

Distribution of heavy metals in recent sediments in the Archipelago Sea of southwestern Finland

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The distributions of organic carbon, sulphur, phosphate, and heavy metals (Ni, Co, Cu, Zn, Pb, Cd, Mn, Fe) were analyzed in marine surface sediments in the Archipelago Sea of southwestern Finland. Variations in heavy metal contents are caused mainly by physical not chemical processes. Lateral transport processes of particulate matter, including organic matter, strongly influence the distribution pattern of heavy metals in the study area. In addition, variable environmental conditions between stations contribute to differences in heavy metal contents. In the harbor, close to the mouth of the Aurajoki, there is a relatively high potential for the binding of heavy metals by oxides/hydroxides. In contrast, sulphide precipitations of heavy metals in the sediments may become relatively more important with increasing water depth, i.e. towards the outer Archipelago Sea. For chromium, aluminium, titanium and vanadium detrital binding was considered to be dominant.

Introduction

Studies of heavy metal distributions in recent sediments in different areas of the Baltic Sea have shown that the sediments in these regions differ in heavy metal concentrations. This is because of different source areas and different sedimentological conditions (e.g. Brügmann and Lange 1990, Salonen *et al.* 1995, Müller 1996, Neumann *et al.* 1996, Neumann *et al.* 1997, Leivuori 1997, Emeis *et al.* 1998, Neumann *et al.* 1998). This study presents new geochemical data from recent sediments in the Archipelago Sea off southwest Finland (northern Baltic Sea). Since the investi-

gation of Heino (1979), who addressed heavy metal distributions in sediments in this area, analytical methods have improved, and the international knowledge on the topic of heavy metals in sediments has grown considerably. The overall purpose of this present paper is to make a contribution to a modern regional database for this area of the Baltic Sea. This paper first describes the vertical and horizontal distributions of environmentally important metals in the sediments of the study area. Another objective of the paper is to examine binding forms of heavy metals in the sediments. To fulfil these objectives, the distributions of heavy metals in the sediments are compared to

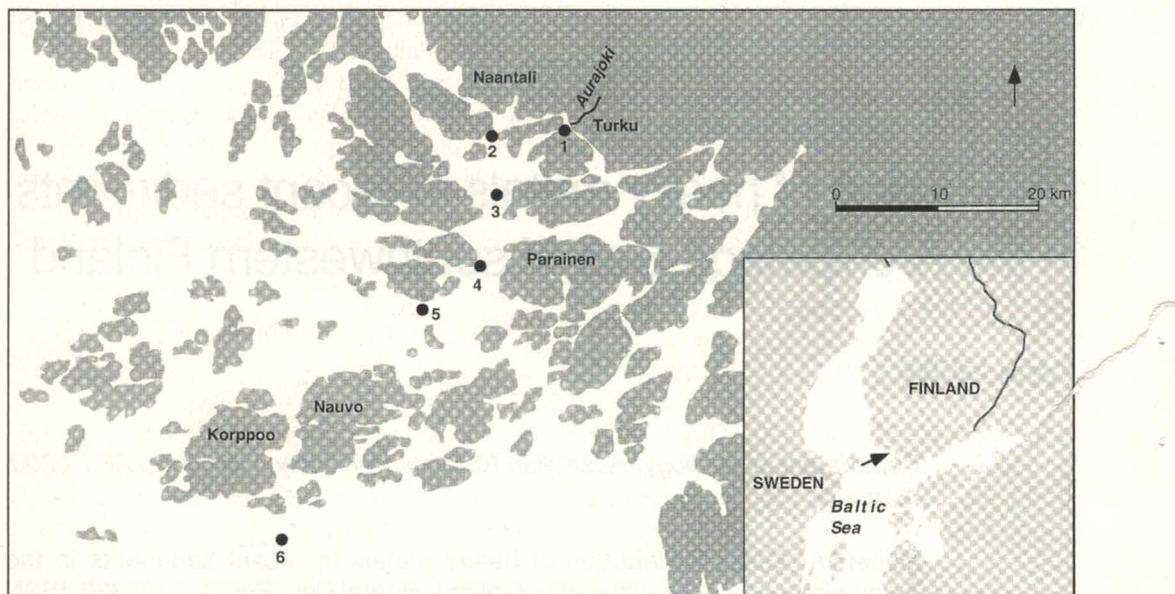


Fig. 1. Study area and sampling locations.

organic carbon, sulphur and phosphorus contents. The results are discussed in relation to the geomorphological and hydrographical conditions of the study area, which have been presented in a previous paper (Müller 1997). Within the study area there is significant variation in the natural environment reflecting the transition from a river mouth to the open Archipelago Sea.

The data presented here can be used for comparison with data of environmental studies that have recently been pursued in coastal areas of mainland Finland. A number of recent studies aimed to increase the knowledge on mobilization, redistribution and dispersion of chemical elements caused by the oxidation and subsequent acidification and weathering of sulphide-bearing sediments. Oxidation and weathering of sulphide-bearing fine-grained sediments due to natural and artificial drainage are causing environmental problems in coastal regions of Finland and Sweden. For example, in the coastal area of Ostrobothnia in western Finland, abundant sulphide-bearing fine-grained sediments have a negative impact on the quality of surface waters (e.g. Åström and Björklund 1995, 1996, 1997, Åström and Åström 1997). This present study aims specifically to acquire information on abundances, forms and be-

haviour of chemical elements, and will contribute to understanding their distribution in the seaward parts of the coastal areas.

Study area

The central part of the study area comprises part of the inner Archipelago of southwestern Finland. The investigations were extended 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, due largely to three factors. First, there is the large number of sills and basins in the crystalline basement. Second, there is continuing isostatic uplift resulting in erosion. Finally, there is an introduction of particulate matter from the mouth of the Aurajoki in the north, and locally variable currents occur in the area.

The sea bottom in the study area is almost completely covered with clay-like sediments, which

belong both to the Aegyulus and the Litorina-stages of the Baltic Sea. Erosion and accumulation of material occur close to each other. In the parts where accumulation takes place both new material and older erosion products are buried. 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 urban areas, towns such as Turku and Naantali (approximately 160 000 and 12 000 inhabitants, respectively), may cause direct pollution to this area. As well, the study area is also influenced by the Aurajoki, a number of smaller rivers and by agricultural cultivation within the drainage area (Kalankasvatuksen vesiensuojelu-suunnitelma 1991).

In the north of the study area, the Aurajoki 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). The horizontal water exchange and ship traffic may cause resuspension of sediments in the north and transport of particulate matter towards the outer Archipelago Sea (Müller 1997). In addition, dredging and dumping of sediment material influence the sediment cover in the harbor (Friman and Mäkinen 1990).

Material and methods

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

Sediment samples were taken with a sediment corer (Niemistö 1974), which 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

Table 1. Latitude and longitude of sampling locations and hydrographical parameters in surface and bottom waters (50 cm above sea floor): temperature in °C, pH, salinity in ‰, oxygen content in mg l⁻¹ and oxygen saturation in %. Data from Müller (1997).

Station	Lat. N	Long. E	Water		Temp. (°C)	pH	Salinity (‰)	Oxygen	
			depth (m)	layer				content (mg l ⁻¹)	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

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 H₂O₂-solution (30%). Ultra-sonic vibration was used for 15 minutes. For determination of phosphate, the sediments were combusted at 550 °C, boiled in 2N HCl for 15 minutes, filtrated and neutralized in NaHCO₃. The solution was then measured photo-spectrometrically after molybdate-blue formation (German Standard DIN 38 405-D 11-3). The analysed fraction is comprised of orthophosphate and hydrolizable phosphate. Organic carbon (total organic carbon after removal of carbonates with HCl) was 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 location; 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:

$$y = -0.3723 + 0.6701x$$

where y = salinity (%) and x = electrical conductivity (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.

Analysis of heavy metals and sulphur was carried out on freeze-dried sediment of the fraction < 63 µm. Total sulphur was determined by combustion (LECO CS-analyzer at 850 °C). For heavy metal analysis, sediment aliquots of 0.5 g were digested in 3 ml HCl-HNO₃-H₂O (3:1:2) for 1 h at 95 °C, diluted to 10 ml with water and subsequently measured with ICP-AES. This leach dissolves organic matter, metal sulphides and

phyllosilicates such as clay minerals, mica and chlorite, while quartz, feldspars and amphiboles are almost unaltered (Åström and Björklund 1997).

Results and discussion

Environmental conditions

Hydrodynamics and nutrient distribution in the sediments of the study area, including grain sizes and water contents were discussed in detail in Müller (1997). Organic carbon and phosphate contents from Müller (1997) are shown here to allow comparison with the presented data (Table 2). During the weeks before sampling, stormy weathers prevailed leading to a mixing of the water column and a lack of temperature stratification of the waters. Oxygen supply was therefore already above the annual minimum at the sea bottom. Oxygen saturation was highest at station 2 (101.6%, 10.4 mg l⁻¹), and showed a decreasing trend towards the more distal stations in the outer Archipelago Sea (Table 1).

Values of pH for the water in the harbour were rather low having values of 6.6 at the surface and 6.7 at the bottom. Samples from location 2 had a similar pH value of 6.8. All other locations showed pH values between 7.9 and 8.0 both at the surface and at the bottom. Salinity varied between 3.1‰ at location 1 and 6.4‰ at location 6 at the surface (corresponding bottom values 3.8‰ and 6.4‰) (Table 1).

Redox potential in the water column ranged between 231 and 467 mV and indicated oxic conditions. There were no significant differences between the surface and bottom waters at the individual stations. Redox potential in the sediments at 2–4 cm depth ranged from 241 to 467 mV and decreased towards location 6, i.e. with increasing distance from the harbour. There was a color change in sediments from yellow-brown to black (respectively gray at location 5) at 1 to 6 cm depth. Color changes in the vertical sediment column reflected a change from oxic to anoxic conditions. At station 1 in the harbor, where redox potentials in the surface sediments were high, this color change from brown to black occurred significantly deeper (6 cmbsf) within the sediment column com-

pared to the other stations. At station 6, where the change to reducing conditions occurred closest to the surface (1 cmbsf), the smell of hydrogen sulphide could be noticed when sampling the sediments.

Sediments at station 6 showed the highest water content (81.8 weight%) in the uppermost layer (0–2 cm sediment depth). Lowest values were found 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. These cores were obviously taken from a place outside the accumulation area. At locations 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 locations. There were no vertical change and no horizontal differences in grain size distribution of the sediments. Dominating components are clay, fine silt and silt (< 10 µm). There was a very small fraction of sand in some subsamples, reaching a maximum of 7% (Müller 1997).

Sulphur content

Sulphur content was enhanced towards the outer Archipelago Sea both in the surface sediments and in the deeper sediment layer. Vertically (sulphur content in layer 0–2 cm compared with that in

layer 16–18 cm), there was a significant downward increase in the observed values (Table 3). This down-core gradient became greater towards the more distal stations. One sample at station 5 did not show this trend, and was excluded from the following discussion because it was believed to represent material of an older age.

Organic carbon content increased with increasing distance from the harbor, both in the surface sediments (0–2 cm) and deeper in the sediment column (16–18 cm) (Müller 1997). Higher organic carbon values may enhance the depletion of oxygen in the bottom water and in the surface sediments. Under reducing conditions, organic matter decay is used by sulphate reducing bacteria, resulting in the formation of hydrogen sulphide (H_2S). H_2S reacts with iron, leading to the precipitation of FeS , which undergoes further reaction to form FeS_2 , pyrite. Sulphur compounds with other metals can also occur, and these compounds can be very stable (Förstner and Patchineelam 1976, Morse *et al.* 1987). At the time of sampling, oxygen saturation decreased towards the more distal stations (Müller 1997). This trend is further pronounced when the thermocline exists. Sulphate reduction may become increasingly important as organic matter decay proceeds. The field observations and the sulphur data suggest that, towards the more distal stations, an increasing amount of hydrogen sulphide is available for sulphidic precipitation. Within the sediment, a fraction of reduced metal-sulphur-compounds (Niedermeyer

Table 2. Organic carbon and phosphate contents (in %) in the sediments. Data from Müller (1997).

Sediment depth (cm)	Station					
	1	2	3	4	5	6
Organic carbon (%)						
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
Phosphate (%)						
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

and Lange 1989, Huerta-Diaz and Morse 1992) is more likely to build up away from the harbor. Such a conclusion is supported by the color and redox changes in the sediments.

Relationship between phosphate and iron contents

Average phosphate values of all the stations were 0.22% in the surface sediments (0–2 cm), and 0.14% in the 16–18 cm layer (Table 2). The highest correlation coefficient ($r = 0.89, p < 0.05$) of organic carbon and phosphate was found at station 1. At this station in the harbor there were good conditions for binding of phosphorus at the sediment surface. This is because an oxic sediment surface offers favourable conditions for the removal of phosphorus and iron from the water column and for the binding of a phosphate fraction with iron (or manganese) oxides and hydroxides. In the northern Gulf of Bothnia, this process is supported by a relatively high natural supply of iron (Niemistö and Voipio 1981). Under reducing conditions, Fe(III) is reduced to Fe(II) and iron-phosphorus-compounds are destroyed in these sediment layers. Part of the iron fraction can be fixed in the reducing sediment layers in the form of iron sulphides. Both phosphorus and iron can migrate upwards in the pore waters towards the sediment surface. Phosphorus and iron migrating from the

anoxic to the oxic zone of the sediment column can be reprecipitated at the sediment surface. Under suboxic conditions, which do not allow a reprecipitation, these elements and associated trace metals can be released into the water column (Förstner and Patchineelam 1976, Suess 1976, Froelich *et al.* 1979).

Heavy metal contents and their lateral variations

Binding forms of heavy metals

Linear regression was used to infer relationships between chemical elements in sediments (e.g. Leivuori 1997). In this study the calculated correlation coefficients (Table 4) were used, in addition to the results of the heavy metal analyses (Table 3), as indicators of similar distribution patterns of chemical elements. It has to be taken into account, however, that natural environments may differ among stations so that links between elements may also differ from station to station. Interpretations given here about proportions of certain bonds or the dominance of detrital bonds respectively are based on previously published articles (e.g. Förstner 1976, Niemistö and Voipio 1981, Brügmann and Lange 1990, Perttilä and Brügmann 1991, Neumann *et al.* 1997).

There was no correlation between organic mat-

Table 3. Calcium, sulphur, manganese, iron, nickel, copper, cobalt, zinc, lead, cadmium, chromium, aluminium, titanium and vanadium contents in the sediments (in % or ppm of dry weight respectively).

Station	Sediment depth (cm)	Ca (%)	S (%)	Mn (ppm)	Fe (%)	Ni (ppm)	Cu (ppm)	Co (ppm)	Zn (ppm)	Pb (ppm)	Cd (ppm)	Cr (ppm)	Al (%)	Ti (%)	V (ppm)
1	0–2	0.41	0.44	390	5.16	42	69	13	305	72	0.5	73	3.21	0.22	57
	16–18	0.33	0.77	296	3.99	29	41	9	134	48	0.5	54	2.80	0.22	49
2	0–2	0.55	0.27	645	6.75	60	60	20	305	45	0.2	105	4.40	0.40	85
	16–18	0.55	0.51	645	6.40	55	85	20	255	45	0.5	100	4.20	0.40	85
3	0–2	0.60	0.19	2835	6.45	50	50	20	245	40	0.2	90	4.20	0.35	80
	16–18	0.55	1.20	1220	6.50	50	50	25	245	45	0.2	80	3.80	0.35	75
4	0–2	0.65	0.34	1380	6.15	65	60	25	275	55	0.5	100	4.00	0.35	85
	16–18	0.60	1.35	1745	7.30	70	65	45	315	55	0.5	90	3.95	0.35	85
5	0–2	0.55	0.45	2575	5.45	55	55	25	240	50	0.3	80	3.40	0.30	70
	16–18	0.65	0.03	1045	6.75	65	65	20	180	35	0.2	110	4.45	0.50	100
6	0–2	0.55	0.57	860	4.25	50	55	15	210	55	0.3	65	2.80	0.25	60
	16–18	0.55	3.18	595	6.30	35	35	15	115	25	0.2	55	2.60	0.25	55

ter and heavy metal contents, which coincides with the results of Heino (1979) from the same area. It is possible that the relationship between organic matter and heavy metals was of different significance at the individual stations depending on varying hydrodynamics and sedimentary environments, and the occurrence of different binding types in different depths of the sediment column.

Iron, aluminium, vanadium, titanium and chromium concentrations were highly correlated with each other. For these metals high proportions of detrital bonds are assumed. Nickel shows associations with chromium, aluminium, vanadium and titanium. This suggests that detrital bonds are important for nickel. The binding behaviour of nickel appears to be similar to that of zinc, copper and cobalt. Binding with iron hydroxides seems possible.

Copper is extensively available in the Gulf of Bothnia. As a result of the high iron, manganese and organic matter content in this area, humus material and manganese/iron-oxides/hydroxides are the most important carrier substances for copper in oxic sediments. Under reducing conditions copper sulphides may be formed (Brügmann and Lange 1990). Looking at the sedimentary environments in the stations, these kinds of bonds seem to be possible. However, associations to chromium

and aluminium point towards the existence of a detrital fraction.

In the case of cobalt, it is only possible to state that partial binding with Mn/Fe precipitates occurs. A detrital fraction, previously described for cobalt (e.g. Förstner 1976), also cannot be excluded. The ratios of cobalt and nickel to organic matter suggest that cobalt has a binding behaviour similar to that of nickel.

Zinc, like nickel and copper, shows partial detrital binding. It is impossible to infer bond types for lead and cadmium from the analyses in this study; however, because of the correlation between these two metals, it is assumed that they undergo proportionately similar binding forms. Perttilä and Brügman (1991) underscore the existence of a relatively high detrital fraction for lead in the Gulf of Bothnia. Lead, like zinc and cadmium, showed only a very small association with organic matter in the investigations of these authors. For cadmium the dominance of binding types with organic matter and a considerable association with Mn/Fe-rich material, i.e. with oxides, hydroxides, and phosphates has been described for the Gulf of Bothnia by Brügmann and Lange (1990). Cadmium is precipitated with sulphides under anoxic conditions (Lapp 1991). It was not possible, however, to infer the dominance of particular bonds for cadmium within the study area.

Table 4. Correlation matrix of calcium, sulphur, manganese, iron, nickel, copper, cobalt, zinc, lead, cadmium, chromium, aluminium, titanium, vanadium, organic carbon and phosphate contents in the sediments ($n = 12$). Underlined values show correlation coefficients significant at the 99.5% level, underlined values in italic show correlation coefficients significant at the 99.9% confidence level.

	Ca	S	Mn	Fe	Ni	Cu	Co	Zn	Pb	Cd	Cr	Al	Ti	V	C_{org}
S	-0.08														
Mn	0.51	-0.22													
Fe	<u>0.71</u>	0.12	0.31												
Ni	<u>0.79</u>	-0.41	0.40	<u>0.66</u>											
Cu	0.23	-0.54	-0.08	0.30	<u>0.58</u>										
Co	0.57	0.05	0.51	<u>0.67</u>	<u>0.76</u>	0.28									
Zn	0.24	-0.46	0.25	0.39	<u>0.63</u>	<u>0.64</u>	0.56								
Pb	-0.34	-0.45	-0.08	-0.37	0.11	0.43	0.10	<u>0.65</u>							
Cd	-0.37	-0.14	-0.26	-0.28	0.01	0.44	0.13	0.29	<u>0.66</u>						
Cr	<u>0.67</u>	-0.58	0.27	<u>0.69</u>	<u>0.85</u>	<u>0.67</u>	0.44	0.57	-0.03	-0.08					
Al	<u>0.61</u>	-0.56	0.33	<u>0.74</u>	<u>0.77</u>	<u>0.58</u>	0.46	0.56	-0.09	-0.13	<u>0.96</u>				
Ti	<u>0.71</u>	-0.39	0.22	<u>0.74</u>	<u>0.75</u>	0.48	0.40	0.24	-0.37	-0.31	<u>0.91</u>	<u>0.90</u>			
V	<u>0.79</u>	-0.44	0.34	<u>0.77</u>	<u>0.88</u>	0.56	0.56	0.44	-0.19	-0.17	<u>0.96</u>	<u>0.94</u>	<u>0.96</u>		
C_{org}	0.15	0.16	0.30	-0.29	0.01	-0.20	0.14	0.14	0.24	-0.03	-0.34	-0.40	-0.45	-0.32	<u>0.59</u>
P	0.14	-0.36	0.30	-0.12	0.12	0.12	-0.06	0.51	0.41	0.06	0.14	0.11	-0.17	-0.02	

Lateral variation of heavy metal contents

In the shallower parts in the north of the study area, deposition of material may partially be prevented. Yet, there is an active water exchange with the outer Archipelago Sea resulting in transport of a large suspended particulate matter fraction in this direction. The depositional environment becomes more suited to the accumulation of material towards the more distal stations. Deposition of this fine-particle fraction becomes more likely in the small basins, which show increasing depth away from the harbor. Towards the more distal stations, a more fluffy texture of the material could be noticed, and a higher water content was measured in the sediments (Müller 1997).

In the case of an input of heavy metals via the Aurajoki, and under the assumption of binding of this heavy metal fraction on suspended particulate matter of the water column, transport processes can be expected to be equivalent to the distribution of organic matter. Consequently, towards the outer Archipelago Sea, one could expect an accumulation of an increasing fraction of these metals. This same trend could be observed if binding with organic matter was dominant.

The upper sediment layer is characterized by a direct interaction with the overlying water body. It therefore has to be considered to what extent the existing binding forms can support or counteract the trend in the horizontal distribution, which is determined by transport processes in the water body of the area. The binding forms may depend on the oxygen saturation state. A high oxygen saturation state can promote a fixing of certain metals in the sediments.

Clearly, migration processes within the pore waters can influence the metal contents of the sediments in vertical profiles and thus also in the transect. One must consider the release of metals from the sediments into the water column, which occurs in connection with migration processes; for example, because of reducing conditions at the sediment surface, or because of redeposition of sediments (Förstner and Patchineelam 1976).

At the time of sampling (October) there were lower salinity and pH in the harbor than at the more distal stations (Müller 1997). According to Förstner (1976), the number of metal ions which can be mobilized by increases in salinity are gen-

erally of minor importance. From the results presented here, it is not possible to infer a possible negative effect of the pH on the binding of metals with clay minerals, humus or oxides/hydroxides as suggested by Förstner and Patchineelam (1976).

Anthropogenic inputs or mobilization processes have been described for some metals analyzed in this study, i.e. nickel, cobalt, copper, zinc, lead and cadmium (Förstner 1976, Niemistö and Voipio 1981, Brügmann and Lange 1990, Perttilä and Brügmann 1991, Neumann *et al.* 1996). In this study, the distribution of these metals (Fig. 2A) is compared to that of organic matter and "non-anthropogenic" metals. The ratios of nickel, cobalt, copper, zinc, lead and cadmium contents to organic matter and titanium contents are shown in Fig. 2B and 2C. Titanium is used as representative of the group of the metals Ti, Al, V and Cr, for which the dominance of a detrital fraction and unchanged natural background contents, both at the surface and at depth, were assumed. In addition, variations of the respective ratios of each of the metals Ni, Co, Cu, Zn, Pb and Cd to Ti, Al, V and Cr, respectively, were almost identical in the transect. Again, the sample from the deeper sediment layer at station 5 is not discussed here.

Ratios of the metals to organic carbon (metal:C_{org}) mostly show a tendency to decrease towards the more distal stations, both at the surface and at depth. For all metals, the ratio is lower in the surface sediments compared to the deeper sediment layer at stations 3 and 4. If cadmium is excluded, there are generally higher metal:C_{org} ratios at the surface compared to the deeper layer in the harbor.

Horizontal variation can be caused by changes in the transport patterns of particulate matter, the occurrence of migration processes and bond types as a result of variable environmental conditions. The available data suggest that the same transport processes are of importance both for metals associated with suspended particles and for organic matter. It has been shown that a larger fraction of particulate matter is transported towards the more distal stations (Müller 1997). In this study, it is not possible to state if, and to what extent, the metal fraction was bound to organic matter. The ratio of metal to organic carbon contents in the surface sediments decreased towards the more distal stations due to an increasing frac-

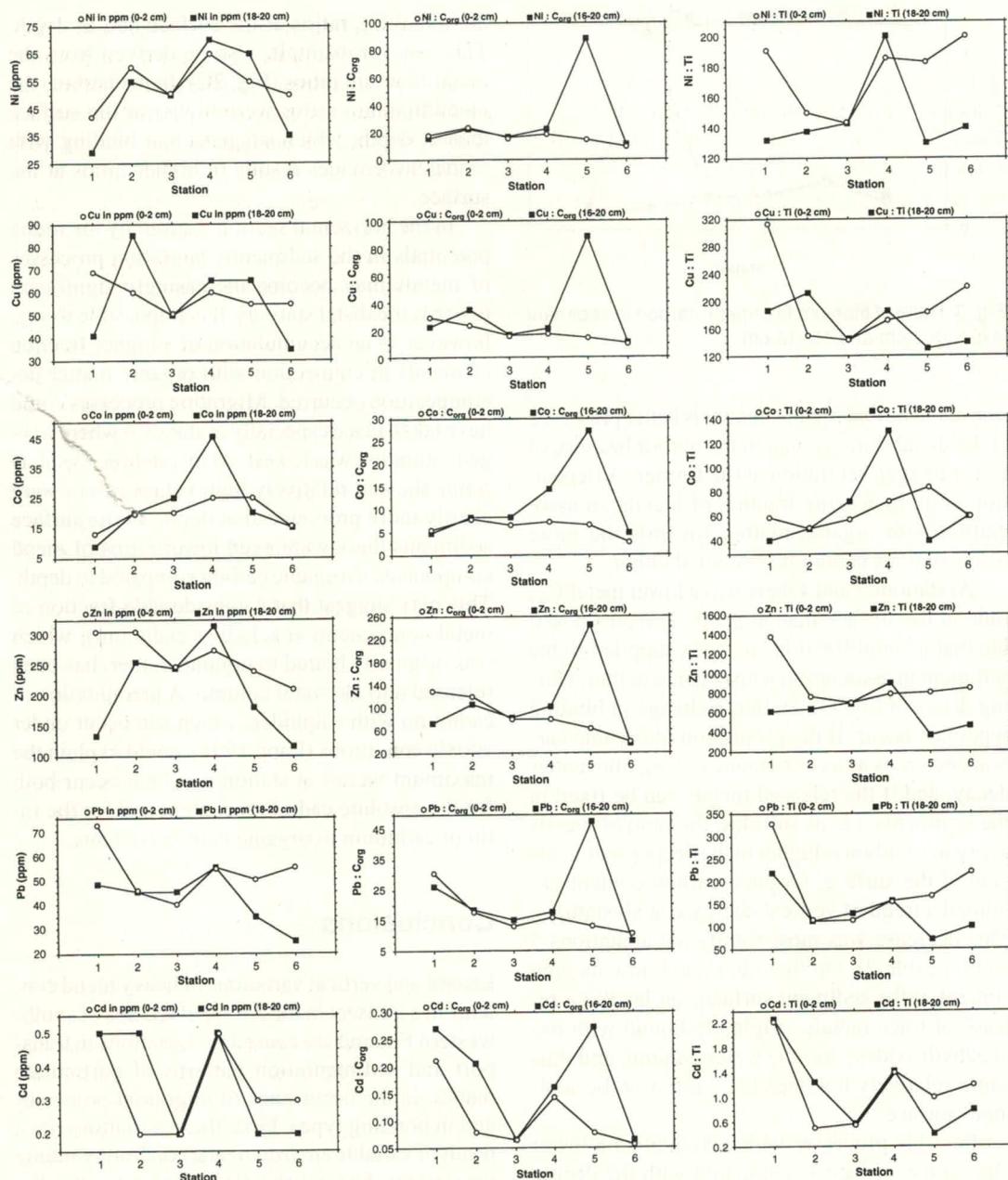


Fig. 2. Heavy metal distribution in the sediments: (A) Nickel, copper, cobalt, zinc, lead and cadmium contents in sediment layers 0–2 cm and 16–18 cm. (B) Ratio of nickel, copper, cobalt, zinc, lead and cadmium to organic carbon contents in sediment layers 0–2 cm and 16–18 cm. Note: Metal contents in ppm (Table 3) and organic matter contents (%) (Müller 1997) were used for the calculation of the ratio as only relative changes of the ratio between the stations are of importance in this paper. (C) Ratio of nickel, copper, cobalt, zinc, lead and cadmium to titanium contents respectively in sediment layers 0–2 cm and 16–18 cm. Ni, Cu, Co, Zn, Pb and Cd contents are in ppm whereas Ti is in %. Note that station 5 partly masks the trend of the other stations due to scaling.

tion of organic matter. This is supported by the ratio of titanium to organic matter, which showed

the same trend (with titanium assumed to be exclusively of natural origin, Fig. 3). One explana-

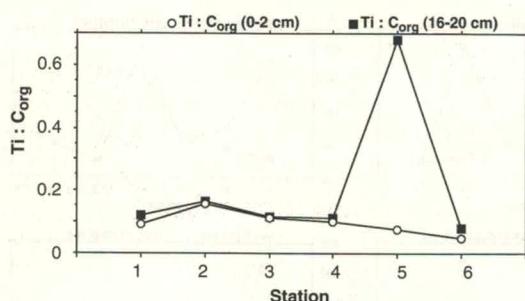


Fig. 3. Ratio of titanium to organic carbon in sediment layers 0–2 cm and 16–18 cm.

tion could be that organic matter is better preserved at the distal stations than in the harbor because of lower oxygen saturation at the former. A deposition of an increasing fraction of metals, in association with organic matter, towards the more distal stations cannot be excluded either.

At stations 3 and 4 there was a lower metal:C_{org} ratio at the surface than at depth. It seems possible that a metal fraction has been supplied to the sediment in association with organic matter. During decay of organic matter, a change in binding types can occur. If the proportion of organic carbon decreases as a consequence of organic matter decay, and if the released metals can be fixed in the sediments, i.e. as sulfides, the ratio of metals to organic carbon is higher in the deeper sediments than at the surface. Organic carbon content exhibited a trend of vertical decrease at all stations. This decrease was most significant at stations 5 and 6 (Table 2). On the other hand, low oxygen content at the sediment surface can lead to a release of trace metals, originally bound with oxides/hydroxides, into the water column, and thus cause relatively low metal:C_{org} ratios at the sediment surface.

Possible processes which counteract a lower ratio at the surface as compared with the deeper sediment layer of this investigation, would be an enrichment of metals at the surface, e.g. because of anthropogenic supply. Another cause could be migration of metals in the pore waters towards the surface and their fixation in the surface sediments.

The dominant binding types at the sediment surface, which are dependent on the current environmental conditions may cause the difference in

the metal:C_{org} ratios at the surface and at depth. This can, for example, also be derived from the metal:titanium ratios (Fig. 2C). In the harbor, the metal:titanium ratios were higher at the surface than at depth, which suggests that binding with oxides/hydroxides results in higher ratios at the surface.

In the horizontal section, caused by the redox potentials in the sediments, migration processes of metals may become increasingly significant towards the distal stations. It is impossible to say, however, if an accumulation of a higher fraction of metals in connection with organic matter decomposition occurred. Migration processes could have taken place especially at station 4 where oxygen saturation was lowest. At this station, metal:Ti ratios showed relatively high values which were clearly more pronounced at depth. In the surface sediments there were even lower ratios of metal components to organic carbon compared to depth. This may suggest that a considerable fraction of metal components (excluding cadmium), which was originally bound to organic matter, has been released into the water column. A precipitation of cadmium with sulphides, which can occur under anoxic conditions (Lapp 1991), could explain the maximum values at station 4, which occur both for the absolute cadmium content and for the ratio of cadmium to organic carbon contents.

Conclusions

Lateral and vertical variations of heavy metal contents in a transect in the Archipelago Sea of southwestern Finland are caused by variations in transport and sedimentation patterns of particulate matter, in the occurrence of migration processes and in bonding types. First, these variations are a result of variable environmental conditions among the stations. Second, the data suggest that the distribution pattern of heavy metals in the study area is linked to that of organic matter. Third, lateral transport processes that are important for the distribution pattern of organic matter in the sediments also strongly influence the distribution of sedimentary heavy metal contents in the study area. The latter pattern is caused mainly by physical not chemical processes. Similar observations have been made in other parts of the Baltic Sea (e.g.

Neumann *et al.* 1996, Emeis *et al.* 1998).

In the harbor there was a relatively high potential for a binding of heavy metals (Ni, Co, Cu, Zn, Pb, Cd) in the sediments. The results suggest that a high proportion of oxic and hydroxic bonds occurred. In contrast, sulphidic precipitations of metals, as indicated by higher sulfur contents in the sediments, may become relatively more important towards the more distal stations. For chromium, aluminium, titanium and vanadium detrital binding was considered to be dominant.

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