., Lampe, R., Matthäus, W., Rachor, E., Rumohr, H., Westernhagen, H.v. (Eds.), *Warnsignale aus der Ostsee*. Parey, Berlin, pp. 74–79.
- Brüggemann, L., Lange, D., 1990. Metal distribution in sediments of the Baltic Sea. *Limnologia* 20, 15–28.
- Callender, E., Van Metre, P.C., 1997. Reservoir sediment cores show U.S. lead declines. *Environmental Science and Technology* 31, 424a–428a.
- Calvert, S.E., Pedersen, T.F., 1992. Organic carbon in marine sediments: is anoxia important? In: Whelan, J.K., Farrington, J.B. (Eds.), *Organic Matter: Productivity, Accumulation and Preservation in Recent and Ancient Sediments*. Columbia University Press, New York, pp. 231–263.
- Canfield, D.E., 1994. Factors influencing organic carbon preservation in marine sediments. *Chemical Geology* 114, 315–329.
- Carman, R., Aigars, J., Larsen, B., 1996. Carbon and nutrient geochemistry of the surface sediments of the Gulf of Riga, Baltic Sea. *Marine Geology* 134, 57–76.
- Carman, R., Aigars, J., 1997. Vertical and spatial distribution of biogenic silica in the sediment of the Gulf of Riga, Baltic Sea. *Toxicological and Environmental Chemistry* 60, 245–259.
- Cato, I., Kjellin, B., 2005. The national Swedish status and trend monitoring programme based on chemical contamination in offshore sediment – an overview of the results from 2003. HELCOM MONAS, vol. 8, p. 17. Available from: <http://sea.helcom.fi/>.
- Conley, D.J., 1997. Riverine contribution of biogenic silica to the oceanic silica budget. *Limnology and Oceanography* 42, 774–777.
- Conley, D.J., Johnstone, R.W., 1995. Biogeochemistry of N, P and Si in Baltic Sea sediments: response to a simulated deposition of a spring bloom. *Marine Ecology Progress Series* 122, 265–276.
- Cowie, G.L., Hedges, J.L., 1992. The role of anoxia in organic matter preservation in coastal sediments: relative stabilities of the major biochemicals under oxic and anoxic depositional conditions. *Organic Geochemistry* 19, 229–234.
- DDTFF, 1992. Deutsch-Dänische Technikergruppe für die Flensburger Förde: Jahresbericht 1992. Sekretariat, Amtsgärden, Aabenraa.
- DDTFF, 1993. Deutsch-Dänische Technikergruppe für die Flensburger Förde: Jahresbericht 1993. Sekretariat, Amtsgärden, Aabenraa.
- Ellegaard, M., Clarke, A., Reuss, N., Drew, S., Weckström, K., Juggins, S., Anderson, N.J., Conley, D.J., 2006. Multi-proxy evidence of long-term changes in ecosystem structure in Danish marine estuary, linked to increased nutrient loading. *Estuarine, Coastal and Shelf Science* 68, 567–578.
- Emelyanov, E.M., 1988. Biogenic sedimentation in the Baltic Sea and its consequences. In: Winterhalter, B. (Ed.) *The Baltic Sea*. Geological Survey of Finland, Special Paper 6, pp. 127–135.
- Exon, N., 1971. Holocene sedimentation in and near the outer Flensburg Fjord (westernmost Baltic Sea). Ph.D. thesis. Christian-Albrechts-Universität, Kiel.
- Exon, N., 1972. Sedimentation in the outer Flensburg Fjord area (Baltic Sea) since the last glaciation. *Meyniana* 22, 5–62.
- Fallesen, G., Andersen, F., Larsen, B., 2000. Life, death and revival of the hypertrophic Mariager Fjord, Denmark. *Journal of Marine Systems* 25, 313–321.
- Filippelli, G.M., Sierro, F.J., Flores, J.A., Vázquez, A., Utrilla, R., Pérez-Folgado, M., Latimer, J.C., 2003. A sediment-nutrient-oxygen feedback responsible for productivity variations in Late Miocene sapropel sequences of the western Mediterranean. *Paleogeography, Paleoclimatology, Paleocology* 190, 335–348.
- Garbe-Schönberg, C.D., 1993. Simultaneous determination of 37 trace elements in 28 international rock standards by ICP-MS. *Geostandard Newsletters* 17, 81–93.
- Gerlach, S., 1988. Eutrophication of Kieler Bucht. *Kieler Meeresforschungen, Sonderheft* 6, 54–63.
- Gerlach, S., 1990. Nitrogen, phosphorus, plankton and oxygen deficiency in the German Bight and in Kiel Bay. *Kieler Meeresforschungen, Sonderheft* 7, 1–333.
- Gerlach, S., 1996. Ökologische Veränderungen in der Kieler Bucht. In: Lozan, J.L., Lampe, R., Matthäus, W., Rachor, E., Rumohr, H., Westernhagen, H.v. (Eds.), *Warnsignale aus der Ostsee*. Berlin, Parey, pp. 259–266.
- GKFF, 1973a. Untersuchungen der Flensburger Förde. Sedimentuntersuchungen. Selbstverlag des Gemeinsamen Komitees Flensburger Förde. Aabenraa.
- GKFF, 1973b. Untersuchungen der Flensburger Förde. Wasseraustausch. Selbstverlag des Gemeinsamen Komitees Flensburger Förde. Aabenraa.
- Graf, G., 1994. Benthic–pelagic coupling: a benthic view. *Oceanography and Marine Biology – An Annual Review* 30, 149–190.
- Haarich, M., Pohl, C., Leipe, T., Grünwald, K., Bachor, A., v. Weber, M., Petenati, T., Schröter-Kermani, C., Jansen, W., Bladt, A., 2003. Anorganische Schadstoffe. In: *Meeresumwelt 1999–2002*. Ostsee. Bund-Länder-Messprogramm für die Meeresumwelt von Nord- und Ostsee, Kiel, pp. 167–194.
- Hansen, J.L.S., Josefson, A.B., 2003. Accumulation of algal pigments and live planktonic diatoms in aphotic sediments during the spring bloom in the transition zone of the North and Baltic Seas. *Marine Ecology Progress Series* 248, 41–54.
- HELCOM, 1993. First assessment of the state of the coastal waters of the Baltic Sea. In: *Baltic Sea Environmental Proceedings*, vol. 54, Helsinki.
- Henrichs, S.M., 1995. Sedimentary organic matter preservation: an assessment and speculative synthesis – a comment. *Marine Chemistry* 49, 127–136.
- Hickel, W., 1967. Untersuchungen über die Phytoplanktonblüte in der westlichen Ostsee. *Helgoländer wissenschaftliche Meeresuntersuchungen* 16, 3–66.
- IMO, 2005. Anti-Fouling Systems. International Convention on the Control of Harmful Anti-Fouling Systems on Ships, 2005 edition. IMO, London.
- Jaeger, D., 1990. TIBEAN: a new hypolimnetic water aeration plant. Internationale Vereinigung für Theoretische und Angewandte Limnologie. Verhandlungen IVTLAP 24, 184–187.
- Jahnke, R.A., 1990. Early diagenesis and recycling of biogenic debris at the seafloor, Santa Monica basin, California. *Journal of Marine Research* 48, 413–436.
- Jenkyns, H.C., 1980. Cretaceous anoxic events: from continents to oceans. *Journal of the Geological Society* 137, 171–188.
- Jørgensen, B.B., Richardson, K., 1996. Eutrophication in coastal marine ecosystems. *Coastal and Estuarine Studies* 52, 1–19.
- Kändler, R., 1963. Hydrographische Untersuchungen über die Abwasserbelastung der Flensburger Förde. *Kieler Meeresforschungen* 19, 142–157.
- Kaupplila, P., Weckström, K., Vaalgamaa, S., Korhola, A., Pitkänen, H., Reuss, N., Drew, S., 2005. Tracing pollution and recovery using sediments in an urban estuary, northern Baltic Sea: are we far from ecological reference conditions. *Marine Ecology Progress Series* 290, 35–53.
- Koop, K., Boynton, W.R., Wulff, R., Carman, R., 1990. Sediment-water oxygen and nutrient exchanges along a depth gradient in the Baltic Sea. *Marine Ecology Progress Series* 63, 65–77.
- Köster, R., 1958. Die Küsten der Flensburger Förde – ein Beispiel für Morphologie und Entwicklung einer Bucht. *Schriften des Naturwissenschaftlichen Vereins für Schleswig-Holstein* 29, 5–18.
- Kremling, K., Otto, C., Petersen, H., 1979. Spurenmetall-Untersuchungen in den Förden der Kieler Bucht: Datenbericht von 1977/78. *Berichte aus dem Institut für Meereskunde an der Christian-Albrechts-Universität, Kiel*, p. 66.
- Kristiansen, S., Farbrøt, T., Naustvoll, L.-J., 2000. Production of biogenic silica by spring diatoms. *Limnology and Oceanography* 45, 472–478.
- Krug, J., 1963. Erneuerung des Wassers in der Kieler Bucht im Verlaufe eines Jahres am Beispiel 1960/1961. *Kieler Meeresforschungen* 3, 374–402.
- Kuypers, M.M.M., van Breugel, Y., Schouten, S., Erba, E., Damsté, J.S.S., 2004. N₂-fixing cyanobacteria supplied nutrient N for Cretaceous oceanic anoxic events. *Geology* 32, 853–856.
- LANU, 2001. Deutsch-dänisches Messprogramm Flensburger Förde: Ergebnisse 1996–1997. Landesamt für Natur und Umwelt des Landes Schleswig-Holstein, Flintbek, Kiel.
- LANU, 2003. Jahresbericht 2002. Landesamt für Natur und Umwelt des Landes Schleswig-Holstein, Flintbek, Kiel.
- Leavitt, P.R., 1993. A review of factors that regulate carotenoid and chlorophyll deposition and fossil pigment abundance. *Journal of Paleolimnology* 9, 109–127.
- Leipe, T., Tauber, F., Brüggemann, L., Irion, G., Hennings, U., 1998. Schwermetallverteilung in Oberflächensedimenten der westlichen Ostsee (Arkonabecken, Mecklenburger/Lübecker Bucht und Kieler Bucht). *Meyniana* 50, 137–154.

- Lorenzen, Z., Prein, M., Valentin, C., 1987. Mass aggregations of the free-living marine nematode *Pontonema vulgare* (Oncholaimidae) in organically polluted fjords. *Marine Ecology Progress Series* 37, 27–34.
- MAEWEST, 2007. Western Baltic Model–MAEWEST. The Western Baltic and Belt Sea marine waters operational modeling service, DHI, Denmark. Available from: <<http://www.havmodellen.dk/MAEWEST/>>.
- Meyer-Reil, L.-A., Köster, M., 2000. Eutrophication of marine waters: effects on benthic microbial communities. *Marine Pollution Bulletin* 41, 255–263.
- Müller, G., Dominik, J., Reuther, R., Malisch, R., Schulte, E., Acker, L., Irion, G., 1980. Sedimentary record of environmental pollution in the Western Baltic Sea. *Naturwissenschaften* 67, 595–600.
- Müller, P.G., Schneider, R., 1993. An automated leaching method for the determination of opal in sediments and particulate matter. Deep-Sea Research, Part 1. *Oceanographical Research Papers* 40, 425–444.
- Newman, B.K., Walting, R.G., 2007. Definition of Baseline Metal Concentrations for Assessing Metal Enrichment of Sediments from the South-Eastern Cape Coastline of South Africa. *Water SA*, vol. 33, pp. 675–691. Available from: <<http://www.wrc.org.za>>.
- Nikulina, A., Polovodova, I., Schönfeld, J., 2007. Environmental response of living benthic foraminifera in Kiel Fjord, SW Baltic Sea. *Earth Discussion* 2, 191–217.
- Nixon, S.W., 1981. Remineralization and nutrient cycling in coastal marine ecosystem. In: Neilson, B.J., Cronin, L.I. (Eds.), *Estuaries and Nutrients*. Humana Press, Clifton, New Jersey, pp. 11–138.
- Nixon, S.W., 1995. Coastal marine eutrophication: a definition, social causes, and future concerns. *Ophelia* 41, 199–219.
- Nriagu, J., 1978. Lead in soils, sediments and major rock types. In: Nriagu, G. (Ed.), *The Biogeochemistry of Lead in the Environment: Part A. Ecological Cycles*. Elsevier, Amsterdam, pp. 15–72.
- Pohl, C., Hennings, U., Leippe, T., 2005. Ostsee-Monitoring; Die Schwermetall-Situation in der Ostsee im Jahre 2004. Institut für Ostseeforschung Warnemünde, an der Universität Rostock, 34 pp.
- Ragueneau, O., Chauvaud, L., Leynaert, A., Thouzeau, G., Paulet, Y.-M., Bonnet, S., Lorrain, A., Grall, J., Corvaisier, R., Le Hir, M., Jean, F., Clavier, J., 2002. Direct evidence of a biologically active coastal silicate pump: ecological implications. *Limnology and Oceanography* 47, 1849–1854.
- Reuss, N., Conley, D.J., Bianchi, T.S., 2005. Preservation conditions and the use of sediment pigments as a tool for recent ecological reconstruction in four Northern European estuaries. *Marine Chemistry* 95, 283–302.
- Rheinheimer, G., 1970. Mikrobiologische Untersuchungen in der Flensburger Förde. *Berichte der Deutschen Wissenschaftlichen Kommission für Meeresforschung* 21, 420–429.
- Rheinheimer, G., 1998. Pollution in the Baltic Sea. *Naturwissenschaften* 85, 318–329.
- Schiewer, U., Gocke, K., 1996. Ökologie der Bodden und Förden. In: Rheinheimer, G. (Ed.), *Meereskunde der Ostsee*. Springer, Berlin, pp. 216–221.
- Seitzinger, S., 1988. Denitrification in freshwater and coastal marine ecosystems: ecological and geochemical significance. *Limnology and Oceanography* 33, 702–724.
- Smetacek, V., 1980. Annual cycle of sedimentation in relation to plankton ecology in Western Kiel Bight. *Ophelia* (Suppl. 1), 65–76.
- Vaalgamaa, S., Conley, D.J., 2008. Detecting environmental change in estuaries: nutrients and heavy metal distributions in sediment cores in estuaries from the Gulf of Finland, Baltic Sea. *Estuarine Coastal and Shelf Science* 76, 45–56.
- Virtasalo, J.J., Kohonen, T., Vuorinen, I., Huttula, T., 2005. Sea bottom anoxia in the Archipelago Sea, northern Baltic Sea – implications for phosphorus remineralization at the sediment surface. *Marine Geology* 224, 103–122.
- Wahl, M., 1984. The fluffy sea anemone *Metridium senile* in periodically oxygen depleted surroundings. *Marine Biology* 81, 81–86.
- Wahl, M., 1985. The recolonisation potential of *Metridium senile* in an area previously depopulated by oxygen deficiency. *Oecologia* 67, 255–259.
- Wasmund, N., Uhlig, S., 2003. Phytoplankton trends in the Baltic Sea. *ICES Journal of Marine Science* 60, 177–186.
- Wilson, P.A., Norris, R.D., 2001. Warm tropical ocean surface and global anoxia during the mid-Cretaceous period. *Nature* 412, 425–429.
- Zeitschel, B., 1980. Sediment-water interactions in nutrient dynamics. In: Tenore, K.R., Coull, B.C. (Eds.), *Marine Benthic Dynamics*. University of South Carolina, USA, pp. 195–218.