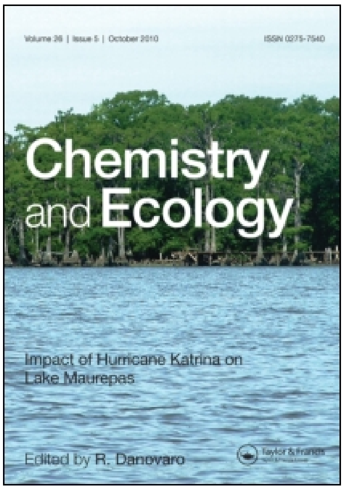

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Impacts of mussel dredging on sediment phosphorus dynamics in a eutrophic Danish fjord

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IMPACTS OF MUSSEL DREDGING ON SEDIMENT PHOSPHORUS DYNAMICS IN A EUTROPHIC DANISH FJORD

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Effects of mussel dredging on sediment metabolism (oxygen uptake and sulfate reduction rates) and phosphorus dynamics (flux across sediment-water interface and sequential extraction) were examined in Limfjorden (Denmark) during spring (May) and summer (August). Sediment samples were taken during mussel dredging and in addition an experimental simulation of the dredging was performed to investigate short-term changes in phosphorus (P) dynamics. Iron-bound P was reduced by up to 2/3 in the surface layer in the dredging track (from 31 to 8 mmol P m^{-2}), whereas the dissolved P-pools and less reactive particulate pools were not affected by dredging. Sediment oxygen consumption was enhanced immediately after dredging, but returned to the initial level after 4 days (20–40 mmol m^{-2} d^{-1}). The enhanced consumption was attributed to reoxidation of reduced compounds released during dredging. Sulfate reduction rates were high in the area (13–15 mmol m^{-2} d^{-1}) and sulfides competed with P for oxidized iron resulting in low iron-bound pools in the area ($<4\%$ of total P pools). Sulfate reduction rates were stimulated by the resuspension of sediments, especially in August, where a subsurface maximum was found, possibly due to a mixing of labile organic matter into these layers. In contrast sulfate reduction rates were reduced in the dredging track due to removal of labile organic matter from the surface layers. The loss of P during dredging was to some extent counteracted by regeneration of iron-bound P pools in the surface layers. The release of P due to mussel dredging was estimated to be in the same order of magnitude as the annual loading from the catchments and point sources to Limfjorden.

Keywords: Phosphorus; Mussel dredging; Sediment; Sulfate reduction; Oxygen consumption

1 INTRODUCTION

Nutrient loading of coastal areas and estuaries with nitrogen (N) and phosphorus (P) is a globally increasing concern due to the negative effects on the coastal marine ecosystem (Conley *et al.*, 2000). In many coastal areas the planktonic primary production has increased dramatically, and the depth limits as well as the distribution of macrophytes and macroalgae have been reduced (Borum and Sand-Jensen 1996). Also the frequency of oxygen depletion events has increased resulting in negative impacts on benthic organisms as well as fisheries. In many fjords, including the Danish fjord, Limfjorden, fisheries and mussel dredging have been significantly reduced during the past decades due to eutrophication (Riemann and

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Hoffmann, 1991; Lomstein, 1999). Mussel dredging is, however, still an important fishery in Limfjorden with 51 licensed boats and an annual harvest of about 100 000 tons (Hoffmann, 1996; Dolmer and Hoffmann, 2000), but there are concerns that this type of fishery accelerates the eutrophication process by increasing the release of nutrients and oxygen consuming compounds from the sediments. Like many eutrophic estuarine systems, Limfjorden suffers from high pelagic primary production during the growth season and oxygen depletion events during summer (Gray *et al.*, 2002; see also Fig. 2). Nitrogen loading from agricultural run-off is particularly high, and the primary production displays a shifting nutrient limitation during the year, with P and/or silicate as the controlling factors in spring, switching to N limitation during summer and autumn (Conley *et al.*, 2000).

Mussel dredging is in Limfjorden carried out from small boats with one to two dredging devices, which are trawled over the seafloor (Dyekjær and Hoffmann, 1999). The dredging process takes a couple of minutes, before the collected mussels are rinsed in the water column and taken on board. Mussel dredging causes resuspension of mud and sand-particles during the dredging and rinsing process, and it is in particular this visible dispersion of particles, which has lead to environmental concern. Dredging has been shown to increase the amount of resuspended particles by up to 1360% in the water column, whereas only minor or no increases in nitrate and phosphate concentrations were measured (Riemann and Hoffmann, 1991; Dyekjær and Hoffmann, 1999). The oxygen consumption increased, but there was no quantitative impact on the oxygen concentration in the water column as the consumption was less than the renewal of oxygen through advective processes. It was concluded that the impact of mussel dredging on water column quality in Limfjorden was minor.

The impact of mussel dredging on sediment conditions is, however, uncertain (Riemann and Hoffmann, 1991). The depth of dredging in the sediment depends upon a number of factors, *e.g.* abundance of mussels and sediment characteristics (mud, silt, sand content). The average dredging depth has been estimated to <5 cm, and the dredging track is expected to last from a few hours to several days dependent upon current, tides and wind conditions (de Groot, 1984). The resuspension of sediment in the dredging track changes the original structure of the sediments, which may give rise to important changes in biogeochemical conditions (Fig. 1). The sediments in Limfjorden have a thin oxic surface layer in the scale of mm's, where oxic respiration takes place (Thamdrup and Canfield, 2000). Below is the suboxic layer of a few cm's thickness, where oxidized compounds such as iron and manganese are important for mineralization pathways. Oxidized iron also participates in the biogeochemical cycling of P and sulfur (S) by binding phosphate and reoxidizing sulfides. The suboxic zone is followed by a reduced zone, where sulfate reduction is the most important mineralization pathway. The thickness of the oxic and suboxic layers changes over the year with maximum extension in winter and minimum in summer (Fig. 1), and may even disappear during oxygen depletion events, which happen for about 30% of the sediments in Limfjorden every year (Limfjordsovervågningen, 1995; 2000). Dredging thus influences the oxic and suboxic layer from autumn until early summer, and the reduced layer in summer (Fig. 1).

The biogeochemical conditions in the sediments may be affected by dredging in a number of ways: (1) The removal of the aerobic sediment surface layer may favour anaerobic processes such as sulfate reduction. (2) Nitrification may be inhibited by removal of the oxic sediment layer, which also inhibits the coupled nitrification–denitrification, and thus lowers denitrification (Rysgaard *et al.*, 1995). (3) Pools of iron oxides are reduced by removal of the oxidized surface sediments (Jensen *et al.*, 1995). Resuspension of the sediments may increase the pools of iron(III) due to oxidation (Spagnoli and Bergamini, 1997). (4) The release of phosphates from the sediment may be enhanced due to exposure of deeper layers with higher porewater concentrations and due to lowered pools of iron oxides (binding site for phosphate) (Jensen

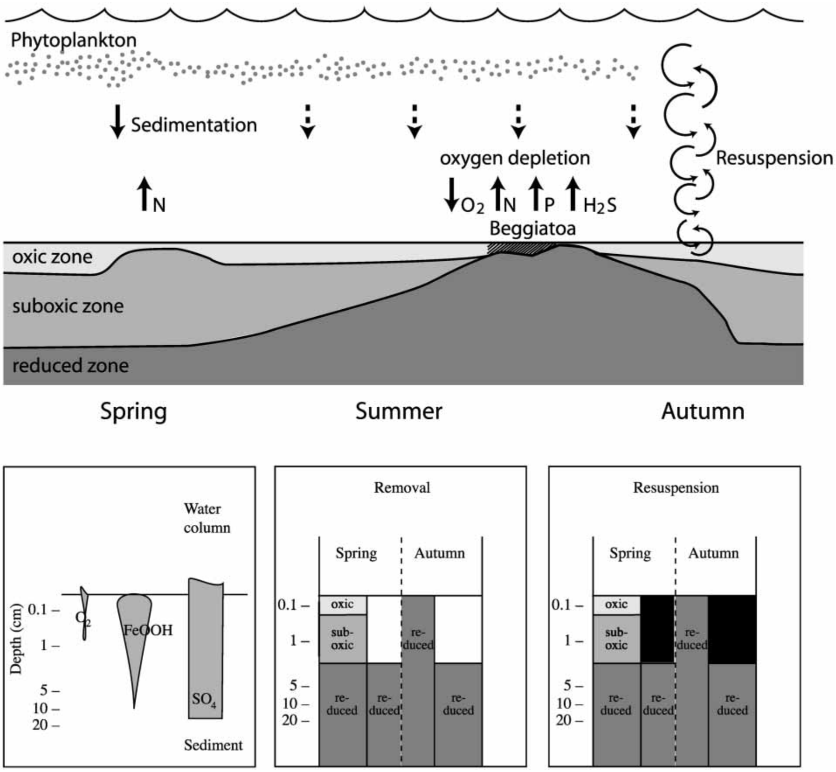

FIGURE 1 A schematic presentation of the seasonal variation in the sediment biogeochemical conditions in Limfjorden and the possible scenarios of mussel dredging. See text for explanation. Modified from Limfjordskomiteen (1990).

et al., 1995). Resuspension may enhance the binding of phosphate in the surface layers. (5) The sediment oxygen consumption may be enhanced when reduced compounds from the anaerobic layers are directly exposed to an oxic water column. (6) Sulfate reduction rates may be reduced due to the removal of labile organic matter from the surface sediment, whereas resuspension may stimulate the rates due to burial of labile organic matter.

The aim of this study was to examine the effect of mussel-dredging on sediment dynamics through simulation of a mussel-dredging event on intact sediment cores collected during different times of the year. Mussel dredging was studied in May (full oxygenated water column) and in August (reduced water column oxygen concentrations) to assess the impacts on phosphorus, iron and sulfur cycling in the sediments. The ecological consequences of mussel dredging are considered in relation to natural processes, *e.g.* resuspension events and to nutrient loading of Limfjorden.

2 MATERIALS AND METHODS

2.1 Study Site and Sampling

Sediment cores and water samples were collected in Lovns Bredning, Limfjorden, Denmark (56°39’5 N, 09°13’5 E) in May and August, 1994 (Fig. 2). Lovns Bredning receives a large amount of fresh water and nutrients from the catchment area and primary productivity and

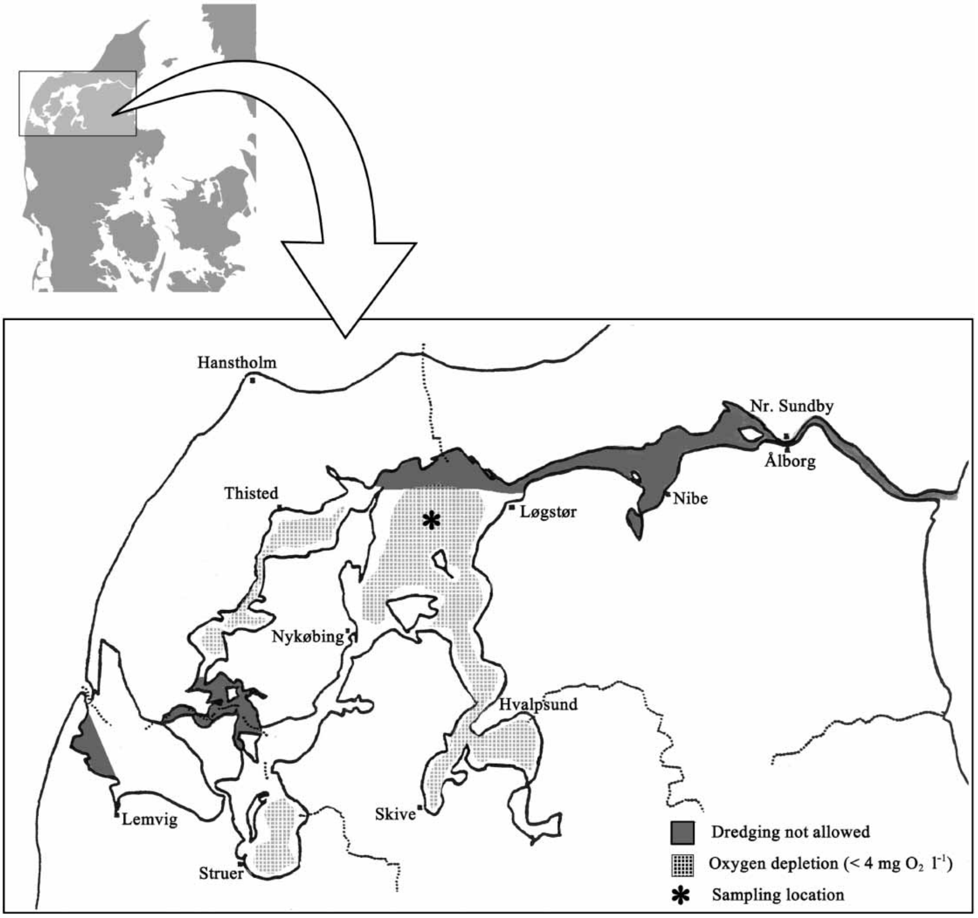

FIGURE 2 Map of Limfjorden showing the sampling location, the area closed for mussel dredging and areas affected by oxygen depletion events for up to 10 weeks in 1994 (Limfjordsovervågningen, 1995).

sedimentation rates are high (Limfjordsovervågningen, 2000). The sediments are characterised as soft reduced muds with a high organic content (8–15% DW). Sediment cores (i.d. = 52 mm) were collected at a water depth of 5 m by scuba-divers. Cores were obtained 4 hours after dredging inside (6 cores) and outside (24 cores) the track. The cores were kept at *in situ* temperature without stoppers until the following day. The temperature was 12.0 °C and 17.5 °C, and the salinity was 21.0 and 23.5 PSU in May and August, respectively. Bottom water for the incubation of the sediment cores was collected at the field site and GF/C filtered before use.

2.2 Experimental Design

Twelve sediment cores collected outside the track were placed in an incubator, where each core was kept in a closed circulation system with a reservoir with 250 ml GF/C filtered seawater from the location (Fig. 3). The water column was stirred by a central magnet (40 rpm) and the water flow through the cores was 2.45 ml min^{-1}. The reservoirs were changed every 2–3 days. The incubator was placed in a climate room to assure temperature

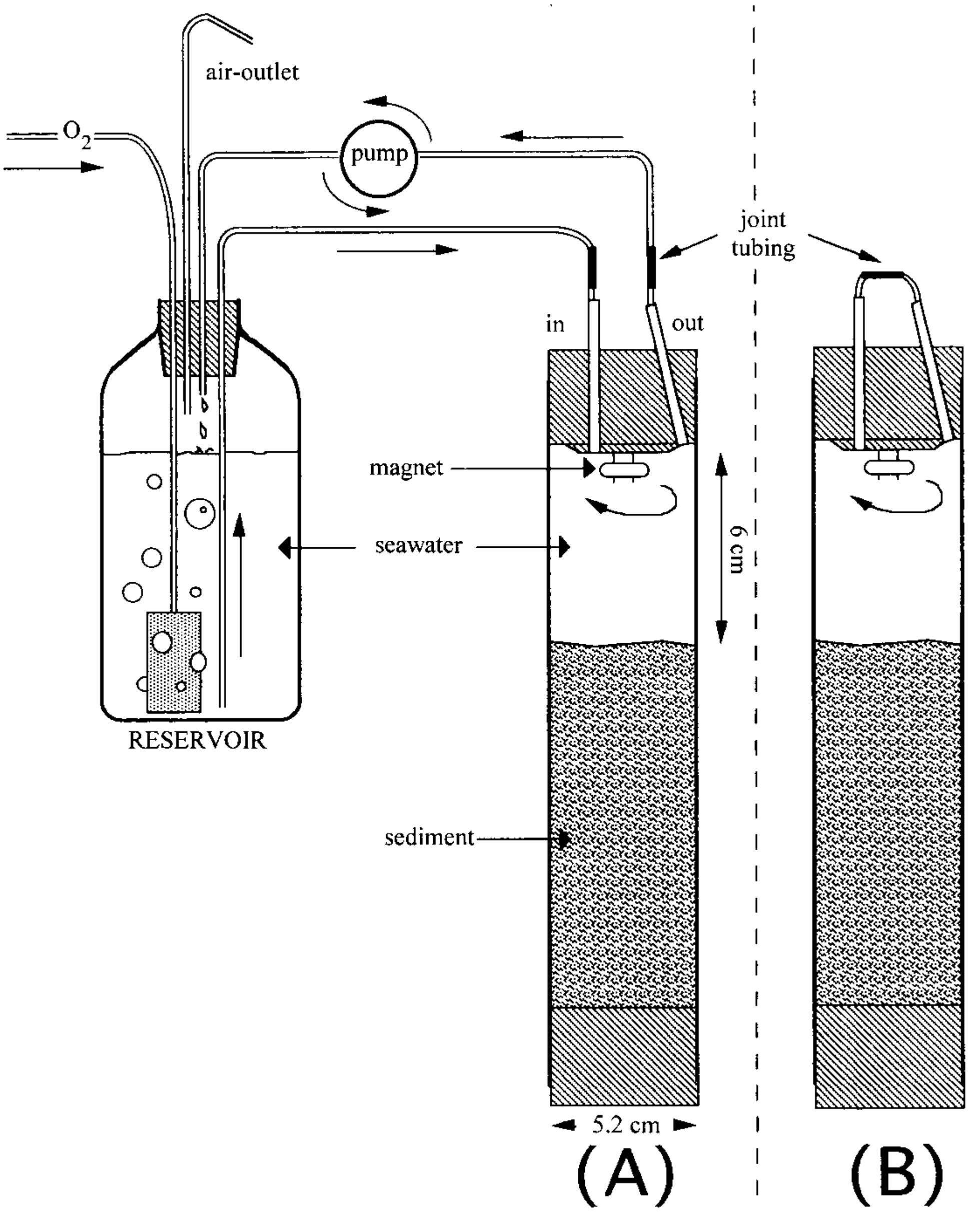

FIGURE 3 Flux cores with reservoir (250 ml). (A) The seawater is recycled in a closed system between sediment chamber and reservoir. (B) Flux incubation with closed sediment chamber.

corresponded to *in situ* (within 2 °C), and the oxygen concentration was kept constant by aerating the reservoirs. The sediment cores were allowed to acclimatize for 5–9 days before initiation of the experiment. Based on underwater observations the sediment cores were manipulated to simulate mussel dredging. Two scenarios were found: (1) A sediment layer with a thickness of 3 cm was removed in the dredging track and (2). The sediment was resuspended for about 2 sec by the mussel bag. The sediment cores were manipulated according to these observations: Three centimeter of the sediment was removed from

4 cores (REM), 3 cm of the sediment were resuspended in 10 sec (RES) and 4 unmanipulated cores served as controls (CON). The experimental resuspension was longer compared to the field observations, as it was not possible to resuspend the sediment down to 3 cm within 2 sec. Abbreviations are shown in Table I.

2.3 Flux Measurements

During the 2 weeks that followed, 6 incubations were performed to obtain sediment oxygen uptake rates (SOU) and fluxes of dissolved phosphate (DIP) across the sediment-water interface. The flux incubations were conducted by disconnecting the sediment cores from the reservoirs, and taking an initial sample from the reservoirs and a final sample from the sediment cores after 3–4 hours of incubation. Oxygen concentrations were measured by the Winkler technique and samples for DIP were GF/C filtered and kept frozen until analysis (see below). After the 2 week period, sediment cores representing the different scenarios were incubated to obtain sulfate reduction rates and sectioned for particulate and dissolved pools of phosphate, iron (Fe^{2+}) and sulfate (SO_4^{2-}).

2.4 Sulfate Reduction Rates (SRR)

Sulfate reduction rates were measured in cores from the field site outside the track (LOT) and from the experiment (REM, RES, CON) with a modification of the core-injection technique (Jørgensen, 1978). The sediment cores (i.d. 52 mm) were subcored with smaller cores (i.d. 26 mm) with silicone-filled injection ports at 1 cm intervals. Two µl of ^{35}S-sulfate (70 kBq) were injected at a 1 cm interval and the cores were incubated in darkness for 6 h at *in situ* temperature. The incubation was terminated by sectioning the cores into 1 cm (0–4 cm) and 2 cm intervals (4–12 cm) and fixing the sediment in 1 M zinc acetate (vol:vol). The samples were stored frozen until distillation according to the 2-step procedure of Fossing and Jørgensen (1989). Pools of acid volatile sulfides (AVS) and chromium reducible sulfides (CRS) were determined by the method of Cline (1969).

TABLE I Acronyms and Abbreviations.

Site and experiment	
LOT	Lovns Bredning outside track
LIT	Lovns Bredning inside track
CON	Control cores
REM	Cores were surface layer is removed
RES	Cores were surface layer is resuspended
Rates and pools	
SOU	Sediment oxygen uptake
DIP	Dissolved inorganic phosphate
SRR	Sulfate reduction rates
AVS	Acid volatile sulfides
CRS	Chromium reducible sulphur
P- and Fe-extraction	
BD-P or BD-Fe	Phosphate or iron extracted in bicarbonate-dithionite. Also referred as iron-bound phosphate or oxidized iron
NaOH-P	Phosphate extracted with NaOH
HCl-P or HCl-Fe	Phosphate or iron extracted with HCl
Res-P or Res-Fe	Residual phosphate or iron

2.5 Phosphorus (P) and Iron (Fe) Sequential Extractions

Inorganic phosphorus (IP) and iron (Fe) were extracted according to the method described by Jensen and Thamdrup (1993) with a few modifications. Three replicate sediment cores were sectioned under a N_2 atmosphere in a glove bag at a 0.5 cm interval down to 2 cm and at a 2 cm interval down to 12 cm. Corresponding sediment sections from the replicates were pooled into one sample and a sequential extraction on 1 g of sediment was done: Step 1: Loosely adsorbed IP was extracted with 1 M $MgCl_2$ for 1 h. Step 2: Fe- and Mn-bound IP was extracted with bicarbonate-dithionate solution for 1 h (BD-P or BD-Fe). Step 3: IP bound in clay-minerals and aluminium-oxides was extracted with 0.1 M NaOH for 15 h (NaOH-P). Step 4: IP and Fe bound with magnesium, calcium and sulfides were extracted with 0.5 M HCl for 1 h (HCl-P(-Fe)). Step 5: Finally residual IP and Fe was extracted from ignited sediment by boiling in 1 M HCl for 10 min (Res-P(-Fe)). Non-acidic extracts were preserved with H_2SO_4 and all samples were stored for later analysis of IP and Fe.

Porewater from the remaining sediment was obtained by porewater squeezing with N_2 according to Reeburgh (1967). The samples were then analysed for DIP, Fe^{2+} and SO_4^{2-}.

2.6 Analysis

DIP and IP were measured by standard colorimetric methods (Koroleff, 1983). Fe and Fe^{2+} were measured by atomic absorption spectrometry (Perkin Elmer, 2100) and SO_4^{2-} was measured by precipitation of barium-sulfate in gelatine solution (Tabatabai, 1974). Porosity and density were obtained by weight of a known volume of wet sediment, followed by drying overnight at 105 °C. Sediment organic content was determined as loss-on-ignition after 6 h at 520 °C.

3 RESULTS

3.1 Solid and Dissolved Pools of IP and Fe in Sediments

There were marked differences in the IP and Fe pools measured inside and outside the track in May (Fig. 4) with much lower pools of BD and HCl fractions in the surface layer of the dredged sediment. The pools were reduced by 85% for BD and 33% for HCl. The experimental cores also showed marked differences, where the REM sediments had 20% lower concentrations in the BD fraction in the 0.5–1 cm layer compared to the CON, and the RES sediments had low concentrations (reduced by 53%) in the surface layer (0–1 cm) and maximum pools in the 1–2 cm layer (enhanced 5 times). The porewater pools of DIP did not show marked differences between cores except for a lower concentration throughout the examined depth in LIT compared to LOT. The DIP concentration was low in the surface layers (10–35 μM in 0–2 cm) and increased to about 55 μM in the deeper parts. In contrast, dissolved Fe^{2+} showed major differences between cores with a subsurface peak at 1–2 cm in LOT and CON of about 125 μM, whereas the LIT and REM had much lower concentrations (<30 μM) throughout the examined depth. The RES showed two subsurface peaks of 75–85 μM at 1–1.5 cm and 2–4 cm, respectively.

The differences between treatments were less notable in August (Fig. 5), and the pools in the BD fraction were generally low in the surface layers compared to May. The REM cores showed lower BD-P concentrations in the surface layers compared to CON, whereas there were no marked difference between CON and RES. The DIP concentration was higher in LOT in August (30–60 μM), whereas only low concentrations of Fe^{2+} (<5 μM) were measured.

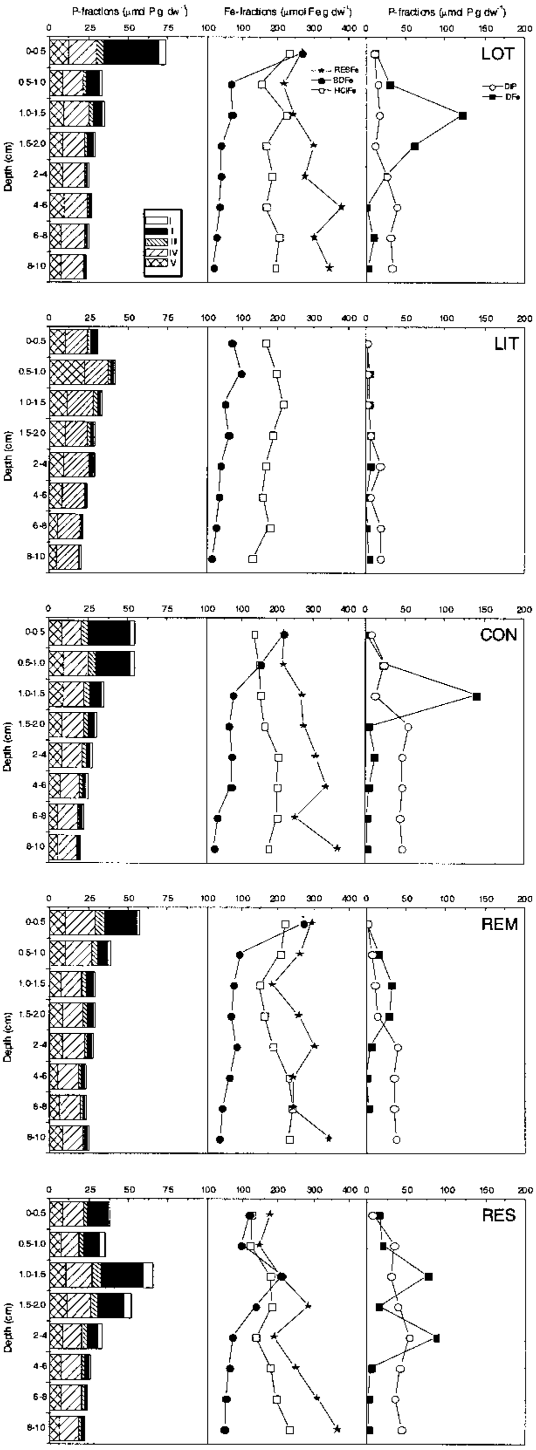

FIGURE 4 Phosphor and iron concentrations in the sediments in dredging area (LOT outside dredging track, LIT inside dredging track) and in the simulated dredging experiment (CON control, REM surface layer removed, RES surface layer resuspended) during May 1994. Left: Sequential P (Step 1–5). Mid: Particulate pools of Fe from the BD-fraction (BDFe, Step 2), the HCl-fraction (HClFe, Step 4) and the residual fraction (ResFe, Step 5). Right: Porewater pools of DIP and Fe^{2+}. Values are pooled from 2–3 sediment cores.

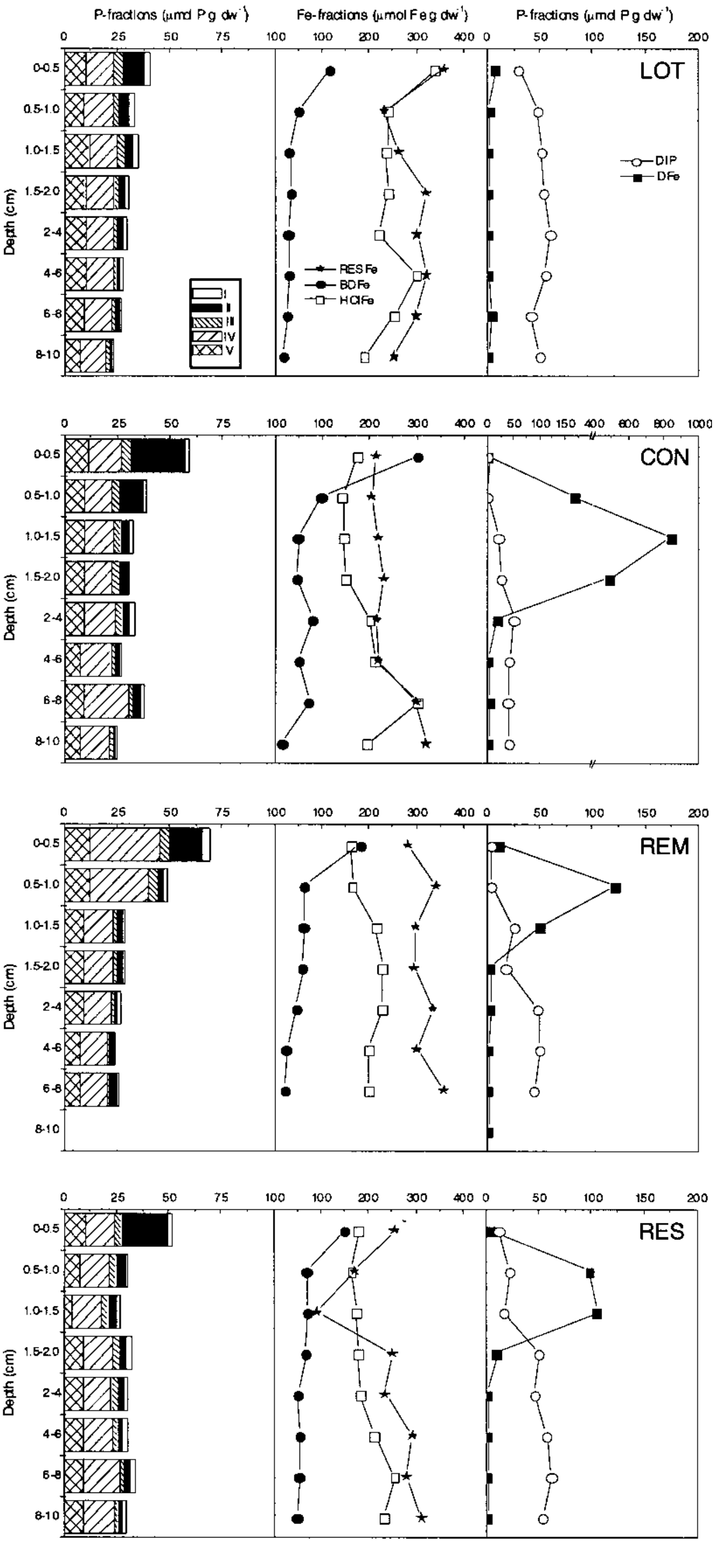

FIGURE 5 As Figure 4 but for sampling in August 1994. Results not available from LIT.

All experimental cores showed low DIP concentrations in the surface layer (4–25 μM in 0–2 cm) and increasing concentrations below (up to 65 μM) with no major difference between treatments. There was a Fe^{2+} subsurface peak in 0.5–1.5 cm in all experimental cores with very high concentrations in CON (up to 842 μM) and lower concentrations in REM and RES, of 125 and 110 μM, respectively.

The total pool of BD-P in the surface layers (0–2 cm) at the field site was reduced by 80% due to dredging in May (Fig. 6). The reduction was less (58%) in the experimental REM cores, whereas the pools increased by 19% during resuspension. The initial BD-P pool was only 1/3 in August compared to May, and the BD-P pool remained at this level in the RES and REM cores, whereas it was almost doubled in the CON cores after 2 weeks of incubation. The Fe:P ratios in the BD-fraction were higher for the dredged sediments and REM (13–23) compared to other scenarios, where a ratio between 8–11 was recorded (Fig. 6). The HCl pool of P was the quantitatively most important fraction and contributed 41–56% of the total pool of P in the upper 10 cm of the sediments (Tab. II). The porewater pools were the smallest (<0.9% of total P pool).

3.2 Sulfate Reduction Rates

Sulfate reduction rates were not measured inside the track at the field site, but the manipulated sediments showed marked differences in May (Fig. 7). Sulfate reduction rates were generally lower in REM (60–100 mmol cm^{-3} d^{-1}) compared to CON sediments (85–175 mmol cm^{-3} d^{-1}), whereas production was stimulated in the 2–4 cm layer in RES (275 mmol cm^{-3} d^{-1}). Sulfate reduction rates, in particular surface rates, increased by up to a factor of 10 between May and August (Fig. 8). Water temperature increased from

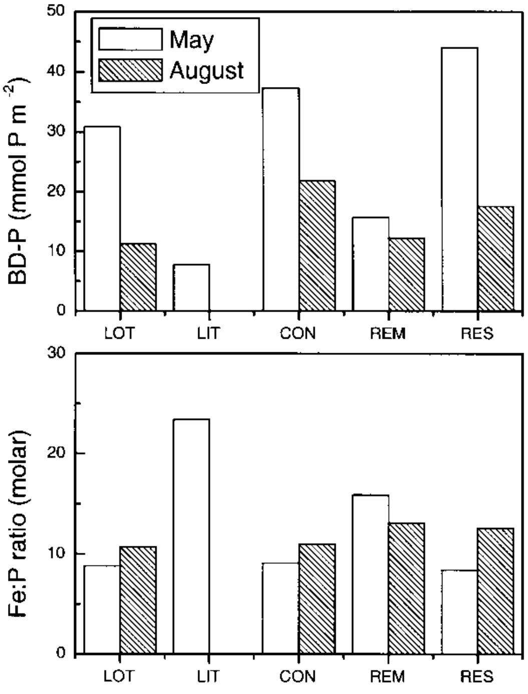

FIGURE 6 Surface pools (0–2 cm) of BD-P (upper) and surface Fe:P ratios (lower) in the sediments from the dredging area and from the simulated dredging in May and August. Values are pooled from 2–3 sediment cores.

TABLE II Depth Integrated P Pools (0–10 cm, mmol P m^{-2}) in the 5 Sequential Extractions and Porewater in May and August at the Field Sites and in the Experimental Cores.

	Porewater	*Step 1*	*Step 2*	*Step 3*	*Step 4*	*Step 5*	*Total*
LOT							
May	2.7 (0.5)	20.2 (3.7)	43.2 (7.9)	25.1 (4.6)	287.3 (52.2)	171.8 (31.2)	550.3
August	4.6 (0.8)	32.3 (5.9)	40.7 (7.4)	34.4 (6.3)	251.6 (46.0)	183.4 (33.5)	547.0
LIT							
May	1.2 (0.2)	11.6 (2.0)	31.3 (5.4)	23.7 (4.1)	326.0 (56.3)	184.8 (31.9)	578.6
August	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CON							
May	4.0 (0.7)	25.1 (4.4)	66.7 (11.7)	41.5 (7.3)	271.2 (47.8)	159.4 (28.1)	567.9
August	3.6 (0.6)	26.6 (4.7)	55.4 (9.8)	39.3 (7.0)	278.3 (49.4)	159.8 (28.4)	563.0
REM							
May	2.9 (0.6)	18.7 (3.8)	41.7 (8.5)	35.0 (7.1)	233.8 (47.6)	159.3 (32.4)	491.4
August	3.8 (0.6)	24.6 (3.8)	63.1 (9.7)	31.3 (4.8)	328.4 (50.4)	200.3 (30.7)	651.5
RES							
May	3.9 (0.7)	33.7 (5.9)	93.9 (16.3)	47.8 (8.3)	237.7 (41.3)	158.3 (27.5)	575.3
August	4.8 (0.9)	38.3 (7.1)	51.8 (9.6)	42.6 (7.9)	250.6 (46.3)	153.5 (28.3)	541.6

Note: The percentage of each fraction of the total is given in parentheses.

12.0 °C to 17.5 °C during this interval. There were marked effects of the manipulations similar to the findings in May with lower sulfate reduction rates in REM and enhanced subsurface rates in RES.

The TRS pools were also influenced by the manipulations in May (Fig. 7), where the REM cores showed high surface pools compared to CON, whereas the RES pools remained high in the subsurface layer (1–4 cm), but were lower below (4–10 cm) compared to CON. In August all TRS pools were generally lower (Fig. 8), which may be due to a slight variation in sampling site, but this does not correspond to observations of other sediment characteristics, *e.g.* solid phase P and Fe pools. The impact of manipulations on TRS pools was less in August than in May, and only RES showed a reduction compared to CON.

The depth integrated SRR (ISRR) reflected the differences found in the depth profiles (Tab. III). ISRR were reduced in the REM treatment, both in May (43%) and August (37%), whereas the rates were enhanced in the RES in August (2.7 times).

3.3 SOU and DIP Flux

Sediment oxygen uptake was high (~32 mmol m^{-2} d^{-1}) right after the manipulation in REM and RES cores, but all cores showed a tendency of decreasing SOU during the first 24 h down to ~12 mmol m^{-2} d^{-1} followed by higher but steady rates during rest of the incubation (~20 mmol m^{-2} d^{-1}, Fig. 9). In August the initial SOU was 2 times higher in the CON cores (~42 mmol m^{-2} d^{-1}) compared to May. SOU was enhanced by dredging and did not decrease until 3 days after the manipulations, and was followed by more variable rates compared to May (40–60 mmol m^{-2} d^{-1}).

Dissolved inorganic phosphate was primarily released from the sediments in May, except around the minimum SOU measured after 24 h (Fig. 10). Here the flux of DIP was close to zero or a minor uptake was measured. DIP was released from the sediments until the last measurement, where the flux was close to zero in the control and a minor uptake was recorded in the manipulated cores. In August a large uptake of DIP occurred in CON and RES during the first 2–3 days of incubation (~600 µmol m^{-2} d^{-1}), which was followed by at period of release and finally the rates changed again to an uptake. In the REM cores

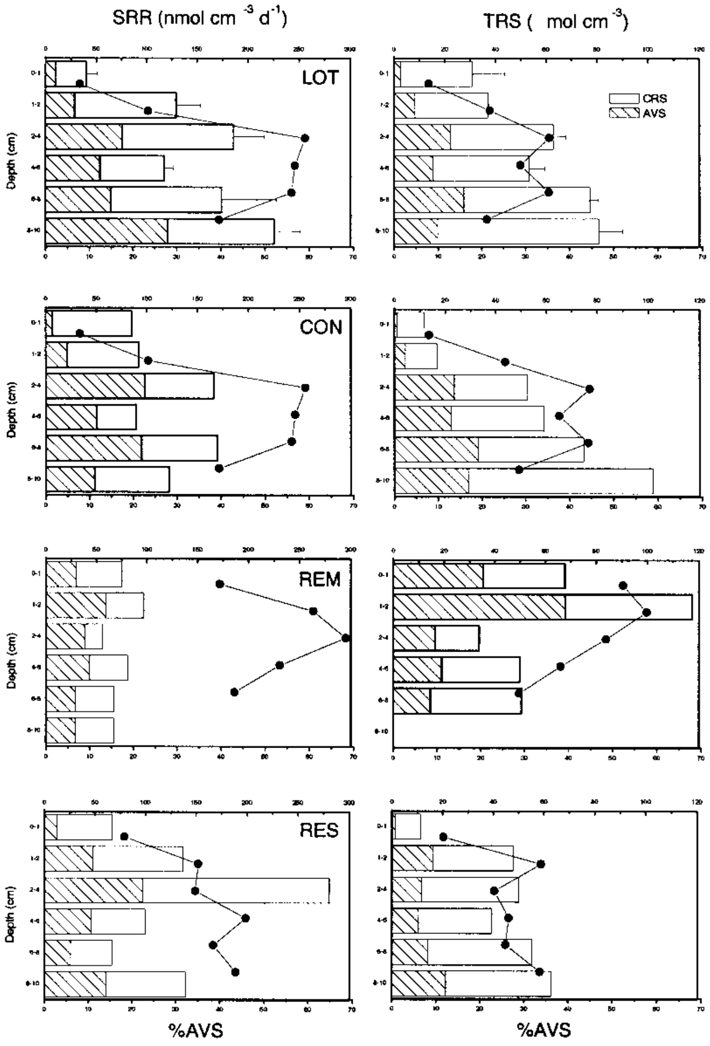

FIGURE 7 Depth profiles of sulfate reduction rates (SRR) and total pools of reduced sulfides (TRS) in the sediments in the dredging area and in the simulated dredging experiment. Rates and pools are given as acid volatile sulfides (AVS) and chromium reducible sulfur (CRS). The percentages of AVS (%AVS) of the TRS (AVS + CRS) rates and pools are given. Values from the field site represent mean of 3 cores (±SD), whereas the sediments were pooled for 2 cores in the experiment.

DIP was released initially (250 μmol m^{-2} d^{-1}) and fluctuated between release and uptake during the rest of the incubation.

4 DISCUSSION

These results indicate that mussel dredging can enhance the release of phosphate from the sediments and thus contribute to the nutrient availability in Limfjorden. The removal and resuspension of the surface sediments during dredging resulted in major changes in the sediment biogeochemical conditions, and contributed to an enhanced sediment oxygen uptake, which may be critical for the water quality during periods of stratification.

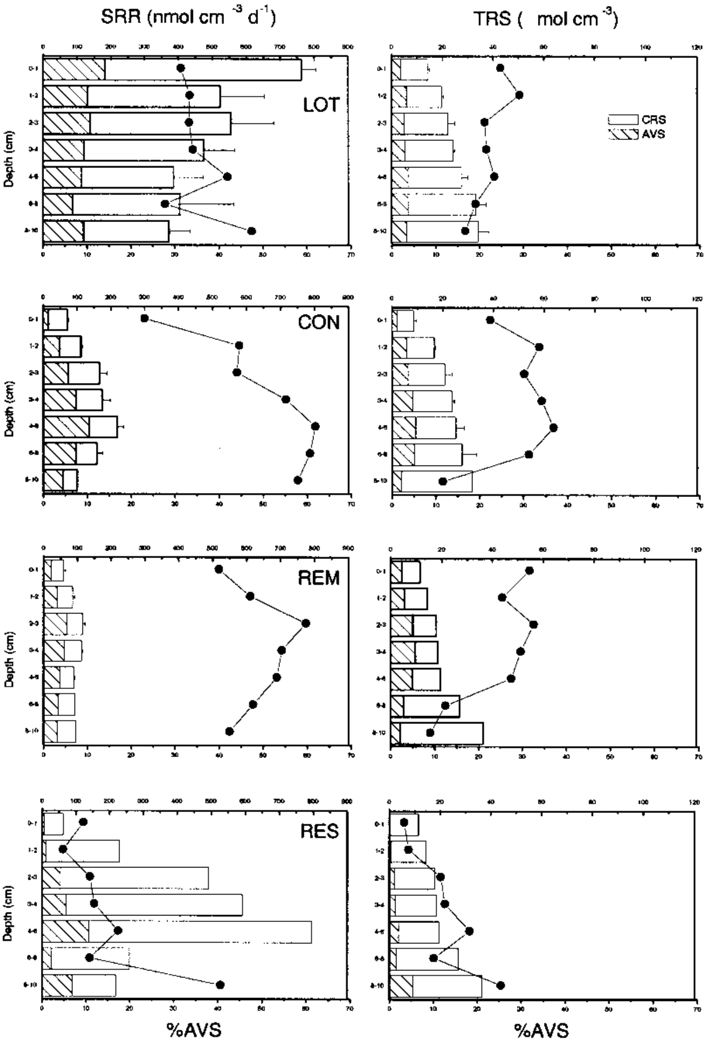

FIGURE 8 As Figure 7, but for sampling in August 1994.

We observed a reduction of the surface pools of P to 1/3 in response to mussel dredging. The concentration of phosphate is usually high in the surface sediments in marine ecosystems due to the binding of phosphate to oxidized iron (Jensen *et al.*, 1995). The observed reduction in P-pools is much higher than the seasonal reduction in iron-bound P pools usually found in temperate sediments (Jensen *et al.*, 1995) and clearly emphasizes the major impact of dredging on P pools in the sediments. A significant fraction of the bound P is generally released from the oxidized iron pools during summer, where high microbial activity in the sediments, stimulated by increasing water temperatures, reduces the oxidized iron pools (Jensen *et al.*, 1995). The release of P from the sedimentary pools, in particular in spring, may contribute to a shift in nutrient limitation of phytoplankton from phosphorus to nitrogen found in many estuaries (Conley *et al.*, 2000). Nitrogen is also released during dredging but only the pore water pools are directly available for phytoplankton growth (Dyekjær and Hoffmann, 1999). Mussel dredging thus enhances the phosphate availability of the coastal

TABLE III Depth Integrated (0–10 cm) Sulfate Reduction Rates (ISRR mmol S m^{-2} d^{-1}) and Pools of Total Reducible Sulfides (ITRS mol S m^{-2}) in May and August at the field site and in the experimental cores.

	ISRR (0–10 cm)		*ITRS (0–10 cm)*	
	AVS	*Total*	*AVS*	*Total*
LOT				
May	6.6 (42)	15.7	1.7 (28)	6.1
August	12.2 (36)	34.3	0.6 (22)	2.7
CON				
May	6.1 (48)	12.7	2.2 (37)	6.0
August	8.1 (55)	14.7	0.6 (26)	2.3
REM				
May	3.7 (51)	7.2	2.3 (42)	5.5
August	4.6 (49)	9.4	0.6 (19)	3.2
RES				
May	5.2 (38)	13.8	1.3 (28)	4.7
August	6.5 (17)	39.2	0.4 (17)	2.3

Note: Rates and pools are presented as acid volatile sulfides (AVS), and total (AVS + chromium reducible sulfur (CRS)). The percentage of AVS of the total SRR or TRS is given in parentheses.

zones by suspending surface sediments with high pools of P, and may in the periods or in areas, where phosphate is the limiting nutrient, stimulate phytoplankton growth.

The experimental manipulations were undertaken to examine the effects of dredging on sediment biogeochemical conditions and to study the recovery of the sediments after dredging events. The experimental removal and resuspension of sediment were consistent with the observations at the field site showing a decrease in the surface P pools. The pools were, however, not as low as measured right after dredging suggesting that the pools of P to some degree recovered after the manipulation. The pools of P even increased in the deeper layers of the resuspended sediment. This pool is, however, most likely temporarily due to enhanced rates of sulfate reduction in the same layers, where the produced sulfides will compete with P for oxidized iron.

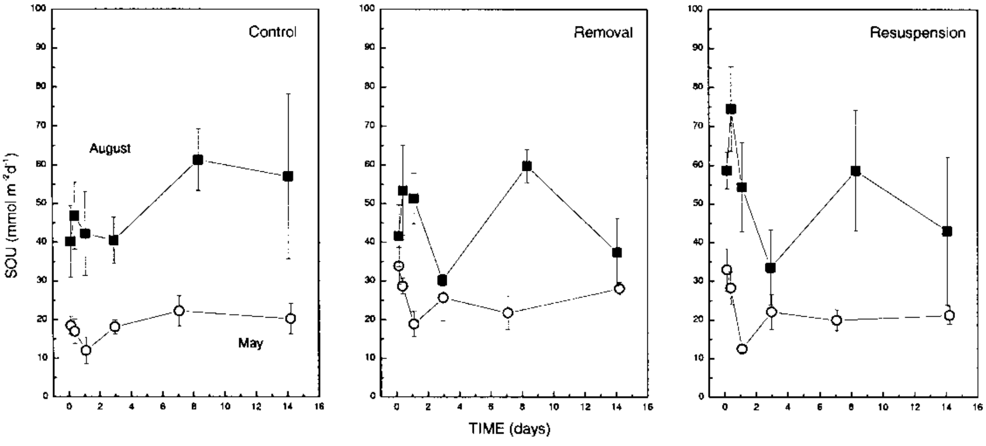

FIGURE 9 Time dependent changes in sediment oxygen uptake during the simulated dredging event in May and August. Values represent mean of 3–4 replicate cores (±SD).

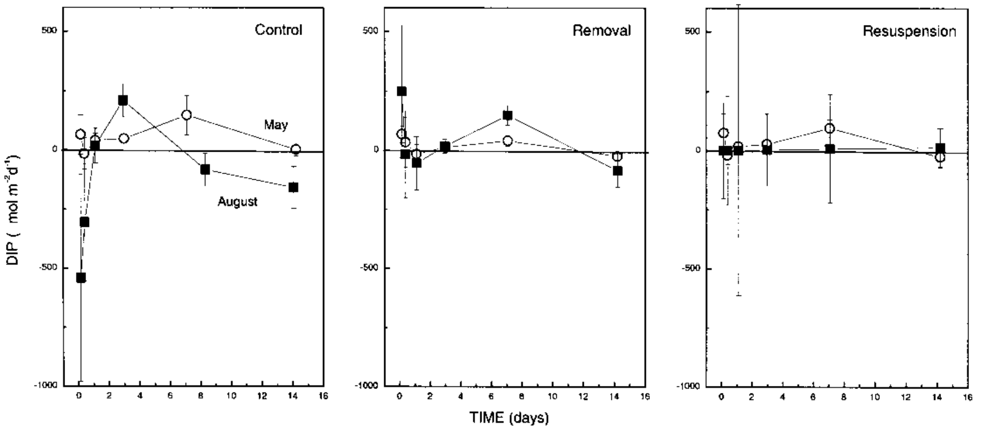

FIGURE 10 Time dependent changes in DIP flux across the sediment-water interface during the simulated dredging event in May and August. Values represent mean of 3–4 replicate cores (±SD). Negative values represent an uptake into the sediments.

The effect of dredging on P pools was similar but less substantial in August. One important factor for this difference is that the iron-bound pools of P were only 1/3 of the concentration in May, and less P is thus removed during dredging. Minimum pools of iron-bound P and maximum release of P across the sediment-water interface are generally measured during late summer (Jensen *et al.*, 1995). The seasonal reduction in iron-bound P concentration in Limfjorden is much higher than found in less eutrophic sediments that have a lower contribution from sulfate reduction to overall metabolism (Jensen *et al.*, 1995), suggesting that sulfide generated during sulfate reduction is a strong competitor for oxidized iron in Limfjorden. Another important factor for the lower release of P was the experimental conditions applied in August. The sediments were kept under full air-saturation to simulate the abiotic conditions encountered during sampling. The sediments had, however, been exposed to 7 weeks of oxygen depletion prior to sampling, which had minimized the pools of iron-bound P in the surface layers (Fig. 2). The surface pools of iron-bound P doubled in the control (non-dredged) sediments during the experimental period of 2 weeks indicating that the iron-bound P pools were restored after the oxygen depletion event. A depletion of porewater P in the surface layers and an uptake of P across the sediment water interface suggested, that P was incorporated into the iron-bound fraction from the dissolved and loosely adsorbed pool and from the water column, where the concentration was high (11 μM) at this time of the year. The recovery was not as fast in the dredged sediments indicating that phosphate remained longer in the water column compared to non-dredged sediments and was thus more available for uptake by phytoplankton.

The changes in the P pools were reflected in the iron pools, and pools of oxidized iron were reduced inside the track and by removal of the sediment, whereas surface pools increased in the resuspended sediment. The Fe:P ratios were relatively high (8–9) in May and similar to other coastal sediments at this time of the year, where the capacity for binding of P in the surface layers is high (Jensen and Thamdrup, 1993; Jensen *et al.*, 1995; Anschutz *et al.*, 1998). This observation is consistent with the low release of P across the sediment-water interface in May. Although both the Fe and P pools were lower in the dredged sediment, the Fe:P ratios were higher suggesting that the potential for P binding increased due to the dredging. This observation is further supported by a low release of P across the sediment-water interface compared to the non-dredged sediment. This result was surprising, as the Fe-pools were expected to be less reactive towards oxidation and binding of phosphate, since the Fe-pools originate from subsurface sediments where the reactivity of iron pools generally is low (Sundby *et al.*, 1992; Jensen *et al.*, 1995; Anschutz *et al.*, 1998). The oxidized iron pools were low in August consistent with the low pools of iron-bound P, and we expected a release of phosphate from the sediments at this time of the year. Phosphate was, however, taken up both in non-dredged and resuspended sediments and a net release was only found from the dredged sediments with the surface layer removed. This uptake of P was most likely caused by reoxidation of the sediments after the oxygen depletion event with binding of P to oxidized iron in the surface layers, and is consistent with an increase in iron-bound P pools during the 2 weeks incubation. The P concentration in the water column was high in August, supporting an uptake of P from the water column. The slower recovery of the iron-bound P pools in the dredged sediments was probably due to the reduced sediment conditions, as reflected by the high percentage of the reduced sulfides in the acid volatile fraction, which may lower the potential for binding of P (Jensen *et al.*, 1995; Anschutz *et al.*, 1998).

There were only minor effects of dredging on the less reactive P pools in Step 3–5 of the sequential extraction (P bound to minerals, magnesium, calcium and residual P) suggesting, that these pools were less affected by the removal and oxidation processes taking place during dredging. The Step 3–5 pools were almost constant with depth, and a removal of the surface layer only had a minor affect on the pool sizes compared to the iron-bound pools, which decreased with depth. The lack of effect of oxidation on Step 3–5 during resuspension can be due to the short oxidation time (<10 s), but Spagnoli and Bergamini (1997) also found relatively small changes in these pools during long-term resuspension of sediments (1–2 hours) suggesting that *e.g.* oxidation of iron-sulfides (Step $4+5$) or mineralization of residual bound P (Step 5) occurs over longer time scales.

Sediment oxygen consumption increased as a result of dredging, but the effect was short lived on the order of hours to days with no major difference between removal and resuspended sediments. Although the sediment oxygen uptake was twice as high in August as compared to May, there were no seasonal differences in the effects of dredging. Oxygen consumption in marine sediments is controlled by both microbial and chemical processes (Thamdrup and Canfield, 2000), and dredging most likely influences both processes. The microbial processes may be affected by altering the organic matter availability and the chemical processes by increasing the reoxidation. We were not able to detect changes in organic matter concentrations in the manipulated sediments, but the organic matter availability was probably reduced under both scenarios, as labile organic matter was removed from the surface sediments in the removal treatment or mixed deeper into the sediment during resuspension. This most likely lowers the sediment oxygen consumption, whereas the exposure of reduced sediment in the dredged track and in the resuspended sediments enhances the oxygen consumption. Riemann and Hoffmann (1991) found that resuspension of particles during mussel dredging in Limfjorden critically influences the oxygen concentration in the water column during periods with low wind-mixing and stratification. Such conditions often occur in the summer and cause oxygen depletion in about 30% of the Limfjorden for several weeks (see Fig. 2 for oxygen depletion in 1994). Riemann and Hoffmann (1991) did not account for enhanced sediment oxygen consumption in their calculations, which add further constrain on the water quality under these critical conditions. Mussel dredging in Limfjorden takes place in areas, where oxygen depletion occur (Fig. 2), but the risk of enhanced oxygen depletion due to mussel dredging has, however, been minimized, as it is now prohibited by law to dredge from the end June until early September (Dyekjær and Hoffmann, 1999).

The contribution of anaerobic mineralization processes to organic matter oxidation is high in Limfjorden, and sulfate reduction accounts for >50% of the sediment metabolism during most of the year (Jørgensen, 1977; Thode-Andersen and Jørgensen, 1989). Similar results were found here, where sulfate reduction accounted for 125% of the sediment oxygen uptake in May and 70% of the CO_2 production in August (data not shown). The effect of dredging was similar in May and August, although the sulfate reduction was 2 times higher in August compared to May. Rates were reduced in the dredged and enhanced in the resuspended sediment. The low rates in the dredged sediments were most likely due to removal of labile organic matter from the surface, whereas the stimulation of sulfate reduction rates in the deeper layers in the resuspended sediment was most probably due to mixing of labile organic matter into these depths. Amendments of sediments with labile organic matter have been found to enhance sulfate reduction rates within a few days (Holmer and Kristensen, 1994). The effect of dredging on the interaction between sulfur and iron cycling appears to be counteractive. Sulfate reduction and production of sulfides were lowered when the surface layer was removed, whereas the exposure of deeper sediment layers with large pools of reduced sulfides increased the consumption of oxidized iron and as a consequence maintained the strong competition between sulfides and phosphate for oxidized iron. Whereas for the resuspended sediment, oxidation of the surface sediments increased potential P-binding capacity, but higher rates of sulfate reduction and thus diffusion of sulfides from the deeper layers, would increase competition between P and S for this reoxidized iron pool.

4.1 Ecological Consequences of Dredging

The pools of iron-bound P were generally low and pools of iron-sulfides high in Limfjorden compared to other coastal sediments, which is a reflection of the major significance of sulfate reduction for organic matter mineralization and the preferential burial of iron with sulfides in eutrophic sediments (Thamdrup *et al.*, 1994; Jensen *et al.*, 1995). Mussel dredging hence takes place in an area, where the retention of P already is constrained by high anaerobic activity and dredging leads to further reduction in the binding of P in the sediments. Dredging primarily affected the iron-bound P pools, which were reduced with up to 2/3 compared to non-dredged sediments. This is similar to the seasonal reduction in the iron-bound P pools between May and August at our sampling location. This location was affected by an oxygen depletion event of 7 weeks duration over the summer, and one dredging event thus alters the pools as much as 3 months of summer with high water temperatures and a long period with oxygen depletion.

Despite this large release of P, the amount of particles suspended during dredging is minor compared to wind-driven resuspension. The contribution of dredging to suspended matter in Limfjorden has been estimated by relatively simple calculations based on a particle model and field observations during dredging (Dyekjær and Hoffmann, 1999). The average particle flux is estimated to 1.4–8.2 $\mathrm{g\,DW\,m^{-2}\,d^{-1}}$, and observations show, that the suspended particles remain in the water column for a maximum of 2 hours. The average concentration of particles in suspension from mussel dredging is thus estimated to 0.11–0.68 $\mathrm{g\,DW\,m^{-2}}$. The measured amount of suspended matter in the water column is 37 $\mathrm{g\,DW\,m^{-2}}$ in the summer (Limfjordsovervågningen, 1995; 2000), and mussel dredging thus only accounts for about 1% of the total amount of suspended matter in the water column. Although the resuspension of particles due to dredging is minor, the area dredged annually is quite large. It has been estimated to $500 \pm 250\,\mathrm{km^{-2}}$, which is about 1/3 of the total seafloor in Limfjorden ($1500\,\mathrm{km^{-2}}$ Dyekjær and Hoffmann, 1999). Our study show, that the loss of P from the sediments during dredging may be up to 23 $\mathrm{mmol\,P\,m^{-2}}$ (estimated as the difference between dredged and non-dredged sediment in May), which corresponds to a loading of Limfjorden with 357 tonnes P $\mathrm{yr^{-1}}$. This recycling potentially corresponds to 68% of the loading from point sources and catchments (Limfjordsovervågningen, 2000). The release of P during dredging of surface layers thus may increase the nutrient availability of Limfjorden significantly, and may stimulate phytoplankton primary production especially in spring, where P is considered to limit primary productivity (Lyngby *et al.*, 1999; Conley *et al.*, 2000). The water column P concentrations are high in Limfjorden in autumn and the release of P during dredging may not be critical for the pelagic primary production, but dredging still contributes to the pool of phosphate in the water column, as the dredged sediments show a slow recovery of the iron-bound pools. Also nitrogen is released during dredging (Riemann and Hoffmann, 1991) and is most likely at maximum during autumn, where the porewater pools are large due to high mineralization activity in the sediments. In conclusion, dredging in Limfjorden occurs in areas subject to eutrophication events and contributes to nutrient loading during critical periods of the phytoplankton growth season.

The results indicate that the sedimentary P pools to a certain extent can be restored. The pools of P recovered relatively fast in May, where conditions were almost back to normal 2 weeks after the dredging event. The high Fe:P ratios in the dredged sediments showed that there was an unused binding capacity for P, and it is likely that the sediments return to the conditions before the dredging event with high pools of iron-bound P in the surface layers. The retention of P in the deeper layers in the resuspended sediment in May was, however, most likely temporary due to high sulfate reduction activity in these layers, and it is expected that P will be released and diffuse to the surface layers, where it can be retained in the iron-bound pool or released to the water column. There was no excess binding of iron-bound P in the deeper layers in August, where the sediments generally were more reduced. A full regeneration of the surface iron-bound P pools in August did not occur within the 2 weeks incubation, suggesting that P was retained in the water column for longer time in late summer. The overall release of P during dredging was, however, less in August due to lower iron-bound P pools in the sediments.

In conclusion, the mussel dredging increased the release of P primarily from the iron-bound pools in the sediments both in the dredging track and in resuspended sediments. The release was one order of magnitude higher than the diffusive flux across the sediment-water interface and contributed significantly to the internal nutrient loading of Limfjorden. Oxygen consumption increased right after the dredging, especially in August where the sediments were highly reduced. The effects of dredging on sulfur cycling were counteractive and did not minimize the strong competition between sulfides and P for oxidized iron in these eutrophic sediments.

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