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Hydrodynamics and nutrient distribution in bottom sediments of the Archipelago Sea, southwestern Finland

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The distribution of nutrients (i.e. water contents, organic carbon, nitrogen and phosphate concentrations) was investigated in the upper 20 cm of coastal marine sediments off southwestern Finland. Bottom sediments were sampled along a transect from the Aurajoki river mouth to the open Archipelago Sea. Towards the Archipelago Sea, sediments showed increasing water and organic carbon contents and decreasing C/N ratios. Phosphate values in the sediments did not show any significant variation along the transect, but increased towards the surface. Most sediments were classified as mud. Resuspension processes can be expected to be dominant in the harbour. Organic carbon contents increase as a result of lateral transport of the lighter fraction towards the more distal stations. Sedimentation is greatest in the small but deep basins in the more distal regions of the transect. The decrease in C/N ratios may be due to the reduced importance of denitrification during the decay of organic matter. Oxygen depletion increases in the sediments because of higher organic carbon contents at the outer stations. Phosphate values increase towards the sediment surface, possibly indicating upward diffusion of phosphorus. Phosphorus depleted surface waters of the Baltic Sea may show greater influence with increasing distance from the harbour. This may be compensated for the higher proportion of fine material which can bind phosphate at the more distal sampling stations.

Introduction

Sediment investigations in the Baltic Sea address the fact that nutrients and heavy metals can be buried in marine sediments for different lengths of time, thus reflecting the environmental status of the area (Niemistö *et al*. 1978, Müller 1996, Neumann *et al*. 1996, Neumann *et al*. 1997). A presupposition for the interpretation of these data is an understanding of the prevailing sedimentary environment. This paper focuses on the nutrient status in the upper 20 cm of marine sediments in a coastal area of the Baltic Sea, southwestern Finland. The purpose of this study was to show the

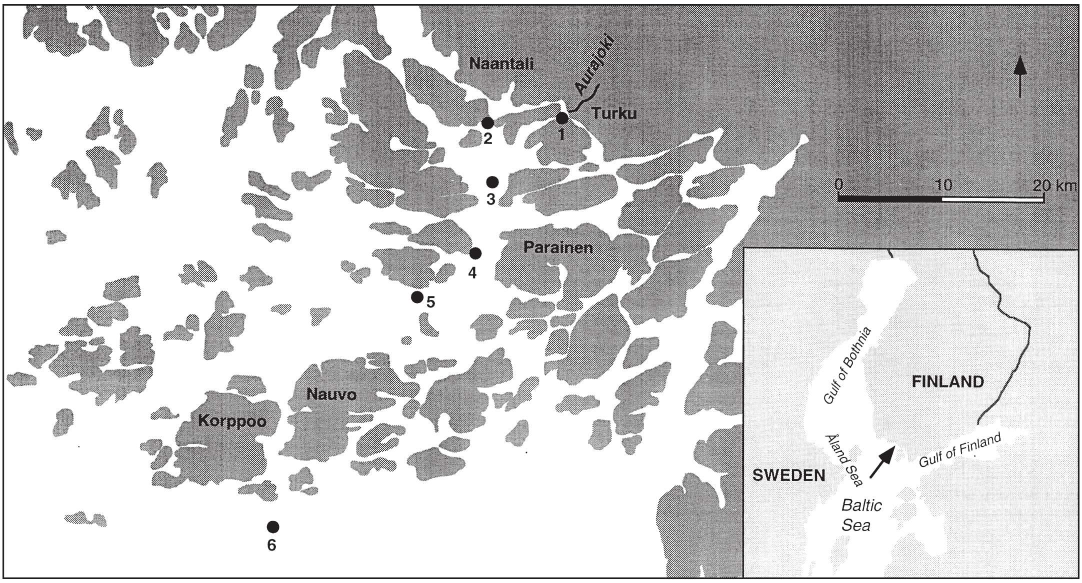

Fig 1. Study area and sampling locations.

magnitude and extent to which sediment parameters change with respect to the natural variations in the study area, corresponding to a transition from a river mouth to the open Archipelago Sea. The results of the sediment investigations are discussed in relation to geomorphological and hydrographical conditions in the area.

Study area

The central part of the study area comprises part of the inner Archipelago of southwestern Finland. The investigations were extended to the southwest, resulting in an approximate 50 km long profile reflecting changing natural conditions (Fig. 1). The area can be divided into two parts with different water depths. The western part consists of a deep channel running from north to south reaching water depths between 40 and 100 m, and the eastern part is shallower than 20 m (Heino 1973). Sedimentation patterns are complicated, largely due to three factors. First, is the large number of sills and basins in the crystalline basement. Second, there is continuing isostatic uplift resulting in wave erosion. Finally, there is an introduction of particulate matter from the mouth of the Aurajoki river in the north, and locally variable currents occur in the area.

Echo sound profiles showed that the bottom is almost completely covered with clay-like sediments which belong both to the Ancylus and the Litorina-stages of the Baltic Sea. Erosion and accumulation occur close to each other. In the parts where accumulation takes place both new material and older erosion products are buried (Niemistö 1982). Sedimentation can be expected in small basins that are not subject to erosion from strong currents. Accumulation can also occur at the marginal slopes of the basins (Winterhalter 1972).

Larger cities which may have an impact on the study area are Turku (approximately 160 000 inhabitants) and Naantali (almost 12 000 inhabitants) (Kalankasvatuksen vesiensuojelusuunnitelma 1991). In the north, the Aurajoki river appears to be a major contributor of particulate matter. In the study area, strong horizontal water movements are characteristic. These occur both in the upper and lower water layers, while the thermocline is in existence. When there is no stratification in the water column, there is a strong vertical water exchange. In the surface water layers there is a dynamic water exchange with the outer Archipelago Sea (Turun Yliopiston Saaristomeren tutkimuslaitos 1979). It can be inferred that this water exchange and the ship traffic in the area promote transport and resuspension of the lighter fraction of suspended material in the water, thus preventing sedimentation.

Sampling and methods

Sampling was carried out in October 1991. Sampling locations were in the harbour of Turku (station 1), off Naantali (station 2), and at increasing distances from Turku harbour (stations 3, 4 and 5). Station 6 was off Korppoo in the open Archipelago Sea (Fig. 1). Water depths ranged from 3 to 57 m (Table 1).

Sediment sampling was done with a sediment corer (Niemistö 1974). The corer sampled bottom water, an intact sediment surface and up to 30 cm of underlying sediment. The cores were divided into subsamples at intervals of 2 cm and stored in air tight plastic boxes. All sediment samples were deep frozen immediately after sampling and freeze dried. Water contents of the samples were determined by measuring the weight of the samples before and after freeze drying. For all further analyses, subsamples of the depths 0–2 cm, 4–6 cm, 8–10 cm, 12–14 cm and 16–18 cm were used. Grain size distribution was measured with a Sedigraph (L.O.T./Galai.-CIS-1). All samples were pretreated in distilled water and H_2O_2 solution (30%). Ultra-sonic vibration was used for 15 minutes. For determination of phosphorus, the sediments were combusted at 550°C, boiled in 2M HCl for 15 minutes, filtrated and neutralized in $NaHCO_3$. The solution was then measured photospectrometrically after molybdate-blue formation (German Standard DIN 38 405-D 11-3). The analysed fraction is comprised of orthophosphate and hydrolizable phosphate. Nitrogen and organic carbon (total organic carbon after removal of carbonates with HCl) were determined with a CHN-Analyzer (Foss Heraeus CHN-O-Rapid). All values are given in percent of dry weight (%).

Water samples were taken with a Ruttner sampler at every station; both at the surface and close (approximately 50 cm) to the sea bottom. The temperature of the water samples was measured on board. Oxygen (Winkler method), pH and electrical conductivity were measured in the laboratory on the same day. Salinity was calculated from electrical conductivity after a formula for brackish water from Husö Biological Station, Åland:

$$y = -0.3723 + 0.6701x$$

(y = salinity in ‰, x = electrical conductivity in mS cm^{-1}).

Measurements of redox potential of the water (surface and bottom waters) and sediment samples (surface samples at 2–4 cm depth) were carried out onboard the research vessel immediately after sampling. A platinum electrode was used, with a silver/silver chloride electrode as reference, for the redox measurements.

Results

Values of pH for the water in the harbour were rather low being of 6.6 at the surface and 6.7 at the bottom. Samples from station 2 had a similar value (6.8). All

Table 1. Latitude and longitude of sampling locations and hydrographical parameters in surface and bottom waters (50 cm above sea floor): temperature, pH, salinity, oxygen content and oxygen saturation.

Station	Latitude N	Longitude E	Water depth (m)	Water layer	Temperature (°C)	pH	Salinity (‰)	Oxygen content (mg l^{-1})	Oxygen saturation (%)
1	60°26´1˝	22°04´3˝	3	surface	8.2	6.6	3.1		
				bottom	8.2	6.7	3.8		
2	60°25´4˝	22°04´6˝	26	surface	9.1	7.8	5.6	9.0	81.4
				bottom	10.8	7.9	5.6	10.4	101.6
3	60°21´8˝	22°05´9˝	49	surface	9.7	7.9	5.8	9.5	84.6
				bottom	10.2	7.9	6.1	11.3	99.5
4	60°18´4˝	22°02´4˝	57	surface	9.4	7.9	5.8	10.2	90.5
				bottom	10.0	7.9	6.1	10.4	90.7
5	60°16´2˝	21°56´9˝	40	surface	10.0	8.0	5.9	10.8	95.6
				bottom	9.8	8.0	6.2	10.8	95.7
6	60°02´8˝	21°40´9˝	47	surface	9.6	8.0	6.4	10.9	95.3
				bottom	9.3	8.0	6.4	10.7	93.9

other stations showed values between 7.9 and 8.0 both at the surface and at the bottom. Salinity varied between 3.1‰ at station 1 and 6.4‰ at station 6 at the surface (corresponding bottom values 3.8‰ and 6.4‰) (Table 1).

There were colour changes in the sediments from yellow-brown to black at 1 to 6 cm depth, except for those of station 5 which changed to grey. Redox potential in the bottom waters increased towards station 6, i.e. with increasing distance from the harbour. There was no significant vertical variation of redox conditions in the water column. Redox potential and oxygen saturation indicate oxic conditions in the water. Redox potential in the sediments at 2–4 cm depth showed a trend similar to that of the water column.

Sediments at station 6 showed the highest water content in the uppermost layer (0–2 cm sediment depth). Lowest values were found at station 1 in the harbour with 53%. At all other stations, values between 70 and 80% were dominant. However, one core from station 3 and one from station 5 did not show this general trend. Their water contents were relatively low. Obviously, these cores were taken from a place outside the accumulation area. At stations 5 and 6 water contents became significantly lower with depth (locally up to 20% difference). However, this trend could not be observed at the other stations (Table 2).

There were no vertical changes and no horizontal differences in grain size distribution of the sediments. Dominating components were clay, fine silt and silt (< 10 μm). There was a very small fraction of sand in some subsamples, reaching a maximum of 7%.

Organic carbon values were between 2.4 and 5.3% at the sediment surface (0–2 cm). Organic carbon contents increased away from the harbour. At 16–18 cm depth there was the same trend along the transect (Table 3). In general there was a vertical decrease in organic carbon content from the surface to the deepest sediment layer at 16–18 cm depth. This trend was especially significant at stations 5 and 6. At stations 2 and 3 vertical differences were less significant.

Values for total nitrogen increased in surface sediments away from the harbour. In the harbour there were values of 0.20% while values for station 6 in the outer sea were about 0.77%. Vertically there were small variations without significant trends at stations 2 and 3. All other stations showed the same decreasing trends with depth as described for organic carbon (Table 3).

Phosphate contents in the surface layer of the sediments were in the range of 0.20 to 0.26%. The highest value occurred at station 4. There was no obvious trend for phosphate values along the transect. Vertically, all values decreased significantly with increasing depth in the sediment. Sediments in the deepest layer (16–18 cm) ranged between 0.08 and 0.18% (Table 3).

Discussion

Water column and sedimentary environment

Because of heavy winds during the weeks before sampling, there was no temperature stratification in

Table 2. Water contents (% of dry weight) in the sediments.

Depth in sediment (cm)		Station 1			Station 2			Station 3			Station 4			Station 5			Station 6		
	Core No.	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
0– 2		51.5	53.0	54.6	74.7	71.9	70.9	39.2	76.5	78.7	75.1	74.5	71.1	77.1	78.8	47.4	81.8	80.6	81.6
2– 4		51.5	51.7	51.9	73.3	71.7	72.3	45.9	58.1	73.5	73.9	72.9	72.0	72.1	72.2	49.3	78.0	77.6	78.0
4– 6		49.4	48.9	54.2	75.7	77.2	74.1	40.8	47.2	75.4	75.4	75.0	71.9	68.4	68.4	49.7	75.6	74.3	71.0
6– 8		50.8	43.3	55.9	73.0	74.9	70.1	44.1	59.3	77.1	76.6	74.6	71.3	52.6	50.1	47.9	76.9	73.6	69.5
8–10		56.5	42.6	59.5	78.2	76.7	69.2	46.1	70.0	76.7	75.9	73.7	70.7	53.7	51.0	49.4	76.8	72.8	67.1
10–12		55.8	42.6	56.6	76.0	75.6	67.5	46.0	72.9	80.5	74.8	72.4	71.8	52.4	53.4	48.3	77.0	72.4	65.5
12–14		48.8	43.4	55.2	80.9	72.3	66.5	44.9	73.9	76.4	73.0	70.8	70.7	51.6	50.2	53.9	77.0	72.7	61.6
14–16		49.7	43.6	53.9	74.5	71.4	65.7	32.9	75.1	79.3	72.8	71.9	70.7	52.9	56.0		76.6	69.6	63.1
16–18		46.6		54.5	73.2	69.1	65.5	41.6	76.5	79.4	71.9	75.4	70.6	54.0	54.9		75.2	68.9	64.1
18–20		53.3			82.2	66.4	68.9	37.0	78.0	79.8	71.0	76.1	70.1	54.1	53.8		74.7	74.5	62.3

the water column. The oxygen supply of the water was already above the annual minimum. Oxygen investigations of the Archipelago Research Institute of the University of Turku point toward an intense but slow water exchange in the deeper water column between the inner and the outer Archipelago Sea. At shallow locations, where there is no temperature stratification, there is a good oxygen supply because of vertical water movements and strong water exchanges with the outer Archipelago Sea (Turun Yliopiston Saaristomeren tutkimuslaitos 1979).

The color variations in the sediments are due to changing oxidation states within the sediments. At station 1 in the harbour (the station with the highest redox potential) the color change was significantly deeper in the sediments than at the other stations. There was abundant particulate matter in the water column at stations 1 and 2. Because of the intense decay of organic matter during August, a minimum in the redox potential of the sediments can be expected in autumn. Oxygen supply to the sediments is highest at the end of winter. This is due to complete mixing of the water column and the lack of phytoplankton production (Laakkonen *et al.* 1981).

Reducing conditions in the sediments especially occur if there is significant degradation of organic matter. Thus, sediments at stations 2 to 6 were anoxic and slightly reducing at 2–4 cm (compare Bågander and Niemistö 1978). Sediments at station 1 were suboxic to oxic. Color change in the sediments, however (see above), indicate oxydizing conditions at the surface and a change to reducing conditions between 1 and 6 cm depth. The zero-millivolt-line, the parameter for comparison of stations 1 to 6, was closest to the surface at station 6.

An explanation for the low and vertically stable water contents in the harbour could be the low water depth and the intense ship traffic. Light material is possibly in resuspension.

During grain size analysis possible aggregates were destroyed, which makes it difficult to draw conclusions on the sedimentation patterns. There was, however, little variation which points toward similar mechanical processes for the detrital mineral fraction during erosion. According to Perttilä and Brügmann (1991) most of these sediments can be classified as mud.

Organic carbon contents in relation to hydrodynamics

During sedimentation organic matter can be buried in the sediments in different amounts. This amount can depend on the autochthonous primary

Table 3. Organic carbon (A), total nitrogen (B) and phosphate (C) contents (% of dry weight) in the sediments.

(A)	Station	1	2	3	4	5	6
Sediment depth (cm)							
0– 2		2.35	2.54	3.08	3.49	3.85	5.31
4– 6		2.10	2.67	3.00	3.34	2.98	3.40
8–10		2.03	2.82	3.10	3.26	2.00	3.58
12–14		2.06	2.74	3.07	3.34	0.69	3.11
16–18		1.84	2.43	3.01	3.10	0.73	3.13
(B)	Station	1	2	3	4	5	6
Sediment depth (cm)							
0– 2		0.20	0.30	0.42	0.48	0.60	0.77
4– 6		0.18	0.34	0.40	0.48	0.39	0.47
8–10		0.16	0.33	0.43	0.45	0.32	0.52
12–14		0.17	0.35	0.40	0.47	0.07	0.52
16–18		0.16	0.31	0.43	0.40	0.06	0.49
(C)	Station	1	2	3	4	5	6
Sediment depth (cm)							
0– 2		0.20	0.21	0.23	0.26	0.20	0.21
4– 6		0.16	0.21	0.19	0.18	0.26	0.18
8–10		0.12	0.21	0.24	0.18	0.39	0.18
12–14		0.12	0.20	0.21	0.18	0.08	0.11
16–18		0.12	0.18	0.18	0.12	0.08	0.13

production. It may also depend on the organic material supplied by rivers, which may be especially significant in coastal areas. The organic matter content in the sediments is also dependent on the supply of other biogenic and terrigenous particles (Seibold and Berger 1982). Organic matter is biochemically altered in the water column and on the sea floor before burial in the sediments (Lahdes 1982). Distribution patterns of organic matter are often discussed by using the organic carbon parameter.

Primary production in the northern part of the Baltic Sea is restricted to between five and six months. A large amount of organic matter is produced in spring after the ice has melted, because the water contains abundant inorganic nutrients for primary production (Laakkonen *et al.* 1981). In summer, when the water column is thermally well-stratified, primary production is low and there is a rapid decay of organic matter. The results of investigations in sediment traps in the euphotic water layer at a station in the coastal waters of the Gulf of Finland showed a second but lower maximum of production in late summer. The thermal stratification is usually destroyed in early autumn. Resuspension of material from the sea bottom starts around September. For 1979 it was estimated that at least 20% of the primary production was permanently buried in the sediments (Laakkonen *et al.* 1981).

Even if autochthonous biological production in the Gulf of Bothnia is low because of climatic conditions, silty sediments contain up to 7% organic carbon. This value is of the same order as the values for sediments in the southern Baltic Sea (Neumann *et al.* 1996). This relatively high amount is partly due to the impact of a large amount of organic matter delivered by rivers (Perttilä and Brügmann 1991). This is especially true for coastal areas. Organic carbon contents at stations 5 and 6 are also high due to the reasons given above. It is, however, necessary to explain horizontal variations of organic matter contents. Values are enhanced with increasing distance from the harbour. This may be due to the following reasons. First, primary production in the harbour may be lower because of light restriction. There is significant resuspended material in the water column. Suspended material is supplied by the Aurajoki river and may be resuspended by ship traffic. The water became clearer towards the more distal stations. Because of sewage input into the region, nutrient availability is not a restricting factor for primary production (Turun Yliopiston Saaristomeren tutkimuslaitos 1979). Light restriction may be especially significant during periods of increased river flow. However, this does not influence the general trend of mean annual primary production, which is highest in the harbour and decreases towards station 6 in the open Archipelago Sea (Lounais-Suomen Vesiensuojeluyhdistys 1992). Second, resuspension due to ship traffic may restrict sedimentation in the north. Strong water movements between the harbour and the outer Archipelago Sea may cause the transport of the lighter material fraction towards the more distal stations. Good conditions for sedimentation are offered by the large number of small basins which show increasing depth with increasing distance from the harbour. Thus, more organic carbon is buried in the sediments at the outer stations. Water contents of the sediments support this trend.

Nutrient status: Organic carbon to nitrogen ratios

In this study, the ratios of organic carbon to total nitrogen were chosen over the ratios of organic carbon to organic nitrogen (see Hebbeln 1991 and Fischer 1989). These authors showed that this ratio can be used instead of the organic carbon to organic nitrogen ratio originally introduced by Müller (1977) when interpreting changes in sedimentation patterns of organic material.

C/N ratios decreased away from the harbour (Fig. 2). Vertically there were no significant changes (station 5 will not be discussed here as water contents of the sediments from the deeper layers are unusually low).

Vertically, almost constant C/N ratios are usually due to the fact that, during the decay of organic matter, carbon and nitrogen are remineralized or preserved at the same ratio (Dungworth *et al.* 1977, Henrichs and Farrington 1987). Also, Kähler (1990) described little vertical changes in C/N ratios for sediments from Kiel Bight in the southern Baltic Sea.

During the decay of organic matter nitrogen is mineralized. It appears in the sediment as ammonium which is converted by oxygen into nitrate. The following denitrification (the reduction of nitrate to elemental nitrogen, e.g. Kähler 1990), is the precondition for removal of nitrogen from the sediments. Decay of organic matter happens both in the water column and at the sea bottom; it is not restricted to conditions of good oxygen supply. If oxygen is depleted, nitrate and sulfate become important agents for the decay of organic matter (Emerson *et al.* 1980). Sulfate is of special importance in the Baltic Sea sediments (Lahdes 1982, Kähler 1990).

In order to explain the horizontal variation in the C/N ratios the following points have to be considered. Gripenberg (1934) reported a relatively high atomic C/N ratio of 10.5 for sediments of the northern Baltic Sea, including the Åland Sea. Usually, we can expect a higher supply of nitrogen from land in coastal areas, especially in the form of nitrate (Kähler 1990). Consequently, one would expect that C/N ratios would be low at station 1 and increase away from the harbour. However, the opposite trend could be seen in the study area. It is thus necessary to look for factors and processes which may cause the reverse trend in the C/N ratios.

The horizontal distribution of organic carbon (increasing values away from the river mouth) may be significant. It has already been shown that oxygen becomes more depleted towards the outer stations because of increasing water depths and increasing organic carbon contents. This is especially true during the existence of the thermocline. Consequently, nitrate production as a result of ammonium oxidation may be restricted because of the deficiency of oxygen. In this situation, denitrification which may result in the removal of nitrogen from the sediment (Schiewer *et al.* 1994) can not occur. If this happens C/N ratios will become lower with increasing distance from the harbour. Denitrification is replaced by sulfate reduction which increases in importance. This can be inferred from the sulfur values (Müller 1992).

Phosphate distribution in the sediments

The average phosphate values were 0.22% in surface sediments and 0.14% in the 16–18 cm sediment depth interval. These values coincide with

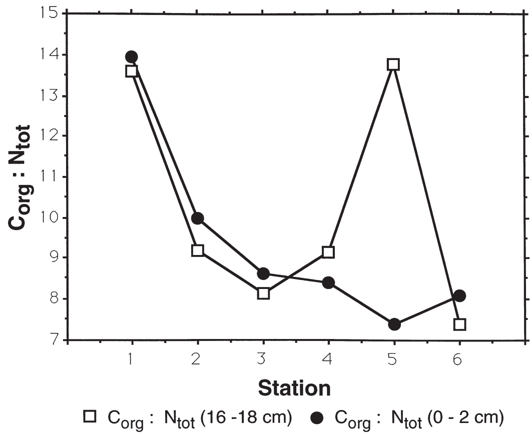

Fig 2. Atomic ratio of organic carbon to nitrogen in the sediments at stations 1 to 6 (depth intervals 0–2 cm and 16–18 cm).

the phosphate contents of 0.2% (uppermost 4 cm) and 0.12% (reducing part in 10–30 cm sediment depth) respectively which were given by Niemistö *et al.* (1978) for the eastern basin of the Gulf of Bothnia.

Towards the Åland Sea and the Finnish Archipelago Sea, the waters of the study area mix with phosphorus depleted surface waters from the central Baltic Sea (Rinne *et al.* 1981). The more distal stations in this study can be expected to be more influenced by the surface waters of the Baltic Sea. That is why one would assume the presence of relatively less phosphorus in the water column at the more distal stations. However, from the transport and sedimentation model, it can be inferred that relatively large amounts of river transported material are deposited at the more distal stations. This material contains a relatively high fraction of particulate matter including organic material.

Laakkonen *et al.* (1981) observed generally higher phosphorus values in sediment trap material than in bottom sediments. In autumn, when primary production was low, there were increased values of particulate phosphorus in the bottom waters and in the water column generally. This was due to the occurrence of inorganic phosphorus bound to particles in the form of iron phosphates and other compounds in connection with a high rate of resuspension of bottom material. Binding of phosphorus occurred mainly on the material in the sediment traps. This binding and relatively high phosphorus values in the water column are the result of a good oxygen supply. Oxygen supply may be less efficient for bottom sediments. Low oxygen levels prevent, to a large extent, phosphorus binding at the bottom. If conditions in the sediments change from oxic to anoxic, phosphate bound with iron can be removed (Froelich *et al.* 1982).

There seem to be two major processes which are responsible for the phosphorus distribution in the sediments: the influence of phosphorus depleted surface waters at the more distal stations; and the transport of phosphorus binding particulate material away from the harbour. The latter seems to compensate for the influence of the phosphorus depleted surface waters of the Baltic Sea, resulting in little horizontal variation in phosphorus values within the study area.

During sampling there were strong water movements, typical of autumn. These movements increased the fraction of resuspended material, which can bind phosphorus, in the water column. This is the reason why phosphate values within the sediments increase vertically towards the surface at all stations.

Towards the outer stations in the Archipelago Sea there was a relative decrease in oxygen supply in the sediments. This prevented phosphorus binding in the sediments and supported the release of a phosphorus fraction into the water column. At this stage, however, it is not possible to say which of the three processes mentioned above is the most dominant nor is it relevant to make quantitive statements about the processes.

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