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Dynamics of P, Fe and Mn along a depth gradient in the SW Baltic Sea

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Diffusive, advective and resuspension fluxes of both dissolved and suspended P, Fe and Mn were measured along a depth transect (16 to 47 m) in the SW Baltic Sea. Sediments were covered by a thin fluff layer, which was functioning as a source of nutrients to the water column. As compared with the diffusive transport, pore water advection can release as much phosphate and redox sensitive elements to the overlying water as 10–1000 days of diffusive flux at undisturbed conditions. Linear correlations between suspended P and Fe suggest that phosphate binding Fe-oxides are the source for suspended P and Fe. There was no P accumulation in shallow water. In the Arkona basin (47 m), gross sedimentation rates of P were 55 P mmol m^{-2} y^{-1} and the DRP diffusion rate back to the water column was 10 P mmol m^{-2} y^{-1} indicating that Arkona sediments are accumulating P. However, episodic resuspension may strongly enrich the water column in this nutrient. The potential resuspension of P varied with the season and a maximum rate of 8 mmol P m^{-2} was registered in June.

Introduction

Phosphorus in natural systems

Phosphorus in natural systems is present in both dissolved and particulate forms. In marine sediments, particulate P can derive from terrigeneous sources (apatite is quantitatively most important), biogenic sources (apatite from bone material, polyphosphates, RNA, DNA and their decomposition products) and authigenic sources. The authigenic P containing particles include apatite and vivianite (Postma 1981, Ruttenberg and Berner 1993), the phosphate fraction adsorbed to/included in authigenic iron oxide (e.g. Jensen *et al.* 1995), manganese oxide (Ingri *et al.* 1991) and calcium carbonate (López and Morgui 1992, Matthiesen *et al*. 2001). Iron(III)oxides can bind phosphate by ion-exchange and this binding capacity decreases with the "age" of the iron hydroxide (Lijklema 1980). Phosphorus adsorption capacity is also influenced by pH, surface area, phosphate concentration and the presence of other ions and humic acids (Torrent *et al*. 1994).

A layer of iron(III) hydroxides can form at the sediment–water interface by the oxidation of upwards diffusing dissolved Fe in the pore water. In a lake water study, Jensen *et al*. (1992) found that for a P:Fe mole ratio < 0.13 in the solid matter such a layer can efficiently bind phosphate in the sediment during oxic conditions. During anoxic conditions the iron oxides can be reduced whereby phosphate is liberated (Einsele 1936). Manganese is similar to iron as oxidized forms can bind phosphate (Ingri *et al.* 1991). However, its capacity is smaller and binding by iron is quantitatively more important in most sediments (Sundby *et al.* 1992, Jensen and Thamdrup 1993).

Resuspension

Sediment resuspension is an important process in coastal areas, affecting boundary layer structure (Gust and Walger 1976), the re-distribution of sediment (Amos and Mosher 1985) and can promote the enrichment of the water column by nutrients (Morin and Morse 1999). The release of nutrients is related to desorption from suspended particles (adsorption is also possible) and to the mixing between pore water constituents and sediment overlying water (Simon 1989). Additionally, high shear stresses affect the dynamics of redox sensitive elements in coastal sediments (Laima *et al*. 1998) and the O_2 penetration into sediments (Christiansen *et al*. 1997). One important ecological consequence of resuspension is the potential enhancement of phytoplankton growth since cells are periodically carried back into the euphotic layer (Garcia-Soto *et al*. 1990). The potential for resuspension may be enhanced through bioturbation by reducing the strength of the cohesive forces in the sediment (Rhoads and Young 1970), and by presence of a fluff layer on the seafloor (Stolzenbach *et al*. 1992). Fluff is unconsolidated material composed of aggregated biogenic and inorganic particles which accumulate on the seafloor during calm weather conditions and is easily resuspended at low current velocities (Emeis *et al*. in press). Similarly, the potential for resuspension can be inhibited or retarded by biofilm growth and algae mats that cover some bottoms (Kornman and De Deckere 1998).

As a consequence of resuspension, it is a general observation that the sediments making up the sea-floor become finer in shallow water to deep water depth profile (Christiansen *et al*. 1997). A decrease of threshold velocities for resuspension is expected from shallow to deep water depth profile, the process being affected by the eventual presence of fluff layers on the bottom.

Transport of particles from oxic to anoxic environments might result in desorption of phosphate from cation complexes, hence increasing the P availability to the water column. Also, transport from anoxic to oxic environments will enhance P adsorption. However, the role of resuspension on the availability of "dissolved reactive phosphorus" (DRP) to the water column is contradictory. In some instances, resuspension promotes the increase of DRP concentrations in the water (Søndergaard *et al*. 1992) sometimes it does not (Holdren and Armstrong 1980). In Mn rich sediments, Mn_{diss} (mostly Mn^{2+}) can be used as a good marker to follow advective transport of solutes in Mn rich sediments (Laima *et al*. 1998), also because Mn^{2+} is oxidized slower

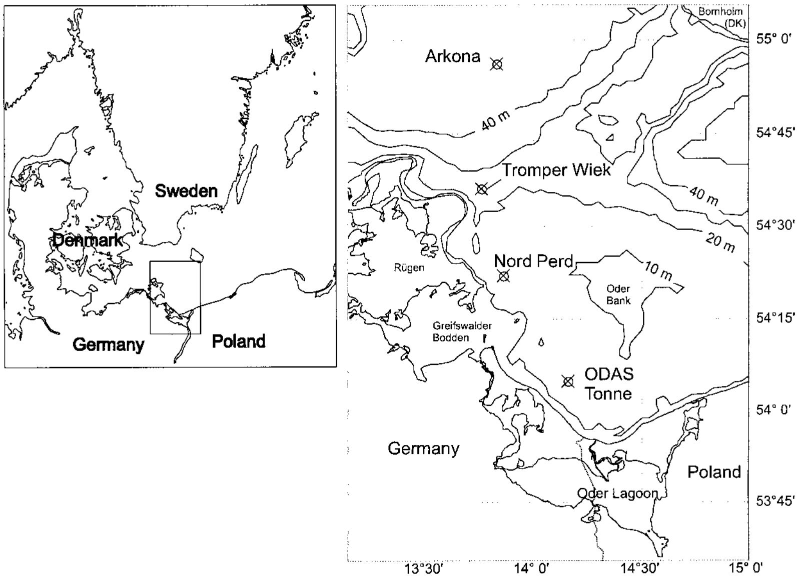


Fig. 1. Locations of the four stations in the SW Baltic Sea.

than Fe^{2+} (Wilson 1980). There is, therefore, more time to measure the high concentration values before Mn^{2+} is oxidized and precipitates.

This study aims at quantifying diffusive, advective and resuspension fluxes of P, Fe and Mn (dissolved and particulate) along a coast-to basin profile in the southern Baltic Sea. This study is a part of a larger interdisciplinary approach focusing on processes and mass estimates (Christiansen *et al.* 1999) and origin and characteristics of the transported material in this region (Emeis *et al.* in press).

Materials and methods

Study area

Four working stations have been selected along a coastal to basin gradient in the southwest Baltic Sea (Fig. 1): Odas Tonne is a mooring station 20 km north north-west of the Oder river mouth. It is a shallow turbulent environment where sand ripples are occasionally overlain by thin fluff, showing great variability in conditions at the sea floor and in sediment type, benthic communities and sedimentary features (Emeis *et al.* 1998). Nord Perd Rinne lies in a morphological depression where material derived from shallow water is channeled during periods of intense near bottom transport, and mud is deposited during quiescent periods (Tauber *et al.* 1999). Tromper Wiek lies at the shoulder of the southern Arkona basin in an area affected by sediment movement during storms (W. Lemke, pers. comm.). Pycnocline depth is around 20 m, giving varying oxygen conditions at the station. Finally, the Arkona basin where the majority of land derived material is deposited after a series of intermediate storage and modification processes (Christiansen *et al.* 1999). Combined the four stations cover the Oder Rinne, i.e the pathway of material emanating from the Oder river to its possible grave in the Arkona basin.

The seabed at the four stations is covered by a very mobile fluff layer which is easily resuspended at shear velocities around 5 cm s^{-1} and is recycled into the suspended matter and benthic boundary layer pools of material (Emeis *et al.* in press). This fluffy material is the main agent for the transport of biogenic material, pollutants and riverine nutrients from the shallow environment near the river mouth to the deeper and calmer sedimentary basins of the southern Baltic Sea.

Sediment traps and surface sediments

A tripod trap system consisting of a stainless steel frame equipped with sediment traps, transmissiometer and Anderaa current meter was deployed and recovered three times at Odas Tonne in 1997: from 11 June to 19 August, from 21 August to 14 October and from 14 October to 6 December. The sediment traps consisted of stainless tubes closed at the lower end, and trap openings were placed 0.35, 0.70, 1.05 1.40 and 1.75 m above the seabed. The traps were 25 cm long with an inner diameter of 5 cm giving an aspect ratio of 5. This is considered as the optimal aspect ratio for measuring vertical fluxes in horizontal flows with moderate up to about 20 cm s^{-1} of current speeds (Hargrave and Burns 1979). Under such moderate conditions, an aspect ratio of 5 has been found optimal for both avoiding overtrapping and preventing resuspension from the traps (White 1990). Sediment trap contents were stored in 2-l plastic flasks at 4 °C. In the laboratory the material was filtered (Whatman 540) and dried at 60 °C for 24 hours. Dry weight was recorded and the material was ground prior to analysis.

Sediment cores were taken manually by scuba divers in shallow water. In deep water, we used conventional box-corers or the hydraulically-damped box-corer (Lund-Hansen *et al.* 2001). Sediments were sampled during cruises in October 1996 (Arkona), four times in 1997 and in June 1998. Sediment samples were sliced into 0.5 or 1-cm slices (0–10 cm) in a glove box under an Argon atmosphere. The slices from muddy sediments were centrifuged ($5340 \times g$, 30 min) in gas-tight containers and filtered (0.45 µm cellulose acetate filters) in the glove box. Pore water from sandy sediments was collected using centrifuge tubes with perforated bottoms and a centrifugation speed of $2300 \times g$ for 30 minutes. Fluff layer was sampled at the Odas Tonne station by divers with a vacuum pump system operated on board the ship. The water was removed using a flow-through centrifuge and the material was stored at –18 °C until analysed.

Diffusive fluxes at non-disturbing conditions

Twenty four small batch cores (5.4 cm i.d., 20 cm long), 6 per station were adjusted to contain 17 cm of sediment overlain by 3 cm of water. The water phase was discarded, except for few ml to avoid sediment disturbance. Fresh bottom water was added to each core, which was then stirred gently with a stirring magnet in a dark temperature-controlled box. A blind core (only water, no sediment) was run as control. The systems were open to the atmosphere except on the June cruise when one core from each station was closed with a lid (no gas phase). Sediment cores were placed around a central rotating magnet and the cores were incubated with a constant water velocity of 0.5 cm s^{-1}. Aliquots from the overlying water were saved for the determination of initial concentrations of DRP, Fe_{diss} and Mn_{diss}, and five to seven 10-ml water samples were withdrawn from each core during a 1–3 day period. Samples were filtered (0.45 µm pore size cellulose acetate filters), acidified to pH 2 and stored at 4 °C in the dark. Oxygen concentration was measured with an O_2 microelectrode. From the cores closed with a lid, oxygen was only measured in the beginning and end of incubation.

Resuspension assays

Three to five wider sediment cores (9.5 cm i.d., 50 cm long) were taken from each station. Their contents were adjusted to contain in height 15 cm of sediment overlain by 10 cm of water. Using the Laberex chamber (Lund-Hansen *et al.* 1999), a resuspension program was run by automatic step increases of velocities from 0 up to 12 cm s^{-1} (equivalent to shear stress range from 0 to 0.04 Newton m^{-2}) at 0.25 cm s^{-1} steps of 12 min each. In June experiments, both ascending and symmetrically decreasing velocities were run. Water samples of 10–20 ml were periodically taken with a syringe and filtered through 0.45 µm pore size cellulose acetate filters. Whereas the filtrates were acidified with HCl to pH 2–3, the filters + suspended matter were transferred to plastic vials containing 10 ml of 0.2 M hydroxylamine hydrochloride ($HONH_3Cl$) at pH = 2 and stored at 4 °C. $HONH_3Cl$ is a suitable reducing solution commonly used to extract iron-bound phosphate from the particulate matter, but it is not selective

(Lucotte and d'Anglejan 1985, Jensen *et al.* 1992).

To investigate whether or not fluff material contributed to increase the concentration of DRP and Mn_{diss} in the overlying water, the lower end of a plexiglass tube (9.5 cm i.d., 50 cm long) was fitted with a lid of a Petri dish to physically simulate the sediment surface. Filtered bottom seawater from Odas Tonne was mixed with fresh fluff layer sampled at this station, to give a final fluff concentration of 0.22 g l^{-1}. The height of water column was set at 10 cm and the suspension was allowed to settle down at 4 °C until complete water clearance was observed. A resuspension program including ascending and symmetrically descending velocities was run for 10 hours in the dark (4 °C). Chamber water was sampled most intensively near the maximum shear velocity of 12 cm s^{-1} and supernatants were filtered with 0.45 µm pore size cellulose acetate filters and analyzed for DRP and Mn_{diss}.

Analytical procedures

Water analyses

Water samples used for analysis of DRP, Fe_{diss} and Mn_{diss} were acidified to pH of 2–3 and stored in the dark at 4 °C. Vials containing filters + suspended matter in $HONH_3Cl$ were heated at 60 °C for 3 hours (Matthiesen 1998). By using the total volume of $HONH_3Cl$ solution (10 ml), the volume of filtered water (10 or 20 ml) and the actual water height in the chamber, the concentrations of Fe_{sus}, P_{sus} and Mn_{sus} were recalculated to the "amount resuspended per area unit".

DRP concentration was measured spectrophotometrically using the phosphomolybdate method (Murphy and Riley 1962). Mn dissolved in the pore water was measured using an air-acetylene AAS. The detection limit was 0.02 µM. No matrix problems were found in using seawater or $HONH_3Cl$ solutions. Dissolved Mn in flux samples was measured with GF-AAS (Perkin Elmer 4100ZL) according to Slavin *et al.* (1982), using $Mg(NO_3)_2$ as matrix modifier. Calibration standards were prepared from commercial standard of Mn(II) in 0.5 M HNO_3, diluted with artificial seawater to get the same salinity as the water samples. Each sample was run in duplicate or until a 3% standard coefficient of variation was obtained.

Pore water Fe_{diss} was measured spectrophotometrically with the 2,4,6-tripyridyl-s-triazine method (Collins *et al.* 1959). Primary standard for Fe was $(NH_4)_2Fe(SO_4)_2.6H_2O$, the detection limit was 2 µM and the relative standard deviation on replicates was below 1% ($n = 3$). The Fe_{diss} pool is mostly Fe(II) but it includes also colloidal Fe(III) as the solubility of Fe(III) is low ($< 10^{-8}$ M) at natural conditions ($6 < pH < 8$). Iron which had been oxidized to Fe(III) during storage was reduced to Fe(II) with $HONH_3Cl$. Lower concentrations of Fe_{diss} were measured with GF-AAS using magnesium nitrate as matrix modifier and a furnace program optimized from Sturgeon *et al.* (1979). The detection limit was 40 nM (2 ppb). A commercial Fe standard from Merck was used as primary standard. Dissolved Cl^- and SO_4^{2-} were measured simultaneously by reverse phase ion-pair chromatography (Perrone and Gant 1984). The detection limit is 1 µM for both Cl^- and SO_4^{2-}. Seawater samples were diluted 50–200 times to avoid problems with too high Cl^- concentrations. Primary standards used were dried NaCl and dried Na_2SO_4, respectively. All vials and glass materials used in this study had been previously stored for 12 hours in a 0.02 M acid bath (HCl or $HClO_4$ depending on analyte) and all chemicals were of analytical grade.

Sediment analyses

Water content (105 °C, 24 h), organic content (550 °C, 6 h) and porosity were determined in duplicates of original sediments. Samples used for total phosphorus determination were exposed to 550 °C for 12 h and extracted with 1 M HCl for 20 minutes at 80 °C (Svendsen *et al.* 1993). Afterwards, acid samples were filtered and total phosphorus concentrations were measured in the supernatants using the phosphomolybdate method of Murphy and Riley (1962). Total organic nitrogen was measured by titration using a Tecator Kjeltec Analyser. Organic carbon was determined gravimetrically from CO_2 evolution (Nørnberg and Dalsgaard 1996). Grain-size distributions of sediments were measured using laser diffraction size analysis (Agrawal *et al*. 1991). Sediment characteristics are shown in Table 1.

Calculations

The exchange of solutes between sediment and overlying water can be expressed as:

$$F_i = dn_{i,\mathrm{w}}/Adt \qquad (1)$$

where F_i is the flux of solute *i* per area unit per time unit, *A* is the sediment surface area and $dn_{i,\mathrm{w}}/Adt$ is the change in number of moles in the water overlying the sediment per time unit. When subsamples are taken from a batch system, $n_{i,\mathrm{w}}$ is the total amount of *i* in the chamber and in the sampled water. $dn_{i,\mathrm{w}}/dt$ was estimated from the curve slope in a $(n_{i,\mathrm{w}}, t)$ plot. Solute fluxes were corrected for adsorption onto core walls by subtracting data obtained from cores incubated with water and without sediment, at the same conditions as intact cores.

The P gross sedimentation rate in the surface sediment layer (*S*) was estimated from the average recent accumulation rate (*R*) of 1 mm yr^{-1} based on ^{210}Pb activity (Christiansen *et al*. 1999) using the relation $S = r_\mathrm{S}cR\ (1 - \Phi)$ (Suess and Djafari 1977) where r_S is the dry density of surficial sediment, *c* the P concentration and Φ the porosity.

Results and discussion

Diffusive fluxes at undisturbed conditions

In general, measured benthic fluxes showed a release from sediment at intermediate depths and incorporation by sediment at both Odas Tonne (exception for P) and Arkona basin (Table 2). Calculated diffusive fluxes towards the sediment-water interface were higher than the measured benthic fluxes, denoting the role of oxidation/reduction processes on the upper sediment horizons. For example, for all stations concentrations of $\mathrm{Mn_{diss}}$ in the pore water were maximum near the sediment surface, suggesting occurrence of Mn(IV) reduction in anoxic pore waters, resulting in higher Mn^{2+} concentrations (Fig. 2). Baltic sediments can be episodically enriched with Fe and Mn following Fe-sulphide precipitation in anoxic bottom waters, and also with Mn-oxides following inflow situations carrying dense $\mathrm{O_2}$-rich water (Neumann *et al*. 1997). It is recognized that microbial mediation of Mn oxidation is an important contributing process to the redox cycling of Mn in the oxic surface layer (Thamdrup *et al*. 1994). In sub-surface layers, Mn presumably precipitated as $\mathrm{MnCO_3}$ (rhodochrosite), as $\mathrm{Mn_{diss}}$ pool alkalinity and pH showed that the sediment pore waters from all stations were all saturated with respect to $\mathrm{MnCO_3}$ ($\mathrm{K_{sp}}^{I = 3.0} = 10^{-9.68}$). Generally, pore water $\mathrm{Mn_{diss}}$ concentrations were highest at Odas Tonne and decreased along the depth transect.

Nord Perd Rinne and Tromper Wiek sediments (0–1 cm) exhibited steep $\mathrm{Fe_{diss}}$ and $\mathrm{Mn_{diss}}$ gradients. At Tromper Wiek, the calculated DRP flux towards the sediment surface was 27 µmol P $\mathrm{m^{-2}\ d^{-1}}$ whereas the actual measured efflux was only 9 ± 17 µmol P $\mathrm{m^{-2}\ d^{-1}}$ at 95% confidence limit (Table 2). Arkona sediments exhibited steep pore water DRP and $\mathrm{Fe_{diss}}$ gradients, at the same time, the lowest DRP diffusive flux to overlying water. Here, the calculated DRP flux towards the sediment surface was 25 µmol P $\mathrm{m^{-2}\ d^{-1}}$ whereas the benthic flux was even negative, –10 ± 4 µmol P $\mathrm{m^{-2}\ d^{-1}}$ at 95% confidence limit (Table 2). Measured benthic fluxes are in agreement with earlier measurements in the Baltic Sea (Koop *et al*. 1990). These data indicate an accumulation of redox sensitive elements in the upper sediment layers, also depicked from the presence of oxic/hypoxic bottom waters at shallow and intermediate water depths in March and June 1997 (S. Jähmlich pers. comm.). In contrast, the presence of hypoxic/anoxic waters in the Arkona basin in later months might result in a DRP release from Arkona sediments.

Pore water $\mathrm{Cl^-}$ concentration profiles give some evidence for intrusions of chloride-rich bottom water in the upper layers of sediment (Fig. 2). This might be attributed to physical forcing effects followed by $\mathrm{O_2}$ advection in the

Table 1. Specific density, porosity (Φ), organic matter (OM) content and sediment grain size fractions (0–1 cm layer) at four sites in the SW Baltic. Properties of near bottom suspended matter (sediment traps) for Odas Tonne are shown. Average data (*n* = 3) for March 1997 and June 1997 are shown. SDs were below 15% of mean values (not shown).

Station	Lat. N	Long. E	Depth (m)	Density (gr cm^{-3})	OM (%)	Φ (%)	Sand (%)	Silt (%)	Clay (%)	C (mmol g^{-1})	N (mmol g^{-1})	P (mmol g^{-1})
Odas (traps)	54°05´18	14°07´99	0.35–1.75 a.b	–	–	–	–	–	–	1883	683	61
Odas	54°05´18	14°07´99	16	1.8	1.1	84	92	6	1.4	301	19	8
(Perd) Rinne	54°21´80	13°51´18	20	1.6	3.1	76	94	5	0.3	387	33	14
Wiek	54°36´04	13°45´62	26	1.3	6.9	70	63	35	2	935	132	20
Arkona	54°56´27	13°49´90	47	1.1	15.4	67	2	79	19	1125	138	91

Table 2. Sediment-water fluxes of DRP, Fe$_{diss}$ and Mn$_{diss}$ at the four stations. Data obtained during cruises in October 1996, March 1997 and June 1997. Calculated diffusive fluxes (inside parenthesis) are based on Fick's law of diffusion using porosity/tortuosity and temperature adjusted diffusion constants (Li and Gregory 1974, Ullman and Aller 1982). *n* is number of cores used in the calculations out of initial six. n.d. = not determined. Units are mmol m^{-2} d^{-1}.

Parameter	Odas			Nord Perd			Wiek			Arkona			
	March	*n*	June	March	*n*	June	March	*n*	June	October	March	*n*	June
DRP flux	0.03 ± 0.022	4	(0.002)†	0.002 ± 0.004	6	(0.011)†	0.009 ± 0.018 (0.027)	5	(0.003)	(0.018)	–0.010 ± 0.004 (0.025)	5	(0.03)
Fe$_{diss}$ flux	n.d.		(0.001)	n.d.		(0.029)†	(0.160)		(0.079)	(0.093)†	(0.160)		(0.07)†
Mn$_{diss}$ flux	–0.001 ± 0.001	6	n.d.	0.008 ± 0.007	6	n.d.	0.009 ± 0.006	4	n.d.	n.d.	–0.012 ± 0.007	6	n.d.

† Based on two concentration data points (bottom water and 0–1 cm).

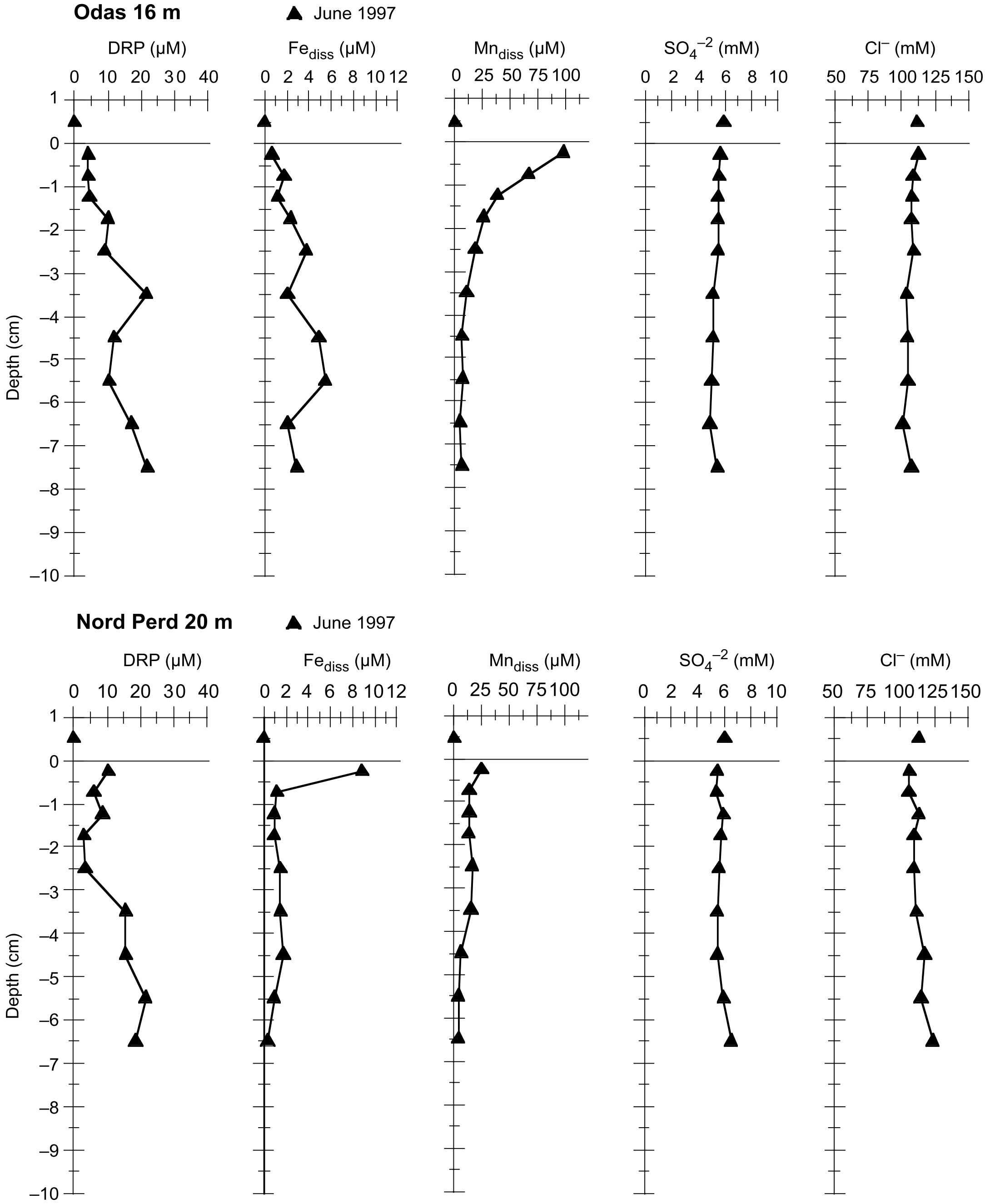


Fig. 2. Depth (0–10 cm) pore water concentrations of PO_4^{3-}, Fe$_{diss}$, Mn$_{diss}$ SO_4^{2-} and Cl^- at the studied sites.

upper layers. Such oxic conditions might promote the oxidation of anoxic minerals such as Mn-carbonates, Fe-sulfides as well as the binding of phosphate to Fe(III)oxides, which explains the lack of Fe$_{diss}$ and P$_{diss}$ gradients in the top layer of Odas and Rinne sediments and resulting in decreasing fluxes to overlying water (Table 2).

Sulphate concentrations were above 4 mM

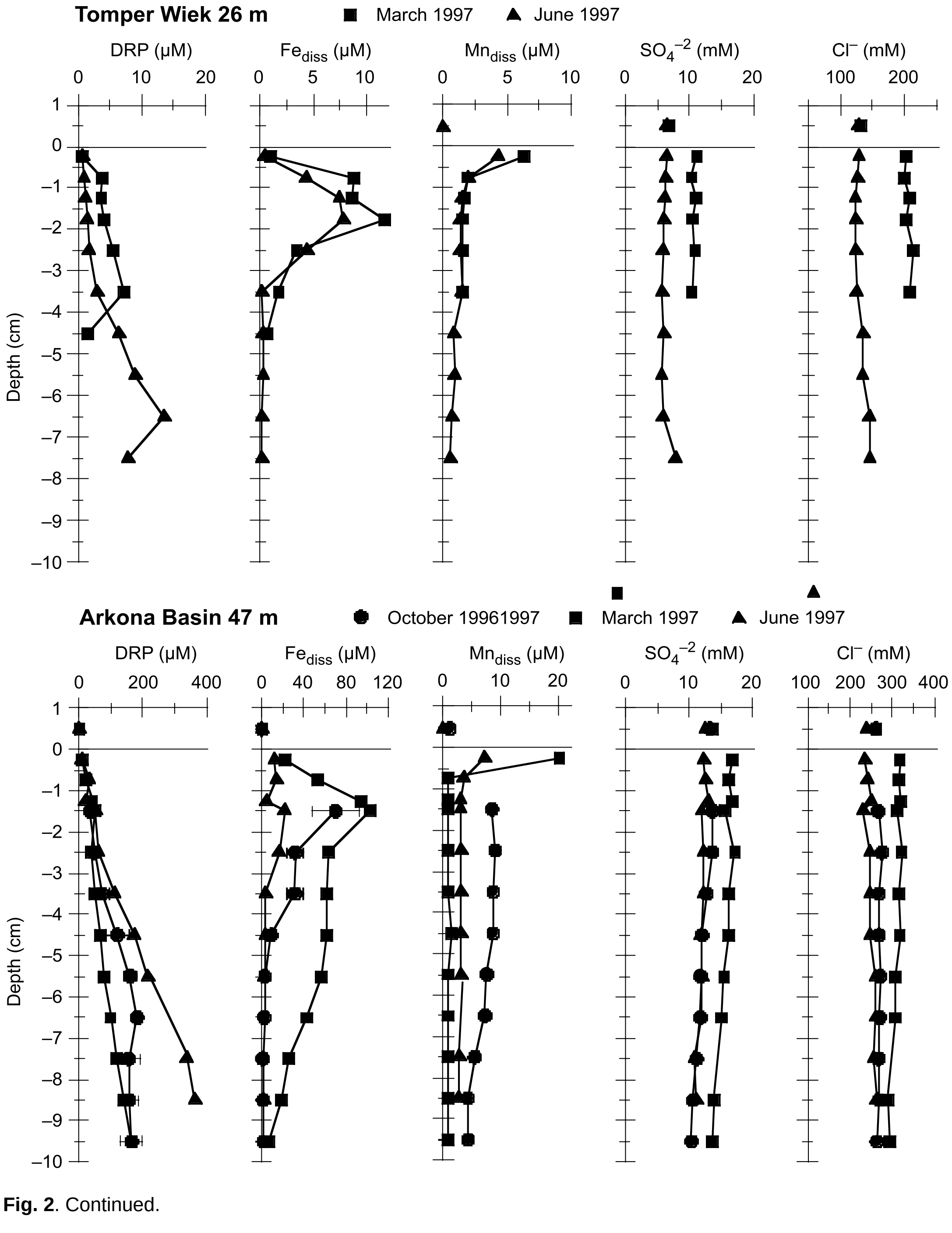
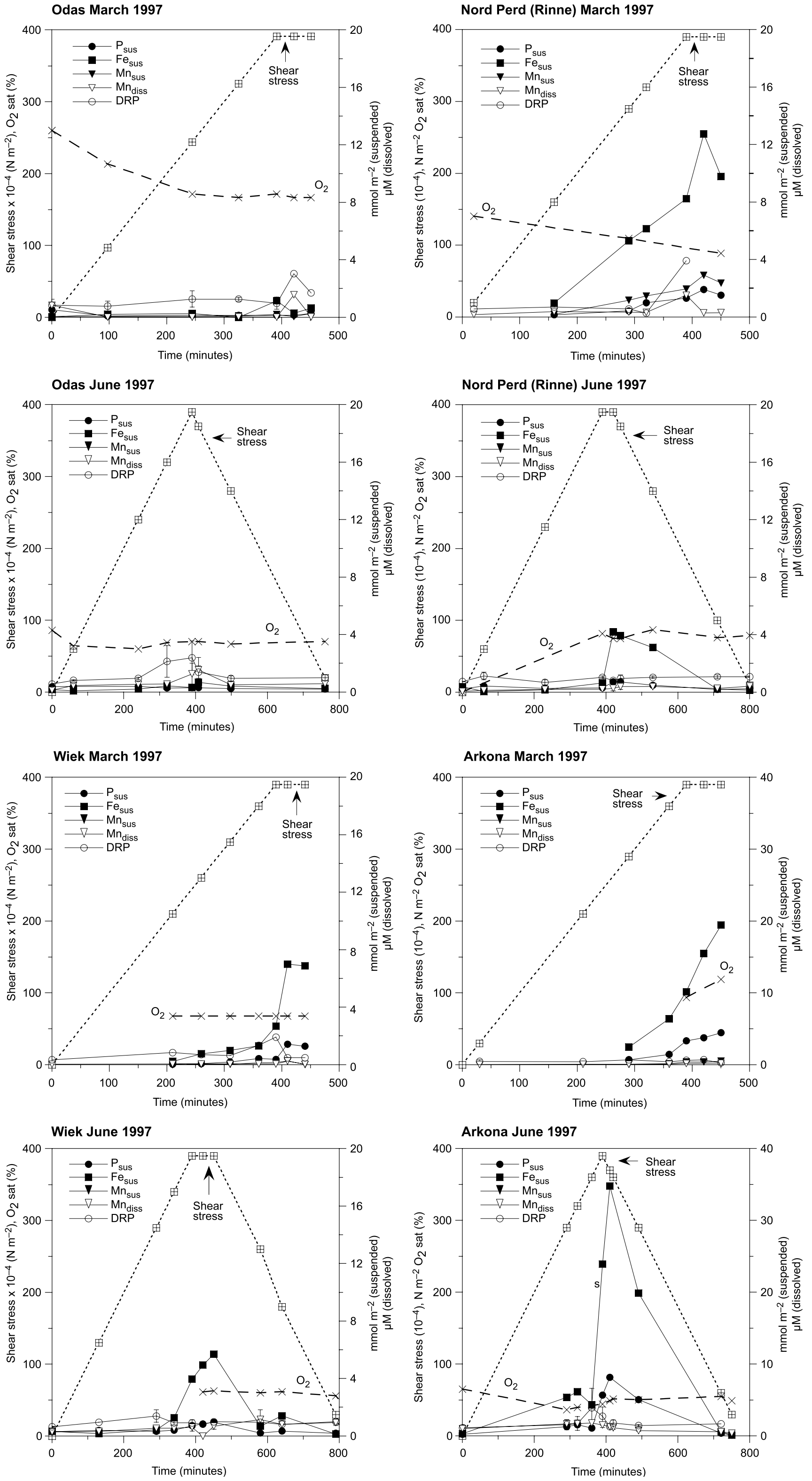


Fig. 2. Continued.

and decreased slightly down to 6 cm depth in shallow and intermediate water depths and to 10 cm in the Arkona sediments (Fig. 2). This means that SO_4^{2-} reduction takes place, which is in accordance to the free energy considerations, where Mn and Fe reduction should anticipate SO_4^{2-} reduction in the oxidation of organic matter (Berner 1980).


Odas March 1997

Nord Perd (Rinne) March 1997

Odas June 1997

Nord Perd (Rinne) June 1997

Wiek March 1997

Arkona March 1997

Wiek June 1997

Arkona June 1997

Fig. 3. Influence of shear stress on the release of P, Fe and Mn at the four stations in March and June 1997.

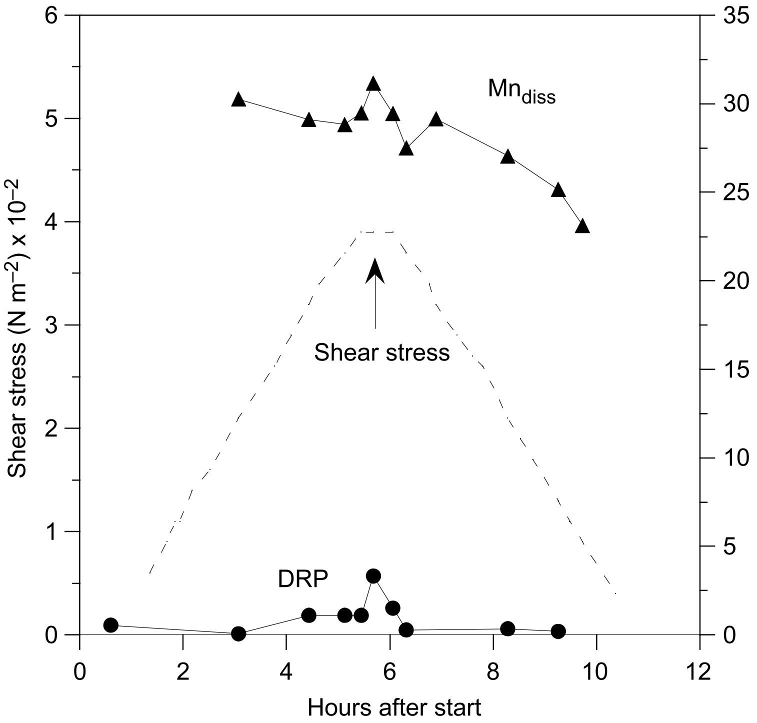


Fig. 4. Results of the Laberex resuspension experiment of fluff without underlying sediment. A rubber stopper was used to physically simulate the sediment surface.

Advective transport of solutes

The release of solutes to the overlying water was influenced by the induced shear stress, in that higher values were registered in March 1997 than in June 1997 (Fig. 3). In general, Mn$_{diss}$ and DRP were released simultaneously to the overlying water. This suggests that the oxidation mechanisms of dissolved Fe into Fe-oxides (and hereby binding of phosphate) were not complete, thus contributing to the phosphate release to water. Eventually new formed Fe-oxides through pore water advection can be hardly detected on the filters because pore water convection and resuspension occurs simultaneously here. Thus 'old' Fe-oxides coming from surface sediment may erroneously elevate the amount formed through pore water convection. It is known that advective currents in centrally stirred chambers are related to radial flows resulting from different hydraulic pressure gradients (Hüttel and Gust 1992) and their magnitude depends on the sediment permeability (Booij *et al*. 1991). The impact of advective currents to the solute release out of sediment is supported by the fact that the concentration of pore water Mn is high enough to explain the Mn concentration increase in the overlying water. On the other hand, there was a release of phosphate and Mn by resuspension of fluff material in the absence of sediment (Fig. 4). These results indicate that fluff layers are a source of DRP and redox sensitive elements in the study area.

The concentration increments and the actual water chamber height can be used to estimate the magnitude of Mn and DRP transport through pore water advection (Table 3). However, it should be noted that these advective fluxes are ephemeral e.g., the released solutes will establish a new equilibria with the surrounding particles. On the other hand, a large peak in DRP concentration detected at Wiek in June (Fig. 3) was not likely to have been caused by pore water advection because there was no concomitant increase of Mn$_{diss}$ in the water. As compared to the diffusive transport, pore water advection can release as much as DRP and Mn$_{diss}$ to the overlying water as 10–1000 days of diffusive flux under undisturbed conditions (Table 3). It is remarkable that such high concentrations of DRP and Mn_{diss} were only detected during a short time period, and concentrations dropped again at high shear stresses (Fig. 4). This evokes a rapid adsorption onto the particulate matter.

After advection, a concentration fall of DRP and Mn_{diss} and a concentration increase of P_{sus} were observed (Fig. 3). This suggests the occurrence of precipitation through surface catalyzed the oxidation of Mn (Wilson 1980) and phosphate binding onto suspended or freshly precipitated Fe-oxides. It should be noted that this relationship is not quantitative since not all the released P was necessarily trapped by $HONH_3Cl$ (Jensen *et al*. 1992).

Resuspension and P transport

The release of particulate forms to the sediment overlying water varied along the depth gradient (Fig. 3). Except at Odas Tonne, linear correlations between P_{sus} and Fe_{sus} were found (Fig. 5). At Odas Tonne, concentrations of P_{sus} and Fe_{sus} were low and no correlation was found between them. This is in accordance with the previous claim that no comprehensive P and Fe accumulation takes place at this station as it is frequently exposed to resuspension events (Laima *et al*. 1999, Emeis *et al*. in press). Also, Fe and P exist in different forms that might not necessarily resuspend together. On the other hand, the positive intercept with the *y*-axis indicates further displacement of P_{sus} from unknown pools in the resuspended matter. Furthermore, a good correlation between Fe_{sus} and P_{sus} shows that the Fe_{sus}:P_{sus} ratios did not depend on the applied shear stress range (Table 4), which in turn indicates a recent origin for this material. On the other hand, Fe_{sus}:P_{sus} ratios were in accordance with those calculated using pore water data (Table 4). This suggests that both P_{sus} and Fe_{sus} stem from locally formed P binding Fe(III) oxides in the upper sediment layers. Using microprobe and SEM techniques, we could identify particles that have been formed at expenses of upwards diffusion of pore water ions followed by P and Fe precipitation at the sediment–water interface (Matthiesen *et al*. 2001). These Fe-P enriched particles (also Fe oxidizing bacteria) formed a reddish band near the sediment surface and were frequently observed in the Arkona sediments. However, it is difficult quantitatively to estimate the proportion of locally formed particulate P and Fe in relation to the total amount present.

Comparison between the sediment trap data and surface sediment (0–1 cm) data showed that, because of resuspension, nutrient concentrations in the suspended matter are much higher than sediment (Table 1). Nutrient concentrations in the upper 0–1 cm of sediment increased along the coast- to basin transect and total phosphorus concentrations in the suspended matter in shallow water and in the Arkona basin are similar (Table 1). This indicates that the Arkona sediments themselves have nearly the same characteristics as the fluff layer material present in

Table 3. Resuspension experiments. Transport of DRP and Mn_{diss} across the sediment-water interface by pore water advections and amount of $HONH_3Cl$-extractable P, Fe and Mn from suspended matter at a water velocity of 12 cm s^{-1}. Two numbers refer to two parallel assays. n.d. = not determined. Data are given as mmol m^{-2}.

Stations	Cruise1997	P		Mn		Fe
		Advection	Resuspension	Advection	Resuspension	Resuspension
Odas Tonne	March	0.34	0.27	0.12	0.27	1.70
	June	0.07/0.23	0.32	0.015/0.015	n.d.	0.68
Nord Perd Rinne	March	3.3	1.90	1.28	2.90	13.02
	June	–/–	0.72	0.03/–	n.d.	4.20
Tromper Wiek	March	–	1.40	0.015	0.27	7.03
	June	–/–	0.96	0.06/–	n.d.	5.70
Arkona basin	March	–	4.50	0.012	0.51	19.04
	June	0.13/0.49	8.20	0.09/0.024	n.d.	35.12

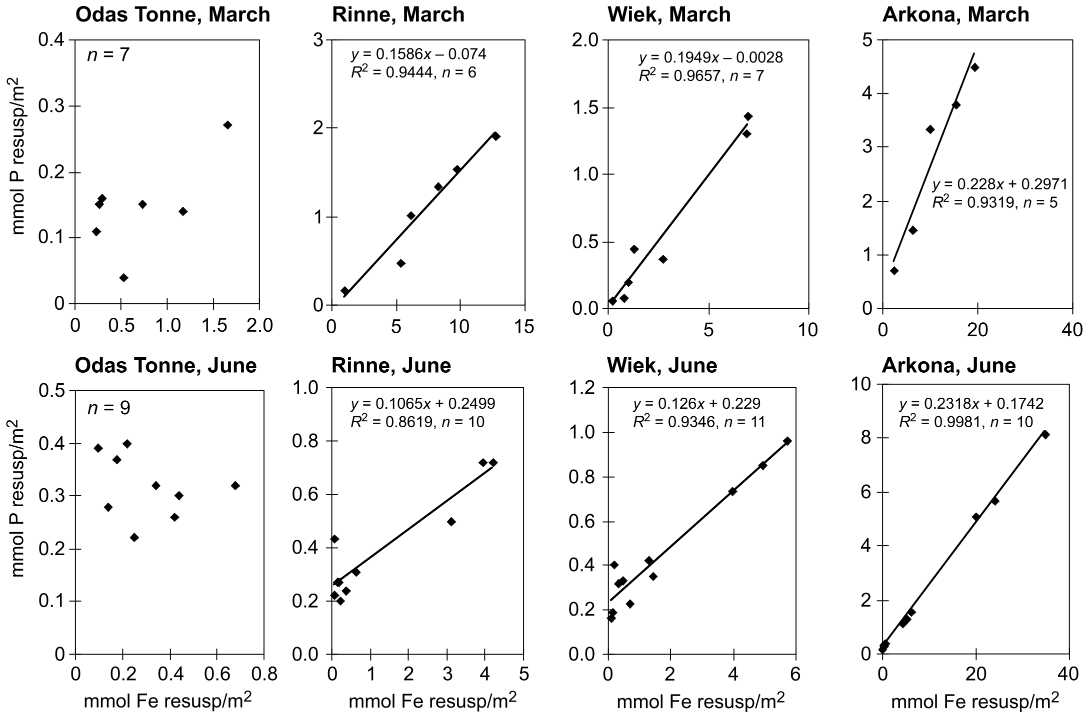


Fig. 5. Correlation between Fe_{sus} and P_{sus} based on $HONH_3Cl$-extraction of suspended particulate matter during Laberex resuspension experiments. The solid line represents the best linear fit of data with the least square method.

shallow water, in agreement with others (Emeis *et al.* in press). On the other hand ^{137}Cs and ^{210} Pb dating methods suggest a residence time of 6 months for the suspended particulate matter in deep water and long-term sedimentation rates of 1 mm yr^{-1} (Christiansen *et al.* 1999).

The net particle transport can be difficult to estimate in confined chambers, because the resuspended particles will settle down on a small surface area. Further, the suspended matter settling velocity is possibly overestimated in the small chamber water volume as an high concentration of suspended matter enhances the aggregation process which in turn increases the

Table 4. Fe:P ratios in the suspended matter and comparison with the expected Fe:P ratios from upward pore water molecular diffusion in the uppermost sediment. Numbers in brackets are uncertain as the pore water profile did not indicate occurrence of diffusion controlled transport. Mean concentration data for October, March and June are shown (*see* Table 2).

Station	Upwards diffusion[1] (mmol m^{-2} d^{-1})			Fe:P ratio in susp. matter (mol mol^{-1})	
	P	Fe	Fe:P	March 1997	June 1997
NPerd (Rinne)	(0.011)	(0.029)	(2.6)	1.09	0.75
Tromp Wiek	0.015	0.12	8.0	11.69	8.00
Arkona Basin	0.024	0.11	4.6	4.81	4.81

[1] Expected (Fick's law of diffusion) upwards in the sedimentary column towards the sediment surface. Average data from October 1996, March 1997 and June 1997 cruises.

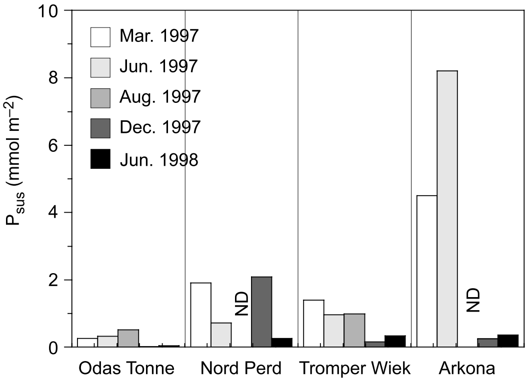


Fig. 6. Average concentration of P_{sus} as function of station and season. Measurements were carried out at constant shear stress of 0.04 N m^{-2} (Lund-Hansen *et al*. 1999).

particle size and sedimentation rate (Stolzenbach *et al*. 1992). Nevertheless, this settling lag is a well known phenomenon and is important in terms of net sediment transport, as in this way the particles can be transported for longer distances (Bearman 1989). Long-term transport processes were simulated by measuring the resuspension potential at constant shear stress of 0.04 Newton m^{-2} (Fig. 6). Season apparently played a considerable role on the resuspension performance and a maximum potential flux of ~8 mmol P m^{-2} was measured in June 1997 in the Arkona sediments. After June 97, the resuspension potential of the Arkona sediments decreased significantly and ~0.2 mmol P m^{-2} was measured in June 98. This apparent decline of the resuspension flux of P might be related to ongoing cohesive processes (or less fluff material) on the upper sediment layers that elevated the resuspension threshold velocity to above the measuring range.

Tentative phosphorus budget in the Arkona sediment

From the evidence of the pore water vertical profiles, the total P availability in the southwest Baltic Sea sediments is highly affected by early diagenetic processes involving P redistribution between solid and liquid phases. The dissolved P concentration in pore water was < 1% of the P concentration in the solid phase. However, following changes in the redox conditions inorganic and organic P compounds must be involved in chemical transformations within the sediment column, and these might lead to partial P release into the overlying water. The fate of P may be determined from the P budget. A tentative budget in the Arkona sediments can be constructed from measured fluxes and assuming steady-state conditions. The calculated *S* value is 55 mmol P m^{-2} y^{-1} which is higher than an earlier reported value of 38 mmol P m^{-2} yr^{-1} (ICES 1992). The maximum yearly diffusion rate of P from sediment is about 10 mmol P m^{-2} y^{-1}. This means that ~20% of P settling down is annually recycled at the sediment-water interface and that ~80% is buried in the sediment. In these calculations, it was assumed that all P associated to sediments, pore waters and diffusive fluxes is produced during undisturbed conditions. However, resuspension experiments have shown that increasing shear stress may themselves be responsible for the transport of significant quantities of Fe and P. For example, using a shear velocity of 12 cm s^{-1} (= 0.0408 Newton m^{-2}) that should be realistic for the Arkona basin (Liljebladh and Stigebrandt 1996), we calculated a resuspension potential of 4.5 mmol P m^{-2} for March 1997 and of 8 mmol P m^{-2} for June 1997. However, the current patterns in the Arkona basin are rather complex (Edelvang *et al.* in press). Therefore, it is difficult to stablish current velocities that are representative for a whole year in the study area.

Conclusion

Fluff layers overlying Baltic Sea sediments are ecologically important as P reservoir. However, the contribution of fluff layers to the P budget is unknown.

The DRP flux out of sediment was highest at Odas and decreased towards the fine grained sediments of the Arkona basin, where the highest P accumulation rates were registered (~0.035 mmol P m^{-2} d^{-1}). The comparatively high DRP efflux at Odas is likely due to the mineralization of recently deposited organic matter resulting from its proximity to a river discharge area.

Advective transport processes take place in the sandy bottoms of the Odas Tonne station. The release of DRP by pore water advection corresponded to approximately 10 days of diffusive molecular flux under undisturbed conditions. Still, such advective mechanisms can importantly contribute to the DRP release from sediment, as resuspension events occur frequently in this area.

At intermediate water depths (20–26 m) and in the Arkona basin (47 m), linear correlations between HONH3Cl-extractable P_{sus} and Fe_{sus} were found for the interval shear stress range between 0 and 0.04 Newton m^{-2}. This suggests a similar origin for the surface sediment particulate matter at these depths, and that aggregation processes are important to the sinking flux of the particulate matter.

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