

Anmärkning.

	betecknar Städer
	Fästningar
	Moderkyrkor
	Capeller
	Gods och Säterier
	Järnbruk
	Gästgärdsgårdar
	Byar och Hemman
	Högden i Fc. silver Ha
	Höjningsömer
	Landsvägar
	Några närmast Ryk

Gränser anmärkte mindre vägar.

Anthropogenic impact on recent sediment in Jätkäsaari harbour basin, Helsinki, Finland: A comparison with the geochemistry of unpolluted glacial clay

Jyrki Rantataro



GEOLOGIAN TUTKIMUSKESKUS
GEOLOGICAL SURVEY OF FINLAND

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Report of Investigation 134

Jyrki Rantataro

**ANTROPOGENIC IMPACT ON RECENT SEDIMENT IN JÄTKÄSAARI HARBOUR BASIN,
HELSINKI, FINLAND: A COMPARISON WITH THE GEOCHEMISTRY OF UNPOLLUTED
GLACIAL CLAY**

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A joint research project in the area of Jätkäsaari harbour basin, close to the centre of Helsinki, was carried by the Geological Survey of Finland and the City of Helsinki Water and Wastewater Authority. The aim of this study was to evaluate the present, recent and natural condition of the harbour basin's sea-floor. Simultaneous echo-sounding and side-scan sonar images were performed along a 6.5 km trackline. Sampling sites were chosen to represent dynamically different parts of the harbour basin. Mineral composition was quite similar both in recent sediment and in glacial clay. In the same sample, elemental concentrations were proportion to aluminium and iron concentrations. The lower unit of recent sediments, which represents material deposited between the 1950s and 1970s, contained more Pb, Zn, Cu, Ag, tot. C, S, P, Ba and Cd than found in the natural state glacial clay. In material being deposited, elemental concentrations, except lead, were near base levels (represented by glacial clay). Lead remained two to three times higher. This decrease in elemental concentrations has been caused by changes in industry and in the use of raw materials around the basin. Since the beginning of 1980s, sewage water has been conveyed to a sewage treatment plant and unleaded fuel has been introduced to Finland. Thus, in a short period, improvements in the control of emissions from industry, traffic and human activity have led to an amelioration of pollution problems.

The study revealed that, by using combinations of strong and weak extraction methods, it was possible to examine elemental components bound to sediment in different ways. In the harbour's uncontaminated glacial clay, total Ni, Co, Cr and V concentrations due to natural geological factors were even higher than those in recent sediment affected by human activity.

However, naturally occurring heavy metals are bound more strongly to the sediment than those with an anthropogenic origin. Therefore, it is essential to establish elemental concentrations, using combinations of strong and weak extractions, both in the natural state and in recent sediments. Only then is it possible to assess human impact on geological processes and compare its significance with that of natural events.

Key words (GeoRef Thesaurus, AGI): environmental geology, harbors, marine sediments, clay, geochemistry, pollution, chemical elements, heavy metals, Jätkäsaari, Helsinki, Finland

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Geologian tutkimuskeskuksen ja Helsingin kaupungin vesi- ja viemärlaitoksen yhteistyönä tutkittiin Jätkäsaaren satama-altaan merenpohjan sedimenttejä. Tutkimuksessa vertailtiin satama-altaan pohjalle nykyään kerrostuvia sedimenttejä muutama vuosikymmen sitten kerrostuneisiin sedimentteihin ja hyvin vanhoihin luonnontilaisiin saviin. Alueella luodattiin 6.5 km pituudelta tutkimuslinjaa yhtäaikaaisesti kaikuluotaimella ja viistokaikuluotaimella. Luotauksien tuloksien perusteella valittiin kaksi näytepaikkaa erilaisilta kerrostumisalueilta. Nuorten ja nykyään kerrostuvien savisedimenttien sekä vanhan glasiaalisaven mineraalikoostumus oli hyvin samanlainen. Näytteiden alkuainepitoisuudet suhteutettiin alumiinin ja raudan määrään. 1950- ja 1970-lukujen välillä kerrostuneessa savessa oli luonnontilaisen glasiaalisaven pitoisuuksiin verrattuna enemmän lyijyä, sinkkiä, kuparia, hopeaa, orgaanista hiiltä, rikkiä, fosforia, bariumia ja kadmiumia. Nykyään kerrostuvan sedimentin pitoisuudet ovat lähellä luonnontilaisen glasiaalisaven pitoisuuksia, mutta lyijyä on edelleen 2-3 kertaisesti luonnontilaiseen saveen verrattuna. Sedimenttiin sitoutuneiden alkuaineiden pitoisuuksien lasku johtuu Jätkäsaaren satama-altaan ympäristön teollisuuden vähenemisestä, teollisuuden raaka-aineiden muuttumisesta, alueen jätevesien johtamisesta jätevedenpuhdistamoihin ja Suomessa 1980-luvun alkupuolella tapahtuneesta siirtymisestä lyijyttömään bensiiniin. Tämän johdosta on ihmisen toiminnasta, teollisuudesta ja liikenteestä aiheutuva saastuminen vähentynyt merkittävästi Jätkäsaaren satama-altaan alueella.

Tutkimus osoitti, että sedimenttiin eri tavalla sitoutuneiden alkuaineiden osuuksia voidaan arvioida tutkimalla alkuainepitoisuuksia samasta näytteestä sekä vahvoilla että heikoilla liuotuksilla/uutoilla. Satama-altaan likaantumattomassa glasiaalisavessa oli kokonaispitoisuutena enemmän nikkeliä, kobolttia, kromia ja vanadiinia luonnollisista geologisista syistä kuin nuorissa ihmisen toiminnan vaikutuksen alaisissa sedimenteissä. Luonnon omista lähteistä peräisin olevat raskasmetallien osuudet ovat kuitenkin sitoutuneet sedimenttiin lujemmin kuin ihmisen toiminnan seurauksena luontoon kulkeutunut raskasmetallien osuus. Tämän vuoksi on tärkeää tutkia samasta paikasta luonnontilaisten sedimenttien ja ihmisen toiminnan aikana kerrostuneiden sedimenttien alkuainepitoisuuksien eri osuudet samalla kertaa sekä vahvalla että heikolla liuotus/uuttomenetelmällä. Vasta tällaisen tutkimuksen jälkeen voidaan arvioida ihmisen toiminnan vaikutuksia luonnollisiin geologisiin tapahtumiin, ja verrata ihmisen toiminnan aikaansaamien muutosten merkitystä luonnollisiin tapahtumiin.

Asiasanat (Fingeo-sanasto, GTK): ympäristögeologia, satamat, merisedimentit, savi, geokemia, saastuminen, alkuaineet, raskasmetallit, Jätkäsaari, Helsinki, Suomi

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1. INTRODUCTION

This paper reports on a joint research project carried out in the area of Jätkäsaari harbour basin, Helsinki (Fig. 1). The participants were the marine geology unit of the Geological Survey of Finland (GSF) and the City of Helsinki Water and Wastewater Authority (HWWA) (represented by Researcher R. Varmo). The aims of this study were to examine the present condition of the harbour basin's sea-floor and to clarify the nature of recent and past changes. Two sample localities were chosen by interpretation of echo-sounding and side-scan sonar surveys. From the sites, R. Varmo (researcher, HWWA) took four

sample-series with a surface-sampler and GSF obtained two profile-samples with a vibrohammer corer. Sampling allowed understanding of the nature of the sediments in the different stratigraphic sequences. This procedure was followed because the base levels of element concentrations characterise samples taken below the surface and/or far from presumed anthropogenic sources (e.g. Leoni et al. 1991). The areal studies were done in Autumn 1990 on GSF's research vessels, r/v *Kaita* and r/v *Geola*. The research results are presented here as diagrams, tables and graphic images.

2. LOCATION AND DESCRIPTION OF STUDY AREA

Jätkäsaari harbour basin is in a marine bay close to the centre of Helsinki. Human activity has long affected the area: e.g. building around Jätkäsaari harbour basin began as early as the beginning of the 19th century (Hakkarainen 1982). An industrial area is on the eastern and northeastern sides of the study area and urban habitation on its northern

side. Until the end of the 1980's, there was a small-scale industrial estate in the north of the harbour basin, west of the study area. The shallow sea areas of the Inner Archipelago are south and southwest of the study area. The harbour basin is on topographic base map 2034 06 and covers about 25 ha (Fig. 1).

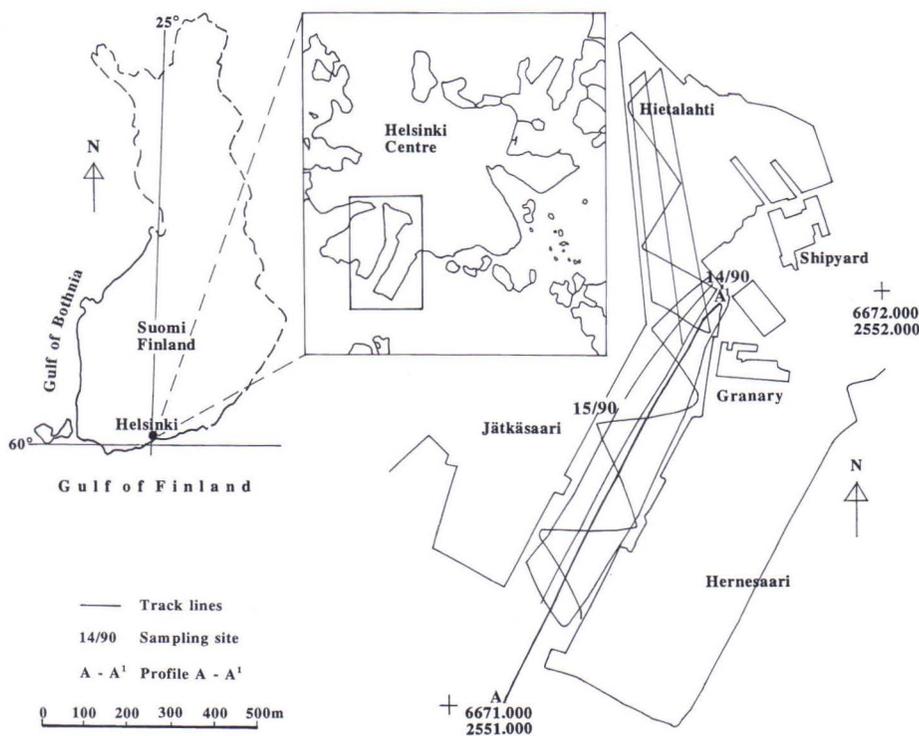


Fig. 1. Location of Jätkäsaari harbour study area. The area is close to Helsinki city centre, on the northern side of the Gulf of Finland. Figure shows track-lines, sampling sites (14/90 and 15/90) and the locations of profile A - A' (see Figs 2 and 3), the shipyard and the granary.

2.1 Construction in the harbour area

Construction in the 19th century did not significantly influence the natural state of the area's coastal forms or the sea floor. Both underwent change during the early 20th century. The construction of Jätkäsaari harbour-basin was in several stages from the 1930's until the 1980's. There were infilling and dredging of the sea inlet only after the middle of this century (Rasanen 1992). The oldest part is a dock built in the 1930s - 1950s, which is on the north side of Jätkäsaari island. Dredging of the basin was done during foundation work on the dock. In the 1940s and 1950s, there was infilling of the area next to the Finnish State Granary as far as the present dock-line and directly on top of the sea-floor clay.

In the 1940s, there was infilling of the middle of the southern part of Hernesaari island. In the 1950s, before infilling with frictional soil as far as today's dock-line, clay was dredged from the western part of Hernesaari island. In the 1950s - 1970s, there was construction on Hernesaari island's northeas-

tern part and the middle part of its eastern infilled area. In the 1950s, infilling was directly on top of the sea-floor clay. Until the beginning of the 1960s, a rubbish dump was sited in the middle of Hernesaari island. The dump was on the southern side of a natural beach. Rasanen (1992) reports that buried metal waste in the dump originates from cars.

In the 1960s, a dock was built in the middle part of Jätkäsaari island and there was dredging of the harbour area during related foundation work. In the 1970s, the southeastern part of Jätkäsaari dock was built with dredging nearby of the sea bottom (Rasanen 1992). In the mid-1970s, there was construction of Masa Yards' ship dock pool on the northern side of the grain silos. However, no dredging was done on the harbour basin side (pers. comm./ Stenroos, Masa Yards 1993). In 1982, there was dredging of a wide area on the northern side of Jätkäsaari harbour basin.

2.2 Waste water load

The sewerage of Jätkäsaari island and its surrounding areas was quite inadequate until the beginning of the 1980s because there were no sewage-pumping stations built until 1979-1984 (Table 1). Before, septic tanks and precipitation wells conveyed the area's waste water to the waterway system (pers. comm., Varmo 1992). The northern

and western sides of the study area were heavily industrialized until the 1980's. Then, the Ruoholahti sewer's opening was at the northern end of the harbour basin. Anthropogenic elements in the study area's recent sediments originated from industrial and domestic waste waters.

Table 1. Construction dates of pumping stations about Jätkäsaari harbour (HWWA 1990).

Location of sewage pumping station	Sewerage area	Construction year
Ruoholahti	Lauttasaari	1979
Hietasaarenkatu	Jätkäsaari	1982
Majakkakatu	Jätkäsaari	1982
Vapaavarasto	Jätkäsaari	1982
Jaalalaituri	Jätkäsaari	1984
Neptunuksenkatu	Jätkäsaari	1984

2.3 Industry

At Hietalahti, Sinebrychoff's brewery (started in the 1820s, closed 1993) and a shipyard (since the 1860's) have been important industrial facilities (Hakkarainen 1982). From the 1910s until 1960, the Finnish Cable Company Ltd. (Suomen kaapelitehdas Oy) operated near Jätkäsaari harbour basin. Karl Fazer Ltd.'s (Oy Karl Fazer) sweet factory operated

from 1891 until 1963 and an oil refinery functioned on Jätkäsaari island in the 1920s and 1930s. In the 1930s and 1940s, there were a forge, an engineering works and an asphalt factory on Munkkisaari and Hernesaari islands. Jätkäsaari mill (Finnish State Granary) has operated since 1935 while the Helsinki Canning Company Ltd. (Helsingin Säu-

lyke Oy) was on Jätkäsaari island from 1925 until the 1950s. Otava print works were at Hietalahdenranta (Hietalahti bay shore) from the 1920s until the end of the 1980s. From 1912, a water main machine shop and workshop have been on the corner of

Kalevankatu and Köydenpunojankatu streets. From the mid-1910s until the end of the 1980s, close to the shore of Ruoholahti bay, there were Valio's dairy, cheese warehouse and biochemical laboratory (Hakkarainen 1982).

3. RESEARCH METHODS

3.1 Sounding profiles

Over two days, 6.5 trackline kilometres were sounded in the area (Fig 1). The research methods were simultaneous echo-sounding (Atlas Deso 10 with 210 kHz and 30 kHz transmitters) and side-scan sonar imaging (Klein 100 kHz).

Echo-soundings clarified the depth below the research vessels and the internal structure and thickness of the soft sediments and, in particular, of the different clays (Fig. 3). The echo sounding plotter results led to conclusions about the sea-bottom's surface structures, topography, and grain composition. Information on factors such as the predominant sedimentary conditions, erosion and the influence of currents was also gathered. The side-scan sonar allowed surveying of the sea-bottom area on either side of the ship. It produced a graphic image printout similar to an aerial photograph (Fig. 2).

This plotter printout allowed interpretation of surface structures and the grade and distribution of surface sediments. Data was also gathered on structures produced on the sea-bottom by human activities (e.g. caused by propeller currents, trawling-tracks and cables).

A positioning system Motorola Mini Ranger III radiolocator (a device accuracy of ± 3 m), was used in acoustic soundings. In practice, the location accuracy was ± 20 m because of errors in location of ground-stations. Exact location was also subject to error because of large buildings (radio-wave reflecting) that surround the harbour basin. Sampling on the r/v Geola used a Syledis SR 3-radiolocator (device accuracy of ± 3 m). This device gave slightly worse location accuracy also due to weakening of radio-waves by buildings.

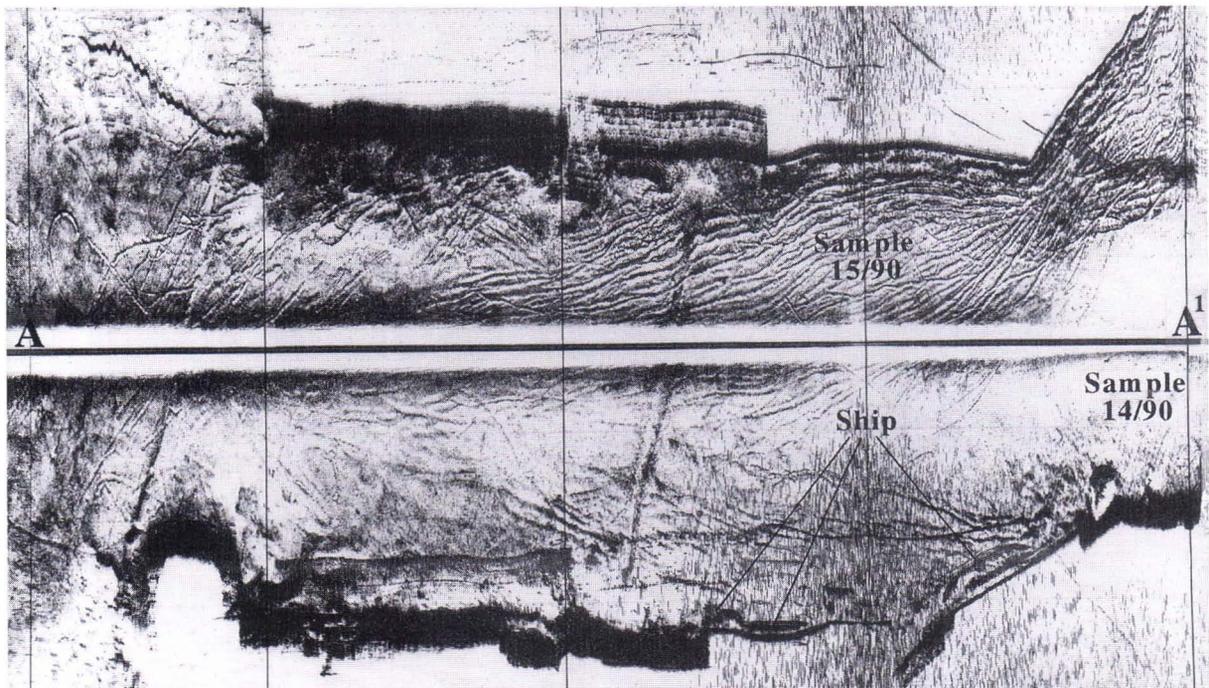


Fig. 2. Side-scan sonar profile A - A' (see Fig. 1) across the southern part of the harbour basin. Sampling site 14/90 is on the smooth sea-floor area. Site 15/90 is on the wavelike and more dynamic sea-floor area. Here, the pattern is due to ships' propeller currents (pers. comm., Häkkinen 1994). The image shows ships berthed in dock.

3.2 Interpretation of soundings

In the selection of sampling site, side-scan sonar printouts helped the interpretation of echo-sounding profiles. The interpreted results of the sounding profiles were used to compile cross-sections that

showed the variation in thickness of sedimentary layers with the rock surface (Fig. 3). The profiles show the extent of the dredged area, depth and the thickness of materials deposited after dredging.



Fig. 3. Echo-sounding profile A - A' (see Fig. 1) across the southern part of the harbour basin. The water depth is on the left. Glacial clays (glclay) are conformable with the underlying unit (bedrock). Irregularities in the sea-floor topography have been smoothed out by "basin fill"-type postglacial clays (postglclay). Recent sediment (recent) occurs on the sea-floor, which has been dredged.

3.3 Sampling

During the study, HWWA took surface samples from two localities with two different samplers, for chemistry and bottom-fauna (macrozoobenthos). HWWA's bottom-sediment samples were taken with a steel Elmgren-corer (internal diameter $\varnothing = 2.3$ cm). The samples represented a thickness of about 5 cm from the surface layers of the sediment. Study samples of the bottom-fauna (macrozoobenthos) were taken with an Ekman-Birge type grab sampler (Varmo 1992). Besides coverage of sampling depth, GSF took two profile samples with a vibrohammer corer (length 6.0 m and diameter, $\varnothing = 110$ mm) from the same locality (Fig. 1).

GSF sample 14/90 (depth 7 m) was taken from the eastern rim of the harbour basin, near the shipyard and State Granary. The sample locality is situated at a curve in the dock protected by shallows. Sample 15/90 (depth 11 m) was from a less protected site on the western rim of the harbour basin (Figs 1 and 2). First, a geological description of the split samples, was recorded on a sample form. The samples were then photographed and then subsamples, for geochemical analysis and grain-size distribution studies, were taken with a pointed injection syringe (volume, 20 ml)(Fig. 4). The subsamples were packed in clean plastic tubes and transported for analysis to GSF's laboratory at Otaniemi, Espoo.

A vibrohammer corer was used to collect samples from sediments deposited after the dredging and building of the harbour basin and from underlying

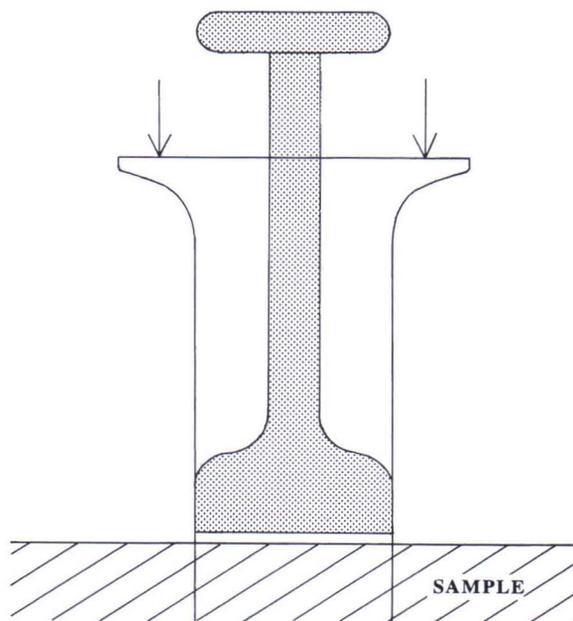


Fig. 4. Subsampling by injection syringe. The head of the syringe is cut off. When the outer shell is pushed into the sediment, the piston remains in place. This action creates a partial vacuum and lifts the subsample.

glacial sediment (age over 10 000 years). In the sampler was a 110 mm diameter steel tube (piston) that contained a plastic tube ($\varnothing = 100$ mm). The sample gently intruded into the sampler when the piston was pushed downwards. A brass stopper at

the lower end of the sample tube stopped the sample from poring out during raising of the tube. In a study in Norway, a similar stopper has not caused significant contamination (Paetzel and Schrader 1991).

3.4 Sample descriptions

Samples 14/90 and 15/90 from Jätkäsaari harbour basin contained a layer of varying thickness sedimented after dredging and underlying older glacial sediments. Additionally, in the western sample (15/90), there was, between the clearly recent sediments and glacial clays, a unit of mixed recent and glacial sediments. This unit was evidently formed by dredging, landslides and propeller currents. In the sample descriptions, the colours of the sediments were determined according to Goddard (1984).

Sample 14/90 is from near the Finnish State

Granary and Masa Yards' shipyard. Its upper part, between zero and 144 cm, consisted of recent sulphide clay and contained organic material. This clay was especially soft and black and sedimented after dredging (Fig. 5). It was gaseous with a clear hydrogen sulphide smell. This recent clay included, between 110 cm and 144 cm, a unit that was mainly grey-black (olive black, 5 Y 2/1) and contained most clay fraction material. The recent clay had a sharp contact with underlying (slightly green) sand (occurred between 144 cm and 157 cm).

There was sulphide clay of possible *Ancylus-*

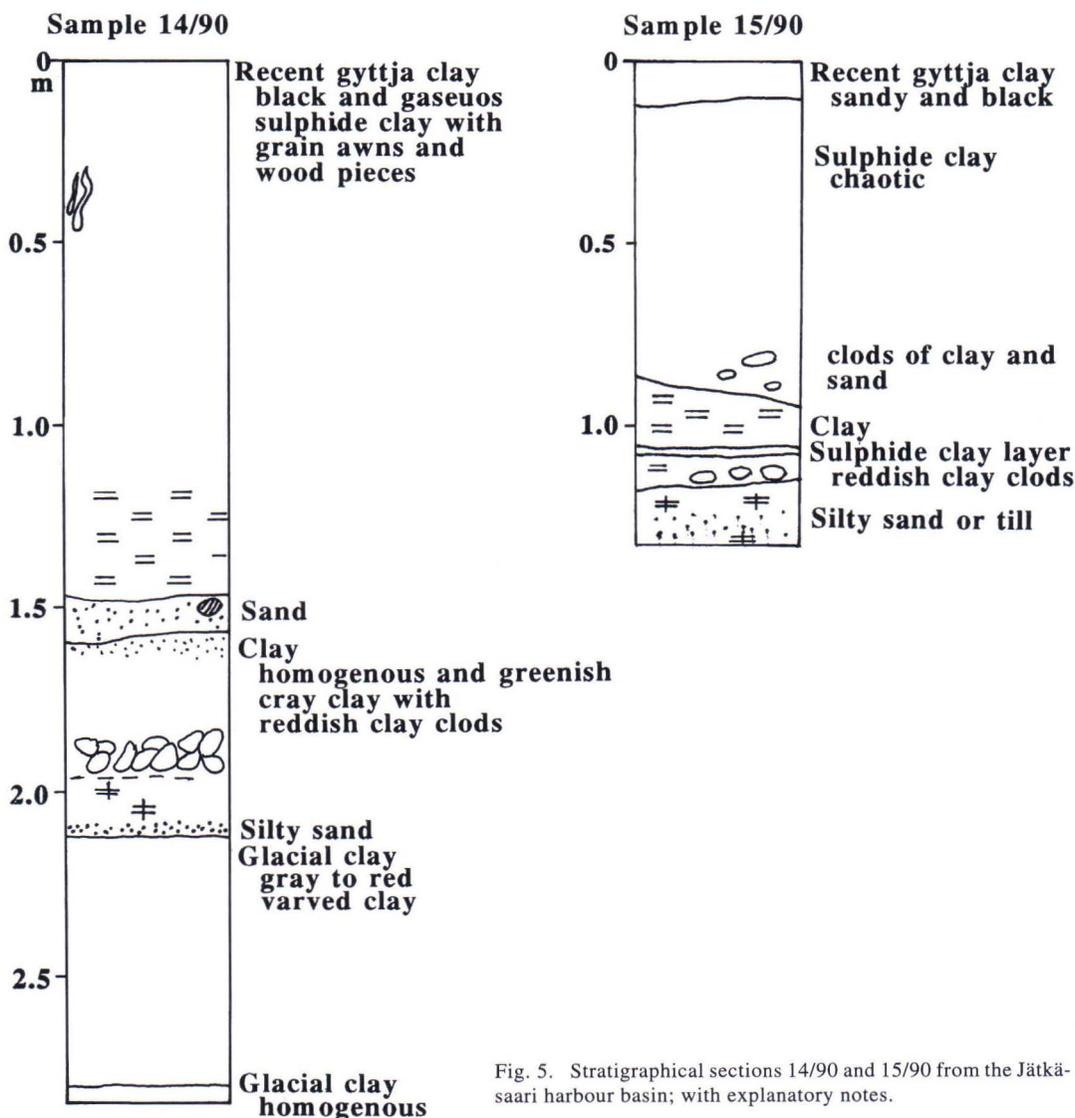


Fig. 5. Stratigraphical sections 14/90 and 15/90 from the Jätkäsaari harbour basin; with explanatory notes.

age (7 500-10 000 years) occurred between 157 cm and 160 cm, below the sand layer and a razor-sharp contact surface. A green-grey (light olive grey, 5 Y 5/2) and nearly homogeneous clay unit occurred between 160 cm and 179 cm. This clay was either the lower part of the *Ancylus*-age unit, or the upper part of the *Yoldia* stage clay (cf. Åker et al. 1988). This unit increased in silt content from top to bottom. Reddish brown, ellipse-shaped clay clods ($\varnothing = 3-5$ cm) occurred between 179 cm and 192 cm in the grey, silty clay. The clay clods were separated from each other by 2-3 mm of grey, silty clay. Clay clods were stratigraphically rip-up clasts and derived from older glacial clay. Silty fine sand occurred between 192 cm and 206 cm and coarse sand occurred between 206 and 208 cm (cf. Åker et al. 1988).

Glacial clay of the *Salpausselkä* stage (pers. comm., A. Rybalko 1990) occurred between 208 cm and 275 cm. It had clear varves and represented the upper part of *Yoldia* stage. The glacial clay was brown-grey (light olive grey, 5 Y 5/2) and contained narrow reddish bands. Quite homogeneous and clearly reddened *Yoldia* stage glacial clay

occurred below the glacial clay of the *Salpausselkä* stage. Subsamples were taken for grain composition (3) and geochemical (11) studies.

Sample 15/90 is from near the middle of the dock in the western part of *Jätkäsaari* harbour basin. The sample's recent surface part, between zero and 11 cm, consisted of very soft and green brown-grey sandy gyttja clay (Fig. 5). Between 11 cm and 92 cm, there was sulphide clay with chaotic structures below the recent clay. Structures ($\varnothing = 0.5-3$ cm) in the sulphide clay's lower portion were similar to rounded brown-grey clay clods (cf. sample 14/90). There was also a small sand clod. This clay unit was chaotic, quite compact and black green-grey. Compact brown-grey clay occurred between 92 cm and 104 cm, below a contact that was probably a slump surface. A sulphide clay layer (2 cm thick) underlay the brown-grey clay. Between 106 cm and 117 cm, there were more clay clods ($\varnothing = 2-3$ cm) in the lower part of the brown-grey clay. The latter was underlain by very tightly compacted silty sand (to 130 cm), which was quite high in sand content below 122 cm. Subsamples were taken for studies of geochemistry (6) and grain composition (1).

4. RESULTS AND ELEMENT-SPECIFIC INVESTIGATIONS

4.1 Surface samples

Surface sediment samples (studied at HWWA) represented the top 5 cm of the bottom sediment. Based on loss of ignition (L.O.I.), the amount of organic material in surface sediment was extremely small (Table 2). The cadmium and lead concentrations of the surface samples were analysed with nitric acid. The analyses were done with a Varian 300/400 AAS-apparatus using the flame method (lead) and a graphite oven (cadmium) and element-specific standards (pers. comm., Varmo 1994).

According to Varmo (1992), the bottom-fauna (macrozoobenthos) in the *Jätkäsaari* harbour basin

is more diverse than has been general in the harbour area. At both localities, there are individuals that belong to seven different species (Tables 3 and 4). Faunal composition shows the area is quite near, biologically, its natural state. The density of faunal (macrozoobenthos) individuals was only a little lower than in the nearby shallow marine bay areas. The biomass in the study area was higher than is usual in other nearby shallow marine bay areas because of the occurrence of the mussel *Macoma balthica* (Varmo 1992).

Table 2. Lead, cadmium and organic matter concentrations in recent surface sediment in the *Jätkäsaari* harbour basin (after Varmo 1992). TS = dry material.

Sample index	Fixed solid % TS	Cadmium(Cd) mg/kg TS	Lead (Pb) mg/kg TS
13401 east	96.3	0.7	72
13402 west	97.0	0.4	130

- GSF's samples 14/90 and 15/90 are comparable to the samples 13401/east and 13402/west.

Table 3. Macrozoobenthos (the means of five sampling) at sampling site 14/90 (after Varmo 1992). SE = standard error of the mean values, Q = number of individuals and W = fresh weight.

Species	Q/m ²	SE	%	W g/m ²	SE	%
<i>Prostoma obsc.</i>	40	23.3	0.5	0.14	0.06	0.5
<i>Nereis divers.</i>	24	16.0	1.3	0.53	0.42	1.8
<i>Manayun. aestu.</i>	208	40.8	10.8	0.02	0.00	0.1
<i>Oligochaeta sp.</i>	920	209.0	47.9	0.32	0.12	1.1
<i>Saduria ent.</i>	8	8.0	0.4	0.01	0.01	0.0
<i>Coroph. volut.</i>	8	8.0	0.4	0.09	0.09	0.3
<i>Macoma balthica</i>	704	67.6	36.7	29.06	12.43	96.3
Total	1920	225.9	100.0	30.17	12.91	100.0

Table 4. Macrozoobenthos (the means of five sampling) at sampling site 15/90 (after Varmo 1992). SE = standard error in the mean values, Q = number of individuals and W = fresh weight.

Species	Q/m ²	SE	%	W g/m ²	SE	%
<i>Prostoma obsc.</i>	8	8.0	1.2	0.03	0.03	0.1
<i>Nereis divers.</i>	8	8.0	1.2	0.01	0.01	0.0
<i>Manayun. aestu.</i>	24	16.0	3.5	0.00	0.00	0.0
<i>Oligochaeta sp.</i>	208	99.9	30.2	0.16	0.08	0.3
<i>Saduria ent.</i>	8	8.0	1.2	0.25	0.25	0.4
<i>Coroph. volut.</i>	56	56.0	8.1	0.17	0.17	0.3
<i>Macoma balthica</i>	376	94.3	54.7	61.84	18.86	99.0
Total	688	170.4	100.0	62.47	18.81	100.0

4.2 Profile samples

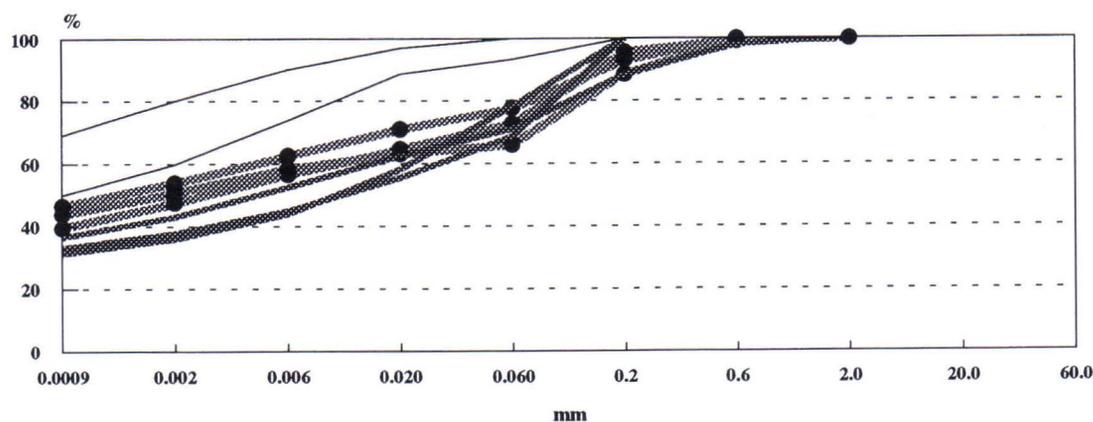
GSF studied the grain-size, mineralogy and geochemistry of the samples from Jätkäsaari harbour basin. The recent sediment was clearly different

from glacial sediment in grain size and geochemistry. However, the mineral composition of fine materials (grain-size < 0.02 mm) was very similar.

4.2.1 Grain size

Based on grain size distribution, the recent sediment, glacial sediment and the western sample's middle unit were each clearly different (Fig. 6).

Grain size distribution was determined by wet-sieving and the fine-grained content (grain-size < 63 µm) was measured by X-ray sedigraph (Micromeritic Sedigraph 500 ET). Recent sediment contained 21.8-29.0 % coarse materials (Ø > 63 µm)



..... Rec. 14/90 Rec. 14/90 Rec. 15/90 — Gl.clay 14/90 — Gl.clay 14/90 ● Mixed 15/90 ● Mixed 15/90 ● Mixed 15/90

Sample 14/90 and 15/90

Fig. 6. Grain size distribution in clay sediments, Jätkäsaari harbour basin.

and glacial clay 0.0-6.7 % (44.0 % in interbedded sand layer). The western sample's middle chaotic unit was similar to recent sediment and contained 22.5-34.0 % coarser materials.

The clay content ($\phi < 0.002$ mm) was different in recent sediment (36.0-43.0 %), glacial clay (59.7-80.0 %) and in the western part's chaotic middle unit (47.5-53.9 %). The forms of the grain-size curves clearly differ from each other in different sediments (Fig. 6). The shapes of the grain-size curves, clay content and coarse material content showed that the western sample's middle chaotic unit formed by mixing, during the area's construction, of recent sediment and glacial clay.

4.2.2 Mineralogy

The mineralogy of two clearly different samples (14/90/30, recent sediment and 15/90/95, glacial clay) was found out by X-ray diffraction of oriented slides (Lintinen 1993b). The mineralogy of the studied slides did not completely correspond to the total mineralogy of the sediments since the studied types were by grain-size < 0.02 mm. Micaeous minerals were abundant. The recent sediment's (sample 14/90/30) specific surface area was $5.9 \text{ m}^2/\text{g}$, which was a typical value for silt or thin clay. The specific surface area of glacial clay (sample 15/90/95) was $18.8 \text{ m}^2/\text{g}$, which showed that this was thick clay (Lintinen 1993b).

Neither samples contained expansible clay minerals (smectite, montmorillonite). The main mineralogical characteristics of the samples were similar. Both samples have relatively little weathered trioctahedral, evidently biotitic, mica as a main mineral. The micas of fine fraction of both clays and moraine are usually trioctahedral (Soveri and Hyypä 1966, Sippola 1974). In glacial clay there were small amounts of chlorite-vermiculite and mica-vermiculite mixed-layer minerals. Thus, the clay was slightly more weathered than the recent sediment (Lintinen 1993b). Both samples contained small amounts of plagioclase, potassium feldspar, quartz (more in recent clay), hornblende and chlorite.

Kaolinite occurred in the samples with clearly more in the glacial clay. The presence of kaolinite was confirmed with an infrared spectroscope. Kaolinite does not form in Finland's present, relatively cold climate since its formation requires a markedly warmer climate (Lintinen 1993a). The kaolinite in glacial clay was presumably derived from sediments older than the last ice age (cf. Lintinen 1993a, 1993b). Kaolinite has not been previously found in Finnish glacial clay (Lintinen 1993b).

Near to the Estonian coast, small amounts of kaolinite, evidently torn off from sedimentary bedrock, occur in all fine-grained sea floor sediments deposited after the last ice age (age $< 13\,000$ years) (Lutt 1992).

The presence of mica- and chlorite-vermiculite and the fact that the samples are sea floor clays suggests that weathering took place in interglacial or interstadial times (Lintinen 1993b). Chlorite may form after deposition if the original sediments have contained sulphides (Lynn and Whittig 1966). At Jätkäsaari, this was unlikely since sulphides have not been found in the glacial clay samples. The fine fraction of moraine has changed only a little in chemical composition (Koljonen and Malisa 1991). At Jätkäsaari, sediments have always been underwater. Therefore, the minerals presumably remained almost unweathered after deposition. The presence of kaolinite in recent sediments showed that there was constant mixing of old and new sedimentary materials in the harbour basin. This conclusion was also inferred from grain-size distribution and variation in trace element concentrations.

4.2.3 Chemical composition

4.2.3.1 General

In chemical analyses at GSF, Espoo, different subsamples were analysed with partial extractions (aqua regia extraction, 1M ammonium chloride extraction and "acid rain"-extraction with $\text{pH}=4.5$) and a $\text{HF-H}_3\text{BO}_4$ -total dissolution. Unsieved samples, which were dried at 70°C , were analysed. Subsamples (0.15 g) were leached in aqua regia extraction for 1 hour at 80°C , after which the cooling solutions were analysed. Subsamples (5 g) were leached in 1M ammonium chloride extraction for two hours at 20°C , after which the elemental concentrations were analysed from the solutions. Subsamples (2.7-5 g) were leached in the "acid rain" water extraction for 2 hours at 20°C , after which the solutions were analysed. In the hydrofluoride boric acid total dissolution, subsamples (0.1 g) were first dissolved for 1 hour at 80°C and then the extraction was continued for 24 hours at 20°C , upon which the solution was analysed. ICP-AES equipment was used in inorganic analysis of the Jätkäsaari samples. A carbon and sulphur analyser (Leco) was used to determine the concentration of carbon and sulphur.

With these analysis methods, it was not possible to reliably analyse cadmium, which was therefore

assessed using GSF's unreliable analyses and HW-WA's analyses. Reliable concentrations for 22 elements were obtained with the total dissolutions and the aqua regia extraction. Reliable determinations for 13 elements were obtained from the weak extraction. The results of analysis of the Jätkäsaari samples are given in tabular form in Appendix 1.

By comparison of concentrations obtained by different extraction methods, the components of anthropogenic and natural material and the role of mobilisation (i.e. if dredged masses of sea floor sediments were transported and dumped in new geochemical environments) could be assessed. Movement of sediment in a geochemically dissimilar environment of deposition, which prevails in the original sedimentary environment, or a change in the physiogeochemical state of a sedimentary environment, can cause a previously bound element to be remobilised (cf. Holm 1988). This is because elements that are bound in sediment always try to reach a state of equilibrium with the dominating conditions.

From the point of view of elemental mobilisation, it is important in what form the element has been bound to the sediment. The element may be bound to the sediments' mineral structure so firmly (e.g. Si, K, Ca, Na and Sr in feldspar) that it becomes mobile only during solution of the whole mineral (Koljonen and Malisa 1991, Erlström and Sivhed 1992). Some dark minerals (pyroxenes, amphiboles, and particularly micas and clay minerals) and ore minerals dissolve particularly easily in aqua regia (Koljonen and Malisa 1991). Pb, Zn, Ni, Cr, Mn and Mg originate from these minerals. By weak extraction (e.g. with an ammonium chloride extraction), information was obtained on the amount of easily leachable and bioavailable components of elemental concentrations, which were adsorbed on the surface of particles and bound to an organic substance, to colloidal particles and to precipitates. "Acid rain" water extraction only liberates to solutions very easily mobile components of the total elemental concentration.

In several studies, it has been shown that the elemental concentration is not necessarily a risk from an environmental point of view (e.g. Leoni et al. 1991). It is more important to know in what forms and in what concentrations an element occurs since a small concentration of an element in an environmentally toxic form may be hazardous to living organisms (Förstner 1987, Leoni et al. 1991). By use of extractions of different strength, it was possible to check that in what form the element was in the sediment under study.

Elemental concentrations derived from human sources are more hazardous to the environment

than corresponding concentrations that originate from natural sources. The human-derived component was generally in the most easily mobilised form and the elemental concentrations could exceed natural background levels, even by several orders (e.g. Förstner 1987, Enckell-Sarkola et al. 1989, Räisänen and Hämäläinen 1991, Erlström and Sivhed 1992).

On the surface of colloidal particles of clay and humus there are negative charges, which are neutralised by electrostatically adsorbing cations (Bache 1986). Because of this clay sediments typically adsorb man-made heavy metals that are in soluble form. Precise analysis of clay sediments and the use of extractions of different strength allows changes in environmental state to be examined. This method is even better than with water samples that give a picture of the controlling situation only at the time of sampling (Paetzel and Schrader 1991).

4.2.3.2 *Element-specific results and their investigation*

4.2.3.2.1 Anthropogenic elements

Lead. In the Jätkäsaari samples, there was 33.8-391 ppm of aqua regia extractable lead in recent sediments, 20.7-39.3 ppm in glacial clay and 18.9-148 ppm in the chaotic unit of the western sample (Fig. 7). There was slightly more aqua regia extracted lead in Salpausselkä clay (27.4-39.3 ppm) than in older homogeneous glacial clay (20.7 ppm). In the northern part of the Bay of Bothnia, the background concentration of lead was 20-40 ppm (Enckell-Sarkola et al. 1989), which corresponded to the glacial clay of Jätkäsaari area. The average concentrations of the central Baltic Sea's different aged clays are 16.0-51.0 ppm (Niemistö and Voipio 1981). The estimated soil pollution's lead concentrations' base value was 100 ppm (Manninen and Willamo 1993), which was clearly exceeded in the lower unit of the recent sediment.

At Jätkäsaari, lead was evidently adsorbed onto grain surfaces and, in comparison to other human-derived elements, it was reasonably firmly bound (cf. Salomons and Förstner 1984). Reliable lead concentrations were not obtained with all extractions from the Jätkäsaari samples. Thus, lead's binding mode to sediments was uncertain.

The greatest part of the lead from the Jätkäsaari recent clay comes from airborne materials in emissions from traffic and power stations and material in waste waters (cf. Salminen 1976, Renberg 1986, Kubin 1991, Leoni et al. 1991, Niskavaara and Äyräs 1991, pers. comm. Varmo 1992).

Lead

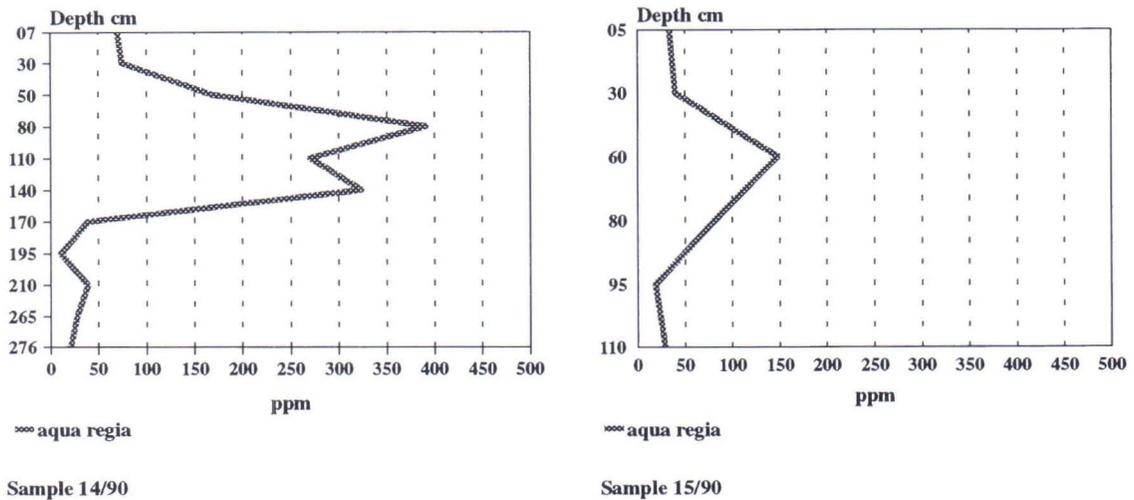


Fig. 7. Aqua regia extracted lead concentrations plotted against depth, which show major upheaval in the recent sediment in the Jätkäsaari harbour basin.

Zinc

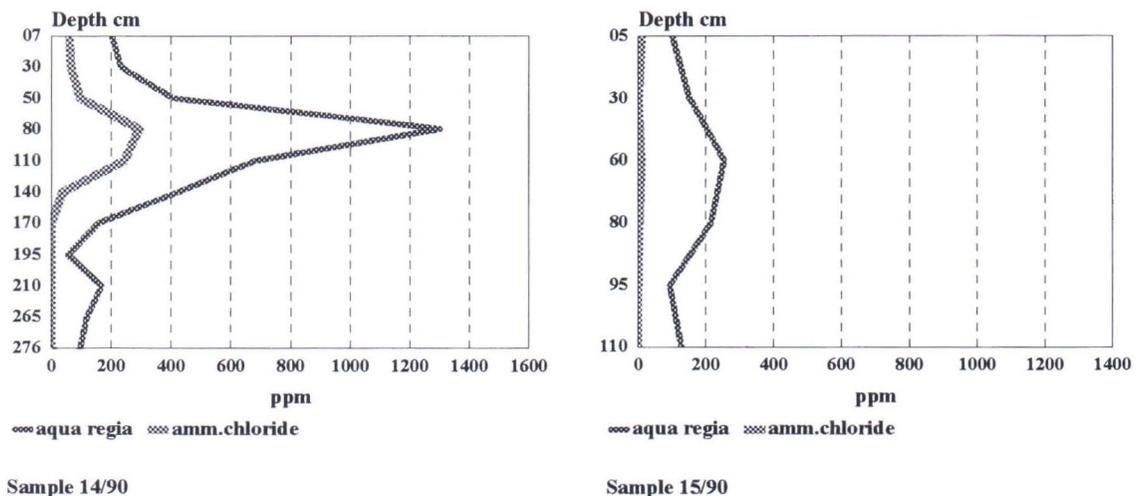


Fig. 8. Zinc concentrations obtained by aqua regia and ammonium chloride extraction clearly show man-made impact on recent sediment in the Jätkäsaari harbour.

The decrease in the lead concentration of the Jätkäsaari recent sediment has been partly a result of the development of sewerage during the 1980's (cf. Varmo and Riiheläinen 1994) and the cessation of use of lead-based paint in the shipyard at the beginning of the 1970' (oral comm., Masa Yards/painting department 1993). In the shipyard, craft have been built and painted in the dry dock since the beginning of 1980's (pers. comm. Stenroos, Masa Yards 1992) and this has also decreased emissions to the harbour basin. Changes in raw materials and work methods and growth in the use of unleaded fuel in cars during the 1970's and

1980's have both partly reduced emissions (e.g. Rühling et al. 1987, Mäkelä-Kurtto and Tares 1987, Verta et al. 1989, Erviö et al. 1991).

Zinc. Variations in zinc concentrations that occurred during recent sediment deposition were seen in sample 14/90 taken near the Finnish State Granary (Fig. 8). In the upper recent sediment there was only slightly more zinc (> 200 ppm) than in glacial clay (97.4-168 ppm). In the northern part of the Gulf of Bothnia zinc's background concentration is 125 ppm (Enckell-Sarkola et al. 1989), which corresponds to the concentration level in the Jätkäsaari glacial clay. In the central Baltic Sea

average zinc concentrations in clays of different ages vary between 106 ppm and 146 ppm and in recent sediment there is on average 245 ppm of zinc (Niemistö and Voipio 1981). At Jätkäsaari, the zinc concentrations in the lower recent unit were between 408 ppm and 1300 ppm. Such levels clearly exceed the value of 150 ppm (zinc) held as a normative base value for unpolluted soil (Manninen and Willamo 1993). The zinc concentration of the western sample's recent sediment was not higher than that of the glacial clay. In the western part's chaotic unit the concentration of zinc (94.0-255 ppm) had been raised.

Based on the Jätkäsaari samples, the zinc concentration in the glacial clay of the Salpausselkä stage (120-168 ppm) was little higher than in other glacial clay (97.4 ppm). In the Jätkäsaari glacial clay there was no zinc that was soluble in a weak extraction. There are also zinc and cadmium in natural-state environments, generally in variable amounts as forms that are in solution and mobile (Sandström 1984, Enckell-Sarkola et al. 1989, Räisänen and Hämäläinen 1991). In the eastern sample of the lower unit of recent clay more zinc was obtained with all extractions. This type of behaviour illustrates that there are differently bound components of anthropogenic zinc and does not reflect differences in concentration of natural and human derived zinc (pers. comm., Salminen 1994).

In the Jätkäsaari sediments, most zinc was in a form soluble in aqua regia and ammonium chloride in minerals, in organic matter and where adsorbed

on the surfaces of particles. The highest zinc concentration was in recent sediments, which also gave the highest organic matter concentration.

Copper. The copper concentration clearly varied in the different aged sediments of Jätkäsaari (Fig. 9). There was copper 34.5-77.9 ppm in glacial clay, which corresponds to the background concentration in clays at the northern end of the Gulf of Bothnia (40 ppm, Enckell-Sarkola 1989) and the average concentration in the sediments of the Gulf of Finland (37 ppm, Niemistö and Tervo 1978). In the central Baltic Sea the average copper concentrations of different aged clays are 31.4-48.0 ppm (Niemistö and Voipio 1981). There was 87.5-672 ppm of copper in the recent material at Jätkäsaari, of which the held normative base value copper concentration for the soil of 50 ppm (Manninen and Willamo 1993) was clearly exceeded. From leaching with ammonium chloride extraction there is on average 1.7 % copper (0.3-3.2 %) concentration obtained by aqua regia extraction in the recent sediment of sample 14/90 and 0.5 % (0.2-1.1 %) in that of sample 15/90. With the ammonium chloride extraction method, copper concentrations in glacial clays were below the detection limit (0.04 ppm).

The largest part of the copper in recent sediment at Jätkäsaari was apparently bound to organic fractions and not to Fe-Mn hydroxides since only a small amount of copper (0.2-3.2 % of total concentrations) leached in ammonium chloride extraction. However, with aqua regia extraction copper

Copper

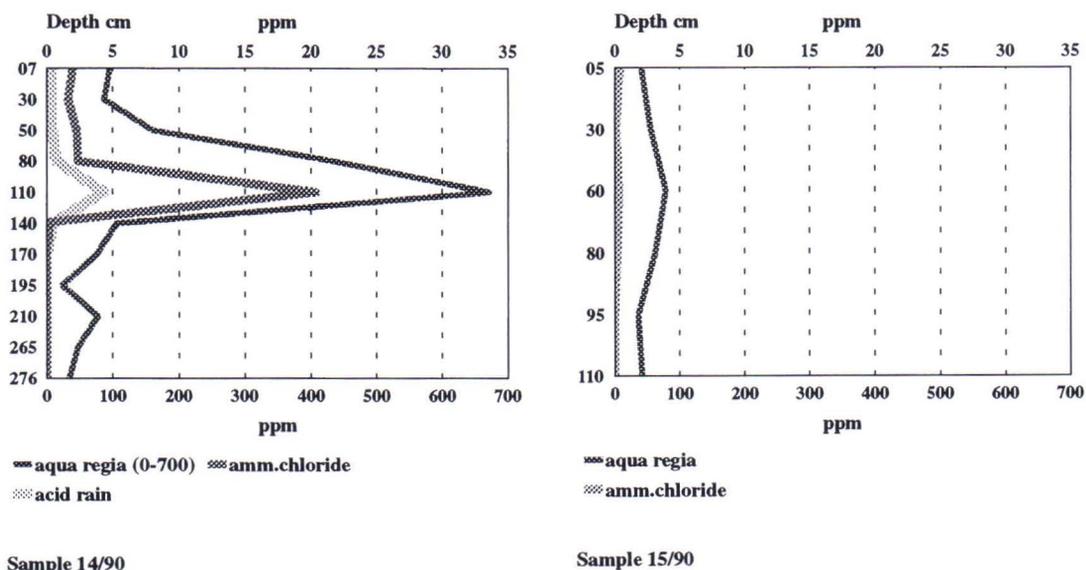


Fig. 9. Copper concentrations in sediments from Jätkäsaari harbour basin. The lower axes of the graphs show values obtained from aqua regia extraction; the upper axes shown values obtained from ammonium chloride and acid rain extractions.

leached very easily.

Copper's behaviour is similar to that of lead in the Jätkäsaari sediments, which may derive from traffic (cf. Niskavaara and Äyräs 1991), waste water (cf. Förstner and Wittmann 1981) or possible oil-emissions (Leminen et al. 1993). There was a more exceptional occurrence in the lower unit of recent sediment (140 cm, sample 14/90), in which copper was low in comparison to lead. In the materials presently deposited, there was only a little more copper than in glacial clay. The location of small foundries and the cable factory near Jätkäsaari island may have affected the copper concentration of the recent sediment (cf. Hickey and Kittrick 1984, Kuo et al. 1983).

Silver. Aqua regia extracted silver concentrations in the lower unit of the recent clay of the eastern sample (< 3-39.6 ppm) and in the chaotic unit of the western sample (5.2 ppm) exceed the detection limit of the analysis method (3 ppm) (Fig. 10). A safe silver concentration for soil considered to be 2 ppm by Koljonen (1992) also exceeds the value obtained with ammonium chloride extraction in the lower unit of the recent clay. Concentrations below the detection limits suggested that the sedimentary units could be separated by their silver concentrations if more sensitive analysis methods were used.

With ammonium chloride extraction (detection limit 0.02 ppm) clearly increased silver concentrations were detected in the lower unit of the recent sediment. Ammonium chloride leached silver was 1.89-15.5 % of the silver amount obtained from aqua regia solution. Based on results, there was

human-derived silver in the recent sediments, which was bound quite firmly to the surfaces of minerals or to organic materials. Anthropogenic silver may be derived from the photographic department of the printing works near Jätkäsaari island. Based on analysis, however, it appears that in the glacial clays of the Salpausselkä phase there is slightly more silver than in homogeneous glacial clays.

Carbon. At Jätkäsaari, carbon was below 0.4 % in glacial clays and above 1 % in recent sediments (Fig. 11). The most carbon was in the lower unit of the recent clay in the eastern sample (1.9-6.1 %). The surface sediment's loss of ignition (L.O.I) was 3.0-3.7 % according to HWWA measurements (Table 2). A moderate amount of organically-derived carbon (2-3 %) does not generally greatly affect heavy metal concentrations in sediments (Tenhola 1988, Paetzel and Schrader 1991). Therefore, organic material could only have affected heavy metal concentrations at Jätkäsaari in the lower unit of recent sediment. At Jätkäsaari, carbon mostly derived from the nearby granary, where there was a mill, and from waste water.

Sulphur. In the lower unit of recent clay there was more sulphur (0.6-1.6 %) than in other units (0.1-0.8 %). At the eastern sample site, the sulphur concentration of recent clay was higher near the granary (0.4-1.6 %) than at the western sample site (0.1 %)(Fig. 11). The sulphur concentrations of glacial clays at Jätkäsaari were between 0.1 % and 0.2 %. According to Manninen and Willamo (1993), the sulphur concentration normative base value for the soil is 200 ppm (0.02 %), which also exceeds glacial clay in the natural state at Jätkäsaari.

Silver

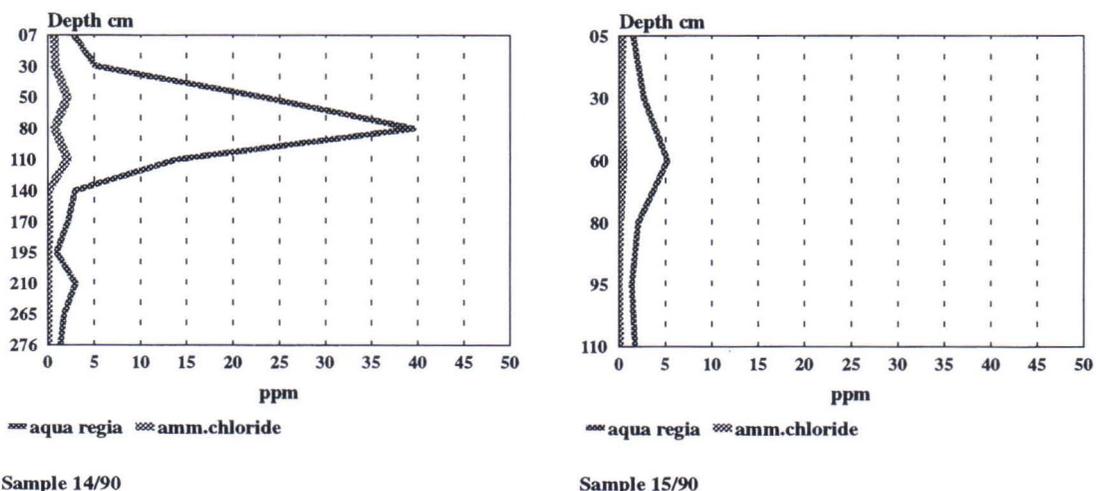


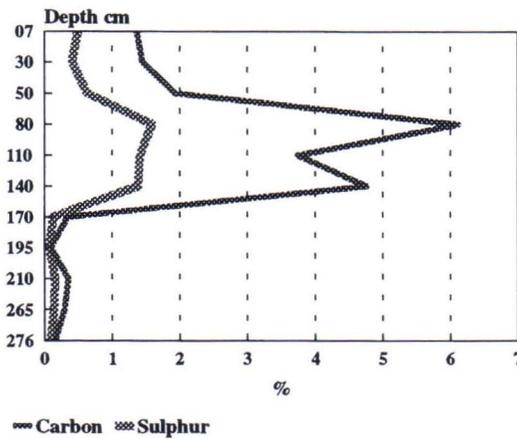
Fig. 10. Silver concentrations in sediments from Jätkäsaari harbour basin. These graphs clearly show the anthropogenic component of silver in the recent sediment.

Dissolved sulphur is precipitated in an oxidising environment as sulphate and in a reducing environment as sulphide (e.g. the vermiform varying-length grains of marcasite in the *Ancylus* stage clays described by Ignatius et al. 1968 and Papunen 1968). Atmospheric sulphur in smoke and industrial gases derived from organic fuels falls back to the earth's surface and enters waterway systems (Salomons and Förstner 1984). Slightly higher sulphur concentrations were found close to peat-fired power stations (Niskavaara and Äyräs 1991), about Jätkäsaari district heating plant (500 m), or where there was grain and flour dust.

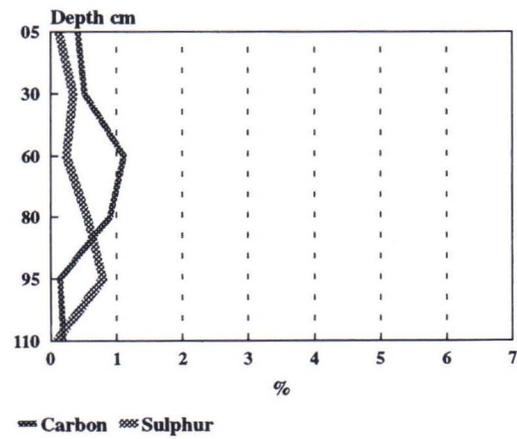
Phosphorus. In the Jätkäsaari samples, the highest phosphorus concentrations (> 1000 ppm) were at the eastern sample site, close to the granary, in the lower unit of the recent sediment. In the eastern sample, the concentrations of the recent sediments upper unit and the glacial clay (667-893 ppm) corresponded to each other. All the phosphorus concentrations in the western sample were also at this level (Fig. 12).

Dissolved phosphorus binds quickly to sediments which consist of both mineralic and biogenic materials. Thus phosphorus is enriched in iron-precipitate, lake mud and clays (e.g. Winterhalter

Carbon and sulphur



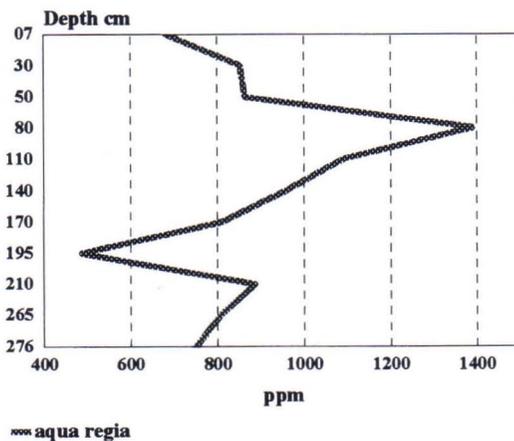
Sample 14/90



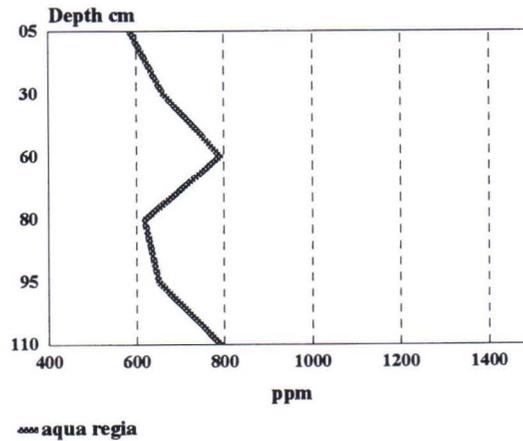
Sample 15/90

Fig. 11. Concentrations of carbon and sulphur in Jätkäsaari harbour basin. These are noticeably higher in the recent sediment than in the glacial clay at the sampling site 14/90.

Phosphorus



Sample 14/90



Sample 15/90

Fig. 12. Concentrations of phosphorus in the sediments from Jätkäsaari harbour obtained by aqua regia extraction.

and Siivola 1967, Koljonen 1992). At Jätkäsaari, the highest phosphorus concentrations were in sediment that contained abundant organic materials, which may have derived from, among others, waste water and organic materials from the granary. Reliable phosphorus concentrations were not obtained with weak extractions.

On the coast of Ostrobothnia (western Finland), the raised concentrations of phosphorus in the fine materials of the coastal region's moraine may be the result of phosphorus enrichment in marine sediments (Koljonen 1992). At Jätkäsaari, at this stage in the research, phosphorus concentrations due to a marine environment of sedimentation were not observed. Aqua regia solubilities were generally over 90 %, which showed that phosphorus was bound to organic materials, apatite and iron manganese hydroxides (cf. Koljonen 1992). In the Jätkäsaari sediments, it was estimated that phosphorus concentrations exceeding 900 ppm in recent sediment equaled the component of anthropogenic phosphorus.

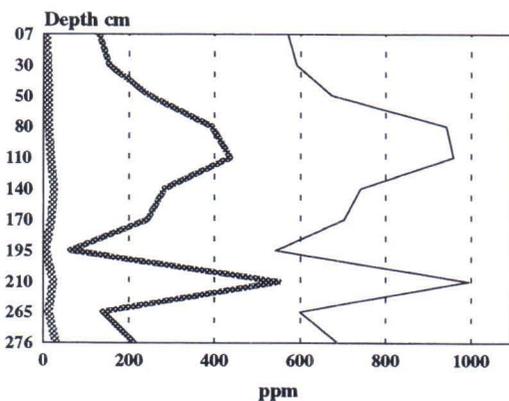
Barium. At Jätkäsaari, the total barium concentrations of recent sediments and glacial clays (570-995 ppm) exceeded the 600 ppm normative base value used in estimating the degree of soil contamination (Manninen and Willamo 1993). However, they correspond to the average barium concentration of sediment of the Gulf of Bothnia (700-1000 ppm, Boström et al. 1978). The high concentration of barium may point to the sediment's origin in a marine environment (Koljonen 1992), but this was not observed at Jätkäsaari. In clay sediments the average aqua regia extractable barium was 32 %

(varies from 18 % to 55 %) and in sand 11.5 % of concentrations obtained by total dissolution (Fig. 13). Barium was bound in the interbedded sandy layer of Jätkäsaari's glacial clay to feldspar that was poorly soluble in aqua regia (cf. Koljonen and Malisa 1991, Koljonen 1992). In the clays, the barium component that was bound to micas was significant.

Barium obtained from ammonium chloride solution was on average < 3.5 % and from "acid rain" solution < 1 % of the total amount. With ammonium chloride extraction there were slight but observable variations in solubility between the sedimentary units. The solubility of barium was lowest in recent clays and in the sandy interbed of glacial clay. In the eastern sample of the harbour basin, barium obtained by ammonium chloride extraction was generally < 3 % (0.9-4.2 %) and in the western sample > 4 % (2.7-9.4 %) of total concentration. With "acid rain" extraction, relatively more barium was leached from recent sediment than from glacial clay.

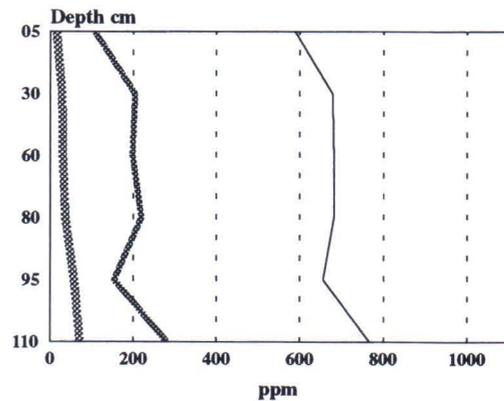
Barium replaces potassium in feldspar and mica lattices. Barium adsorption by clays (cf. Koljonen 1992) was also seen in the Jätkäsaari analyses. Barium moves weakly in ground surface conditions because the greatest part of the barium is in feldspar in a nearly insoluble form. At Jätkäsaari barium behaviour was different from that of potassium in recent sediment, but in glacial clay its behaviour was similar. This shows that barium in glacial clay's K-feldspar lattice replaces potassium. In recent sediment barium was more abundant in micas and was also human-derived barium that may have originated from paint pigment materials and from chemicals required by the photographic works.

Barium



— total dissolution - - - aqua regia
 ···· amm. chloride

Sample 14/90

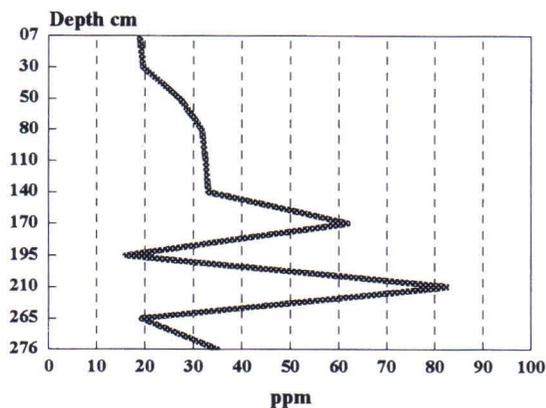


— total dissolution - - - aqua regia
 ···· amm. chloride

Sample 15/90

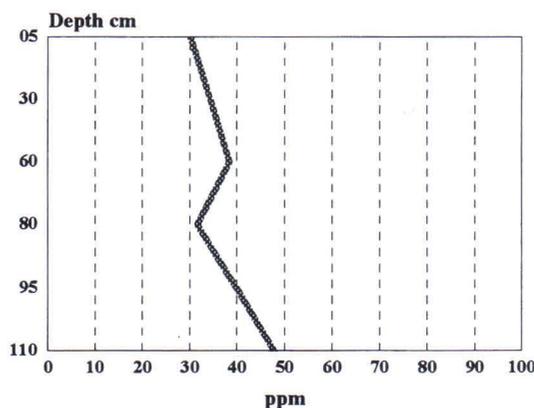
Fig. 13. Concentrations of barium in sediments from Jätkäsaari harbour.

Arsenic



--- aqua regia

Sample 14/90



--- aqua regia

Sample 15/90

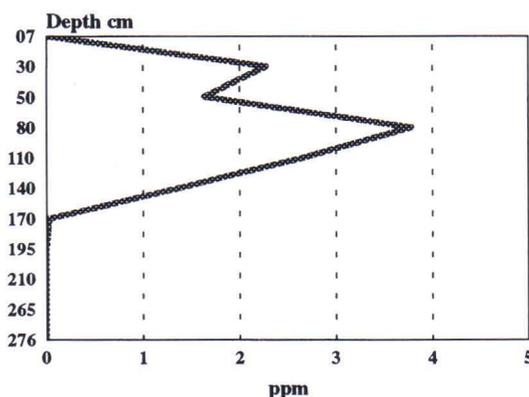
Fig. 14. Arsenic concentrations obtained by aqua regia extraction in the sediments from Jätkäsaari harbour.

Arsenic. At Jätkäsaari there was 18.9-33.1 ppm of aqua regia extractable arsenic in recent sediment, in glacial clay 19.3-82.5 ppm and in the chaotic unit of the western sample 31.6-38.5 ppm (Fig. 14). Such concentrations exceed the 10 ppm arsenic concentration held as a normative base value (Manninen and Willamo 1993) and the background concentration of the northern part of the Gulf of Bothnia (also 10 ppm, Enckell-Sarkola et al. 1989). Concentrations < 40 ppm were unreliable in the analysis method used, but evidently gave guidelines since there were clear concentration differences between units.

Recent sediment can be divided into upper and lower units, if the concentrations that fall below the degree of analytical certainty were in the correct relationships to each other. There was 35-47.9 ppm of arsenic in homogeneous glacial clays and slightly more in the glacial clays of the Salpausselkä stage, i.e. 19.3-82.5 ppm. Arsenic appears bound to clay since in sandy units there was less arsenic. Arsenic concentrations have been observed in polluted sediments to change similarly to lead, copper and zinc (Leoni et al. 1991). At Jätkäsaari there was not, based on the behaviour of arsenic, anthropogenic arsenic since concentrations in glacial clays exceeded those of the recent sediments.

Arsenic concentrations behave in aqua regia extraction in the same way as other elements such as aluminium, calcium, manganese and titanium, among others. Thus, aqua regia solution is suitable for the extraction of arsenic. Because of the analysis method's high limit of reliability (40 ppm) for arsenic concentrations, the neutron activation method (NAA) was clearly suitable in arsenic analysis (cf. Koljonen 1992).

Cadmium



--- aqua regia

Sample 14/90

Fig. 15. Aqua regia extracted component of cadmium concentrations are below the reliable analysis detection limit, but the graph clearly shows that the concentrations in the recent sediment are higher than in glacial clay.

Cadmium. Based on the amount of cadmium in extractions determined with aqua regia, recent sediment clearly differs from glacial clay (Fig. 15). No cadmium was obtained from glacial clay by aqua regia extraction. However, in recent sediment, not counting the surface layer, 1.4-3.8 ppm was obtained. This amount exceeds the ground base value of 1 ppm (Manninen and Willamo 1993). Concentrations in recent surface sediments and glacial clays were at the same level. According to analyses by HWWA's, cadmium concentrations in surface sediment's were reasonably low (0.4-0.7 ppm,

Varmo 1992). They correspond to cadmium background concentrations (0.3-0.5 ppm) in both Finland (Verta and Mannio 1987, Enckell-Sarkola et al. 1989) and the central Baltic Sea (Niemistö and Voipio 1981).

Cadmium concentration has risen mainly during this century, but cadmium emissions to the air and waterway systems have decreased in the latter half of the 1980's (Verta et al. 1989). The effect of these decreases was also seen as lower cadmium concentrations in the surface layers of recent sediment at Jätkäsaari. The clearest reason for the decrease in concentrations was the development of sewerage in the earlier half of the 1980's since high cadmium concentrations are typical of waste water (e.g. Förstner 1987, pers. comm., Varmo 1992). Larger cadmium emissions originate from zinc and copper foundries, from iron and steel factories, from waste incineration facilities and from waste dumps (Kuo et al. 1983, Hickey and Kittrick 1984, Förstner 1987, Mukherjee 1989, Erviö et al. 1991, Niskavaara and Äyräs 1991). The transition and decrease of existing industry and changing raw materials has also affected the lowering of recent surface sediment's cadmium concentrations.

4.2.3.2.2 Heavy metals

Cobalt. At Jätkäsaari, total cobalt concentrations also distinguish different sediments. In recent sediment these are 15.5-20.8 ppm, in Salpausselkä

stage clay 29.9-36.6 ppm and in homogeneous glacial clay 21.8-28.7 ppm (Fig. 16). Cobalt concentrations clearly were below the normative base value for soil (50 ppm, Manninen and Willamo 1993). At Jätkäsaari, cobalt concentrations, especially in Salpausselkä stage glacial clay, were a little higher than concentrations of 16.9-25.9 ppm put forward by Niemistö and Voipio (1981) for clays deposited at different times in the Baltic Sea. Differences in concentration between sedimentary units increase with aqua regia extraction: in recent sediment aqua regia leached cobalt was 62.0-76.8 % and in glacial clay 75.9-95.1 % of the total amount. Cobalt occurred at Jätkäsaari, based on aqua regia solubilities, mostly in micas (cf. Koljonen 1992).

Using a strong acid extraction, the soluble cobalt concentrations were smaller in recent sediment and larger in glacial clays, especially in Salpausselkä stage clay. With weak extractions, cobalt concentrations behave opposite to the way in strong acid extraction. With a weak extraction more cobalt leached from recent sediment than from glacial clay. With ammonium chloride extraction on average 2.9 % (1.4-3.6 %) of the total amount leached from recent clay and from glacial clay on average 0.2 % of total amount (always < 0.3 %). Based on cobalt obtained with a weak extraction, the western sample's middle unit appears to consist of mixed material, of which the solubility percentages were between those of recent and glacial clay. Cobalt

Cobalt

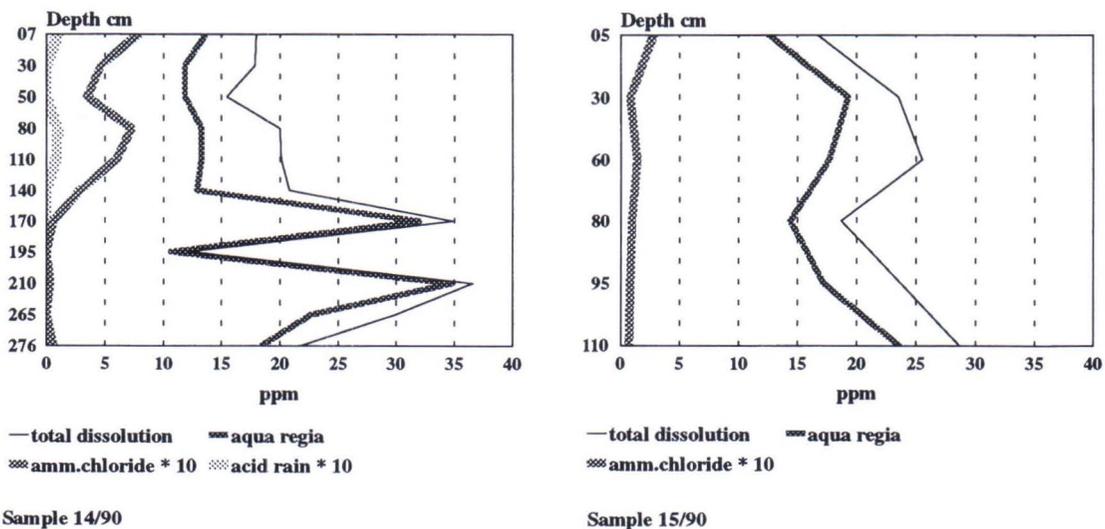


Fig. 16. Cobalt concentrations in sediments from Jätkäsaari harbour determined by various extraction methods. The anthropogenic impact on recent sediment was slight. Total dissolved and aqua regia leached concentrations are shown straight out but cobalt concentrations obtained with weak extractions have been multiplied by ten.

concentrations obtained by "acid rain" extraction were generally below the analysis method's detection limit (0.02 ppm).

Cobalt is adsorbed by clays and Fe-Mn precipitates (Chao 1972, Leoni et al. 1991, Koljonen 1992), which was also seen in Jätkäsaari's sediments. In these, the largest cobalt component was in a tightly bound form, particularly in glacial clay, in which concentrations obtained with a weak extraction were very low. In recent sediment there was, more easily soluble, possibly human-derived cobalt. Near the heavy fuel oil-fired heat-generating power stations as at Hernesaari, moderately increased cobalt concentrations have been reported (Niskavaara and Äyräs 1991).

Chrome. Chrome concentrations in recent sediment (54.2-98.1 ppm) were higher at Jätkäsaari than background concentrations from the northern part of the Gulf of Bothnia (12-45 ppm, Enckell-Sarkola et al. 1989) and in the central part of the Baltic Sea (38-47 ppm, Niemistö and Voipio 1981). However, they corresponded to background concentrations from the Gulf of Bothnia (40-90 ppm, Boström et al. 1978). The chrome concentration of recent sediment was below the normative base value for ground materials (100 ppm, Manninen and Willamo 1993), but glacial clay's concentrations were higher (74.7-132 ppm). On average 72 % (62-85 %) of the total amount of chrome leached with aqua regia (Fig. 17), which indicated that chrome had substituted for iron in micas (cf. Koljonen 1992).

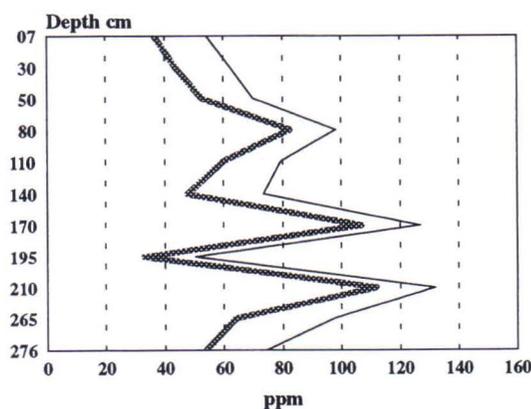
In the lower unit of recent sediment, chrome may

partly be a human-derived material introduced to the environment by human activity and thus adsorbed by grain surfaces. Anthropogenic chrome in recent sediment's was clearly indicated by the relationship of normalised chrome to iron and aluminium (Fig. 31, p. 33). As a pollutant, chrome is generally of only local significance (Förstner 1987). Rarer chrome in oxidation stage +6 is an environmentally very hazardous and toxic element (Förstner and Wittmann 1981).

Nickel. In Jätkäsaari's samples, the Salpausselkä stage glacial clay can be separated from other clays based on its high nickel concentration (58.6-86.1 ppm against 28.2-40.1 ppm) (Fig. 18). Except in Salpausselkä stage clay, the nickel concentrations of the Jätkäsaari sediments fall below the held soil base value of 40 ppm (Manninen and Willamo 1993). In the Salpausselkä stage clay the nickel concentration also exceeds the amount of nickel in the sediments of the Gulf of Bothnia (25-55 ppm, Boström et al. 1978) and the average concentrations of the different aged clays of the central Baltic Sea (34-61 ppm, Niemistö and Voipio 1981). At Jätkäsaari, aqua regia extractable nickel was 62.8-84.8 % of the total concentration. From ammonium chloride solution nickel in recent sediment was 0.7-4.9 % of the total amount and in glacial sediments 0.1-0.6 %.

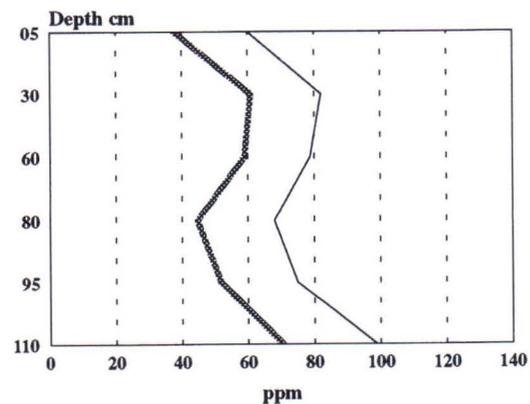
Environmentally significant increased nickel concentrations have been found in the vicinity of heavy fuel oil-fired district heating stations (Niskavaara and Äyräs 1991). At Jätkäsaari, the very low and easily soluble component of anthropogen-

Chromium



— total dissolution - - - aqua regia

Sample 14/90



— total dissolution - - - aqua regia

Sample 15/90

Fig. 17. Chromium concentrations in sediments from Jätkäsaari harbour. Human contamination is shown in the lower part of recent sediment layer at sampling site 14/90.

ling 1985, Boström et al. 1981). At Jätkäsaari, this was seen as a high vanadium concentration in the glacial clays. However, in recent sediment, which contained a higher amount of organic material, there was less vanadium.

More vanadium was extracted with weak extractions from recent sediment than from glacial clay. This is similar to the behaviour of nickel. Concentrations were very low, but, with "acid rain" extraction, concentrations in glacial clays were below the detection limit (0.03 ppm) and recent sediment's concentrations were above it. An increased easily extractable component of vanadium concentrations came from a heavy fuel-fired heating station in the vicinity (cf. Salomons and Förstner 1984, Niskavaara and Äyräs 1991). However, vanadium concentrations obtained with weak extraction from Jätkäsaari's recent sediment are noticeably quite low for the environment.

Manganese. Manganese concentrations also differentiate Jätkäsaari's recent sediment (377-433 ppm) from glacial sediment (400-839 ppm)(Fig. 20). The total concentrations of different units of recent sediment corresponded to one another, but in the sediment's lower unit there was more aqua regia extracted manganese (53.6-58.8 %) than in the upper unit (45.0-47.8 %). There was more manganese in Salpausselkä stage clay than in homogeneous glacial clay.

Aqua regia extracted manganese in recent sediment was 45-58.8 % of the total and in glacial clays 76.5-93.1 % of the total (in the sandy interlayer

60.7 %). The highest solubility percentages were in the Salpausselkä stage clay. In the Jätkäsaari samples, manganese was bound to micas easily soluble in aqua regia, adsorbed on surface of grains and as a precipitate.

In the eastern sample there were amounts of ammonium chloride extracted manganese in the upper unit of the recent sediment that were similar to those in the glacial clay. However, there was less manganese in the lower unit of recent clay. From "acid rain" extraction there was more manganese in recent sediment (0.5-5.9 ppm) than in the glacial clays (0.2-0.5 ppm). This difference is significant in the surface layer of recent sediment, in which the solution's manganese amount is 2-5 times the concentrations of other recent clay and over 10 times that compared to glacial clays. This type of geochemical behaviour can be caused by a diagenetic process, in which manganese is transported to the interface between sediment and water (Davison 1993). Manganese moves easily in reducing conditions (e.g. Davison 1993). These dominated inside the sediment at the eastern sample site of the harbour basin as indicated by a strong smell of hydrogen sulphide during subsampling.

Titanium. There was 2450-3170 ppm of titanium in Jätkäsaari's recent sediment and 3940-5510 ppm in glacial clays (Fig. 21). In recent clay aqua regia extracted titanium was 37.8-44.4 % of the total and in glacial clay 42.9-63.5 %. Most titanium was in the Salpausselkä stage clay (4610-5510 ppm), which also contained, relatively, most titani-

Manganese

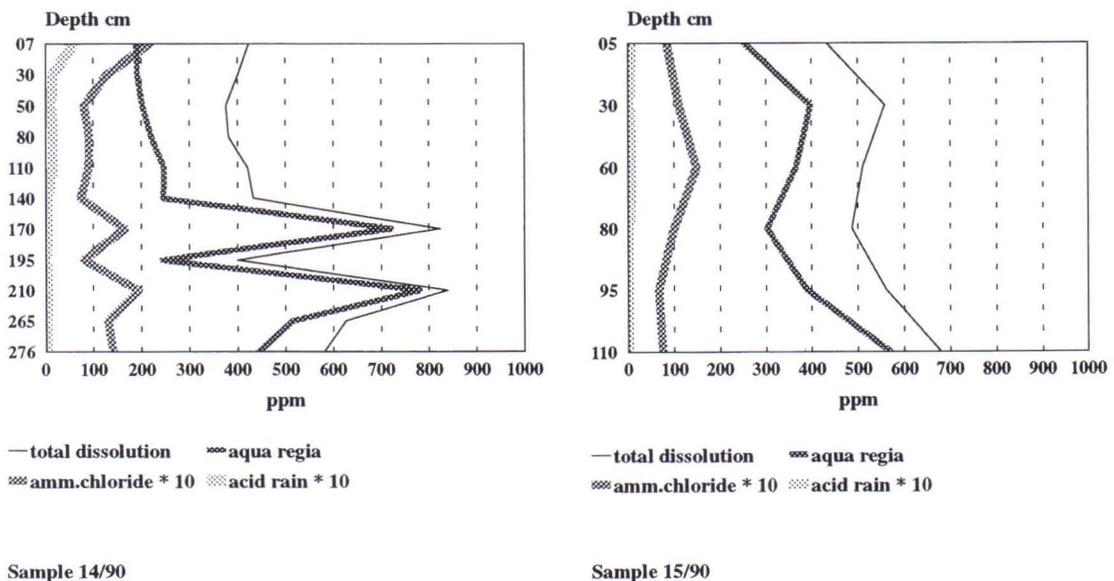


Fig. 20. Manganese concentrations in sediments from Jätkäsaari harbour. Total dissolved and aqua regia extracted manganese concentrations are given straight out but manganese concentrations obtained with weak extractions have been multiplied by ten.

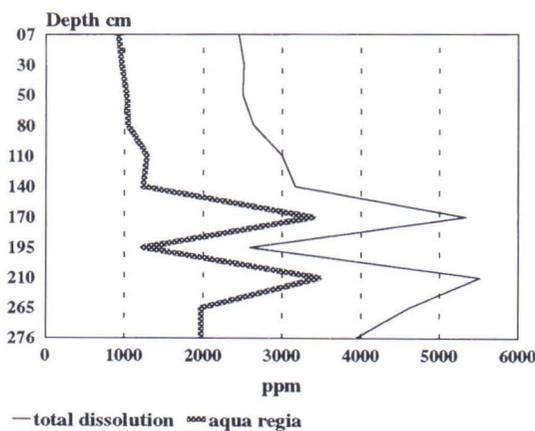
um soluble with aqua regia. These results indicate that the titanium was not derived from human sources.

4.2.3.2.3 Geological elements

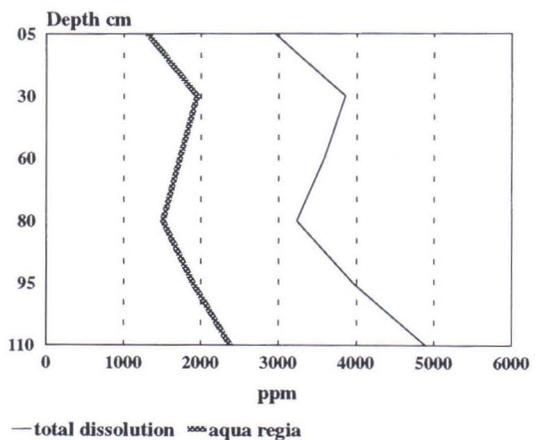
Aluminium. At Jätkäsaari there was, in total, 6.7-7.6 % aluminium in recent sediment and 8.7-10.1 % in glacial clays (Fig. 22). There was most aqua regia extractable aluminium in Salpausselkä stage clay. The aluminium concentration of aqua regia solution illustrates the amount of aluminium

contained in micas because aluminium bound to feldspar is nearly insoluble (cf. Koljonen 1992). In recent sediment, from the surface downwards, the aluminium component of aqua regia solution increases from 16 % to 23 %. Ammonium chloride extraction was not suitable as an extraction method for aluminium in the Jätkäsaari samples since aluminium was always under the 2.00 ppm detection limit. Ammonium chloride extraction may have caused precipitation instead of leaching since "acid rain" extracted aluminium concentrations were only below the detection limit (2.00 ppm) in recent sediment.

Titanium



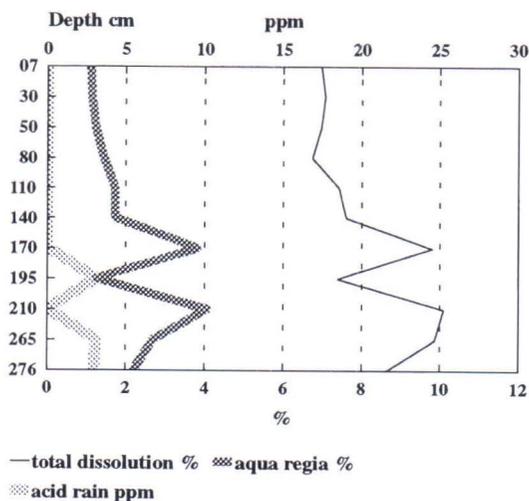
Sample 14/90



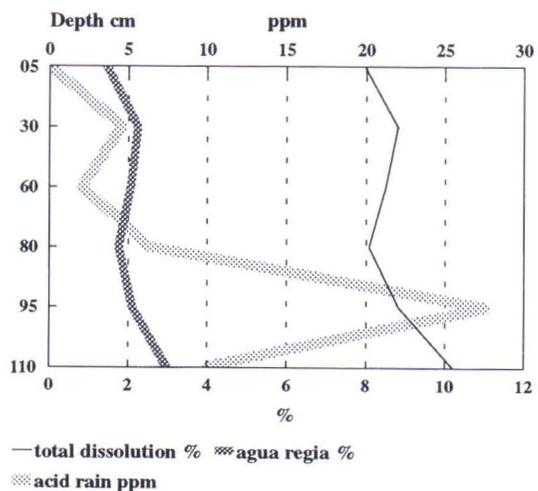
Sample 15/90

Fig. 21. Titanium concentrations in sediments from Jätkäsaari harbour.

Aluminium



Sample 14/90



Sample 15/90

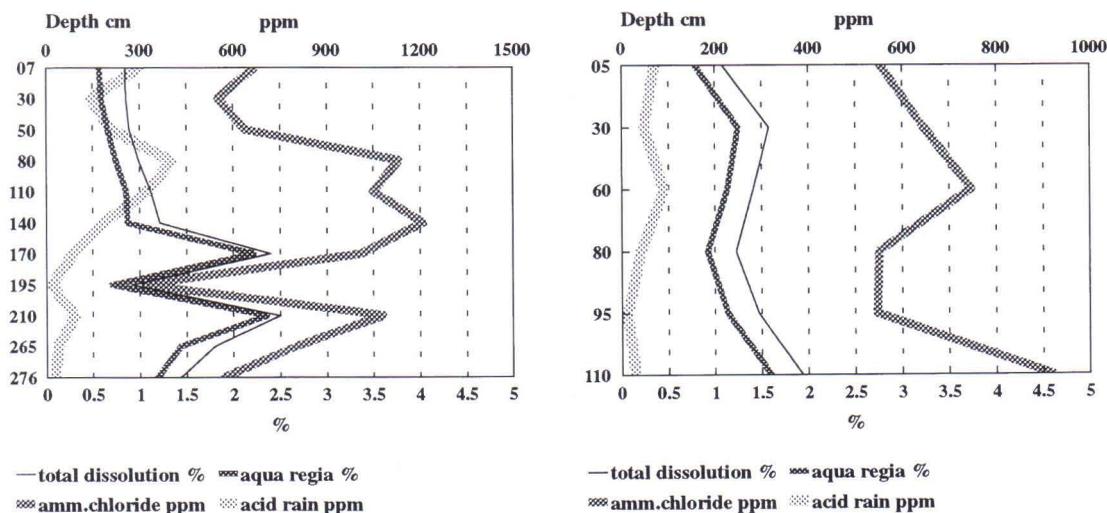
Fig. 22. Aluminium concentrations in sediments from Jätkäsaari harbour. The amounts of acid rain extractable aluminium are given along the upper axes of the graphs (ppm).

Aluminium was in Jätkäsaari's sediments nearly completely in a weakly dissolving form. Biotite, amphiboles, chlorite and anorthitic plagioclase weather easily (Wilson 1986 and Koljonen 1992) and contain conformably-behaving aluminium and calcium in analyses. This explains the high aluminium solubilities of glacial clays in comparison to recent sediments since there was more chlorite and biotite in glacial clay.

Magnesium. There was less magnesium (0.9-1.2 %) in recent sediment at Jätkäsaari than in the glacial clays (1.4-2.5 %) (Fig. 23). The Salpaus-

selkä stage clay was distinguished from homogeneous glacial clay by higher Mg-concentrations. With aqua regia, 82.5-94.4 % of the total magnesium was extracted from glacial clays and 67.1-76.8 % from recent sediment, in which there is a downward increase in both the total amount of magnesium and the percentage extractable with aqua regia. In comparison to the total concentration obtained with ammonium chloride extraction, relatively more magnesium (5.1-11.4 %) was leached from recent sediment than from glacial clay (3.4-4.7 %). From recent sediment, 0.7-4.1 % of the total amount of

Magnesium

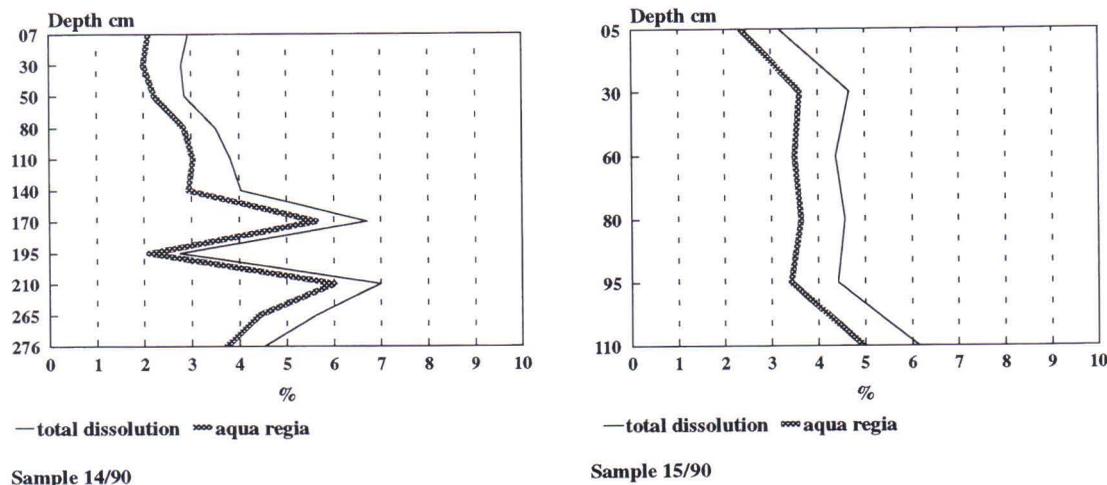


Sample 14/90

Sample 15/90

Fig. 23. Magnesium concentrations in sediment from Jätkäsaari harbour. Total dissolved and aqua regia extracted concentrations are given along the lower axes of the graphs (%). The amounts of magnesium obtained with ammonium chloride and acid rain extractions are indicated along the upper axes of the graphs (ppm).

Iron



Sample 14/90

Sample 15/90

Fig. 24. Total dissolved and aqua regia extracted iron concentrations in sediments from Jätkäsaari harbour.

magnesium was leached with "acid rain" extraction and 0.2-0.4 % from glacial sediment.

More magnesium leached with a weak extraction from the recent sediment with low total concentration than from glacial clay. Nickel and vanadium showed similar behaviour. In the glacial clays, magnesium was bound to mica and clay minerals. In recent sediment there was also magnesium soluble with "acid rain" extraction and clearly adsorbed to the surfaces of grains.

Iron. In Jätkäsaari's glacial clays iron was 4.5-7.0 % and in recent sediment 2.8-4.1 % (Fig. 24). The iron concentration of recent sediment corresponds to the background concentration of the northern part of the Gulf of Bothnia and the central Baltic Sea (cf. Enckell-Sarkola et al. 1989, Niemistö and Voipio 1974), but there are higher concentrations (4.4-7.0 %) in the glacial clays and in the chaotic middle unit at the western sample site. In recent sediment, aqua regia extracted iron was 71.5-81.2 % of the total amount; in glacial sediment 76.1-85.9 % (the lower value is for sand) and in the western sample' mixed unit 77.5-80.1 %. Salpausselkä stage clay leached with aqua regia extraction more iron than from other units. At Jätkäsaari iron that had been bound to the sediments was in practice insoluble with weak extraction.

Potassium. There was 2.0-2.6 % potassium in recent sediment, 2.9-3.6 % in glacial clay and 2.5-2.9 % in the western sample's mixed unit. Recent clay, Salpausselkä stage clay and homogeneous

glacial clay are distinguished from each other by the total concentration of potassium and on the basis of the potassium component obtained with aqua regia (Fig. 25). Aqua regia extracted potassium was 27-45 % of the total amount in glacial clay, 16.3-23.6 % in recent sediment and 24.1-28.6 % in the mixed unit. In the sedimentary series, there was a downward increase in the potassium component of recent sediment obtained with ammonium chloride and aqua regia solutions. Ammonium chloride leached potassium was on average 2 % (1.0-3.2 %) of the total concentration. The potassium component of "acid rain" solution, in relation to the ammonium chloride solution's potassium concentration, decreased with depth in the sedimentary series (46.2 % → 9.66 %, sample 14/90). This showed that potassium was more strongly bound in the older sediments.

Sodium. There was little variation in sodium total concentrations (1.7-2.0 %) in the Jätkäsaari sedimentary units (Fig. 26). Aqua regia extracted sodium was 9.6-21.3 % of total concentration in recent sediment and 13.7-28.7 % in glacial clay. Aqua regia extraction showed the glacial clay's sandy layer to be a weakly soluble unit (8.4 % of total concentration). By leaching with weak extractions there was more sodium in glacial clay than in recent sediment, especially in comparison to the upper unit of recent sediment. In Salpausselkä stage clay, sodium concentration and solubility were higher with both aqua regia and weak extrac-

Potassium

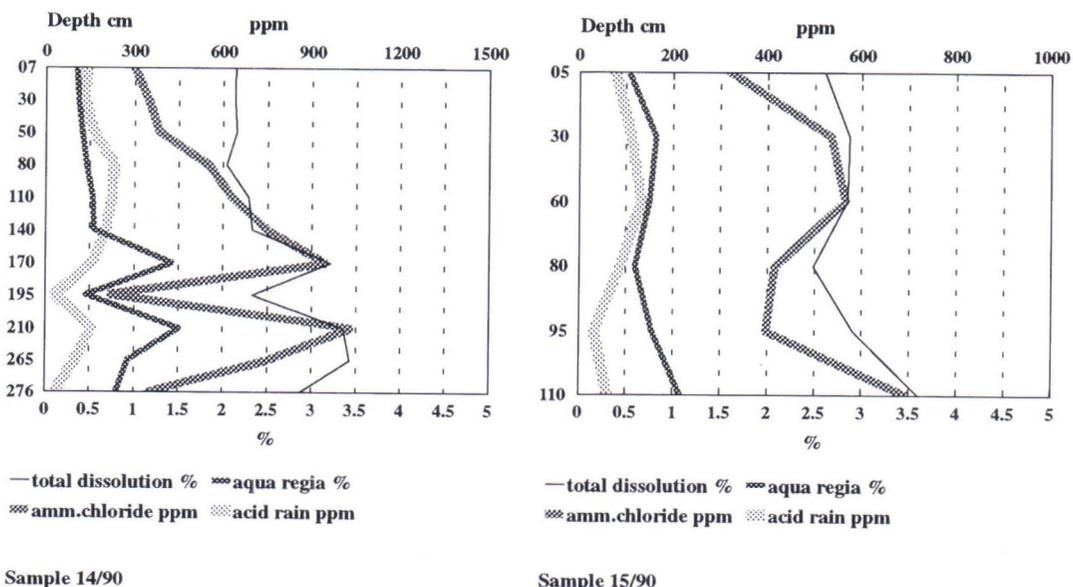


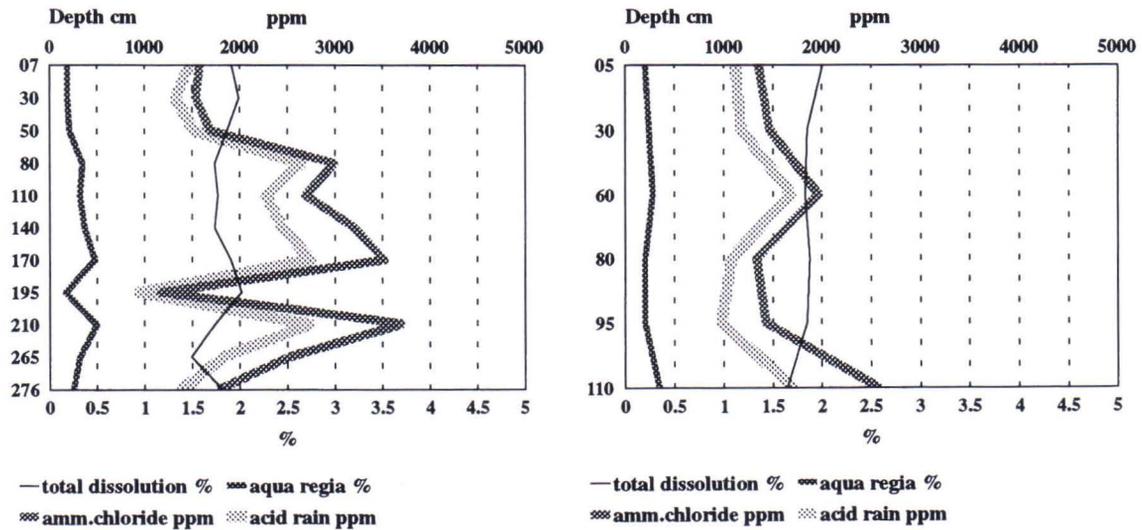
Fig. 25. Potassium concentrations in sediments from Jätkäsaari harbour. Total dissolved and aqua regia extracted concentrations are given along the lower axes of the graphs (%) and the amounts obtained from ammonium chloride and acid rain extractions along the upper axes of the graphs (ppm).

tions. Sodium generally remains in solution and is enriched in sea water. Due to its ease of solution, sodium concentration cannot be used alone as an indicator of a marine sedimentation environment.

Calcium. Recent materials and glacial clay were not distinguished at Jätkäsaari by total calcium concentration (1.1-1.5 %) (Fig. 27). In recent sed-

iment, aqua regia extracted calcium was under 30 % of the total concentration and in glacial clay over 30 %. Ammonium chloride extracted calcium was 3.1-8.8 % of total concentration in recent sediment and 6.0-11.7 % in glacial clays. "Acid rain" extracted calcium was 1.2 % (0.5-1.8 %) of total concentration in recent sediment and 0.6 % (0.3-

Sodium

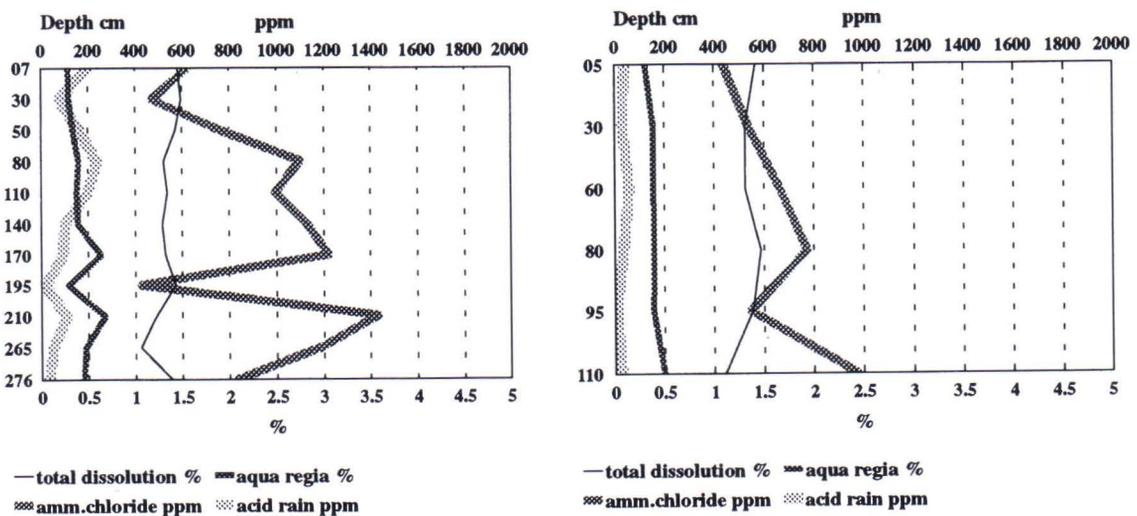


Sample 14/90

Sample 15/90

Fig. 26. Sodium concentrations in sediments from Jätkäsaari harbour obtained by various extraction methods. Total dissolved and aqua regia extracted concentrations are given along the lower axes of the graphs (%) and the amounts obtained from weak extractions along the upper axes of the graphs (ppm).

Calcium



Sample 14/90

Sample 15/90

Fig. 27. Calcium concentrations in sediments from Jätkäsaari harbour obtained with various extraction schemes. Total dissolved and aqua regia extracted concentrations are given along the lower axes of the graphs (%) and the amounts obtained from weak extractions along the upper axes of the graphs (ppm).

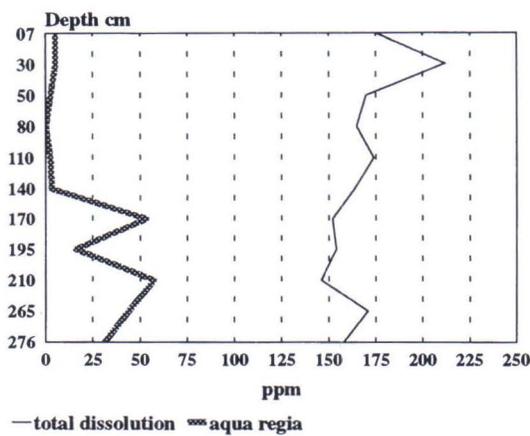
0.9 %) in glacial clays. In recent sediment, within the unit, the component of "acid rain" solution decreased with depth compared to the component obtained with ammonium chloride solution. Thus, calcium was more strongly bound to minerals and grain surfaces in the older sediments.

Zirconium. Recent and glacial sediments were distinguished clearly from each other based on the solubility of zirconium in aqua regia (Fig. 28). In the recent sediment of the

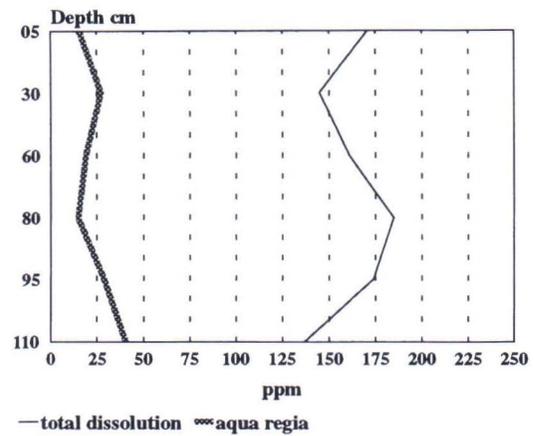
eastern sample, aqua regia extracted zirconium was < 15.7 ppm (0.1-3.0 % of total amount) and in glacial sediments 16.0-57.4 ppm (10.4-39.3 % of total amount). There is not a large difference in total concentrations between recent sediment (164-212 ppm) and glacial sediment (137-171 ppm). These levels correspond to the average zirconium concentrations in sediments from the Gulf of Bothnia (200 ppm, Boström et al. 1978).

The high zirconium solubility (9.2 %) of the western sample's surface sediment, obtained with

Zirconium



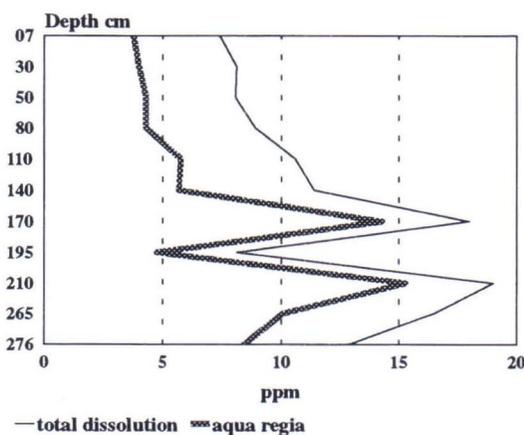
Sample 14/90



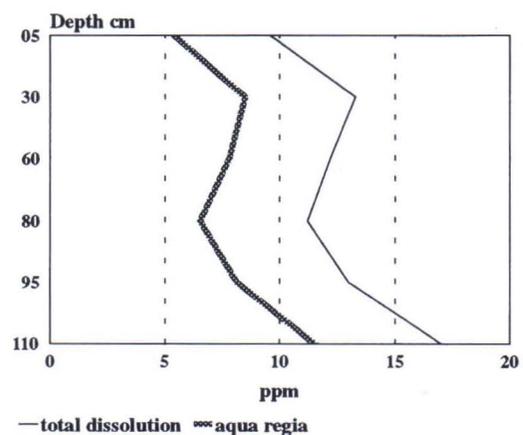
Sample 15/90

Fig. 28. Total dissolved and aqua regia extracted concentrations of zirconium in sediments from Jätkäsaari harbour. Aqua regia extracted component of zirconium concentrations were much higher in glacial clay than in recent sediment.

Scandium



Sample 14/90



Sample 15/90

Fig. 29. Scandium concentrations in sediments from Jätkäsaari harbour.

aqua regia solution from total concentration, is due to the mixing of glacial clay and recent sediment. This mixing has been a consequence of the more dynamic nature of the area and, thus, the glacial clay's characteristics have also affected the recent sediment's behaviour. The aqua regia solubilities of the Jätkäsaari samples were especially high in glacial sediments. However, zircon is one of the most weathering-resistant minerals (Koljonen 1992) and, consequently, the high aqua regia solubilities of Jätkäsaari's glacial sediments' zirconium's are difficult to interpret. Corrosion in aqua regia solution, for example, of crystal surface edges on the surfaces of old sediments' zircon grains may explain such high aqua regia solubilities.

Scandium. There was least scandium (7.4-11.4 ppm) in the recent sediment samples from Jätkäsaari and most in the Salpausselkä stage glacial clay (16.5-19.0 ppm) (Fig. 29). The adsorption of scandium by clays (see Koljonen 1992) was also seen in the Jätkäsaari sediments. There was least aqua regia extracted scandium in recent sediment (49.2-56.4 % of total amount) and most in Salpausselkä stage glacial clay (58.7-80.5 %). There was, in comparison to the total concentration, a high component of scandium in aqua regia solution, which showed that scandium was bound to micas that are easily soluble in aqua regia. Scandium concentrations above the detection limit were not obtained with weak extractions.

5. GEOCHEMICAL ANALYSES AND EVALUATION OF ANTHROPOGENIC COMPONENT OF ELEMENTS

5.1 Effect on results of extraction and analysis methods, geochemical environment and sedimentary character

Compared to total concentration, a larger element component was leached with aqua regia from the fine-grained sediments of Jätkäsaari harbour basin than from moraine fine materials (cf. Koljonen 1992). This disparity is explained by different mineralogy. In moraine, fine materials contain more minerals that are less soluble in aqua regia (amphiboles, pyroxenes, oxides etc.) than clays, in which there are abundant easily soluble micas (cf. Räsänen et al. 1992b).

A sediment's anthropogenic component is determined with weak extractions. This method only establishes those element components adsorbed onto minerals' surfaces and those element components that move in solution within grains interstices. Only one cadmium concentration was obtained that exceeded the reliable detection limit, in the recent sediment of the Jätkäsaari samples, with the analysis methods used at GSF for this research.

Changes that occurred during the processing of the sediment samples have been underestimated as such transformations can be significant if analysis was done a long time after sampling. The total element concentrations remain untransformed, but the way the elements are bound changes into an easily extractable form (e.g. Kersten and Förstner 1986, Förstner 1987). It is assumed that this has happened in the Jätkäsaari samples. The results are, nevertheless, important since they give hints about what may happen during transfer of the area's sediments to a more oxidizing environment (e.g. during dredging).

Alone, total analysis does not give a correct picture of the concentrations of human-derived elements in a sediment (Leoni et al. 1991). However, with extractions of varying strength, different amount of elements can enter solution depending on in which form the elements are bound to the sediment. Sequential extraction serie methods allow study of the way heavy metal concentrations were bound to sediment and estimation of the mobility of an element in chemical and biological processes (e.g. Hickey and Kittrick 1984, Räsänen and Hämäläinen 1991).

Elements can be divided into labile, easily mobile and non-labile and immobile types (Räsänen and Hämäläinen 1991). Easily mobile metals usually show human-derived contamination. Labile metals and elements (Fe, Mn, As, Cd, Pb and Zn) react quickly to changes in sedimentary environment, especially in polluted sediments (Enckell-Sarkola et al. 1989, Räsänen and Hämäläinen 1991, Erlström and Sivhed 1992).

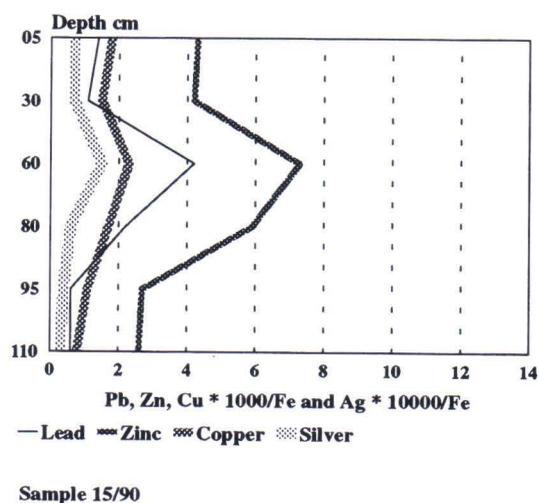
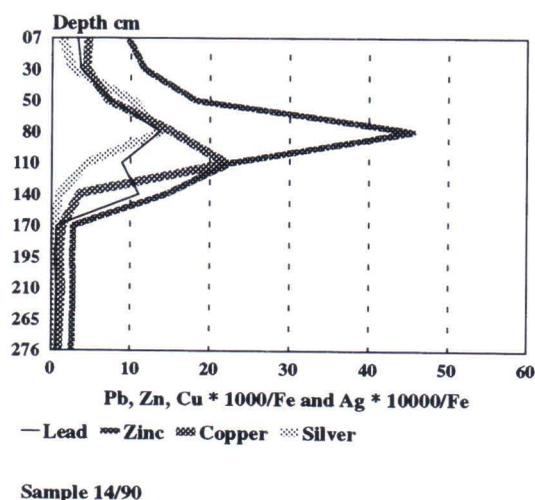
This research used "acid rain" extraction (pH=4.5) in determination of the most easily mobile element components. The components of elements, used by organism, were determined by ammonium chloride extraction. This leached from the sediment the elements' exchangeable ions, elements adsorbed onto the surfaces of sedimentary grains and metallic-organic compounds. In the Jätkäsaari sediments, ammonium chloride extraction leached only those element components that were bound to FeMn (hydr)oxides and mobile with

manganese. This was because manganese was leached from the sediment (under 6 % of total concentration) but iron was nearly immobile. The component of reasonably tightly bound elements was established with aqua regia extraction. This method leached element components that are bound to FeMn hydroxides and organic substances and mafic minerals (e.g. Räisänen 1989). The elements' total concentrations were determined with an HF-H₃BO₄ dissolution.

Selective sequential extraction analysis is clearly a practical method in analysing long term proc-

esses in contaminated sediments. However, this technique includes certain problems (Calmano and Förstner 1983): **1)** reactions are not necessarily selective, **2)** duration of extraction and the ratio of amount of material to amount of solvent affect extraction capability, **3)** in successive extraction processes, elements are re-adsorbed and precipitated and **4)** labile elements can stabilize during the procedure's progress. The concentrations of elements from the Jätkäsaari samples have always been analysed from different extractions and not from the material residues of successive extrac-

Element/Fe ratios



Element/Al ratios

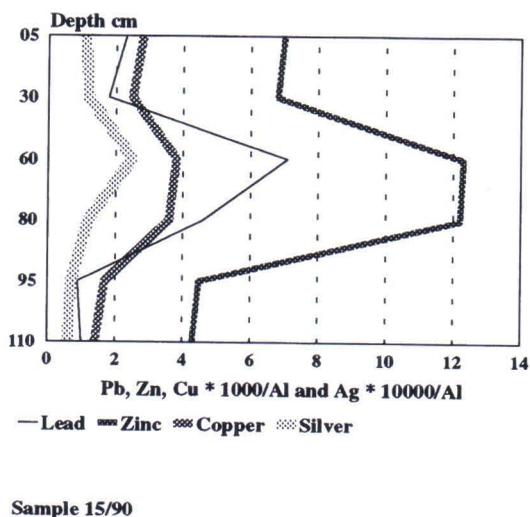
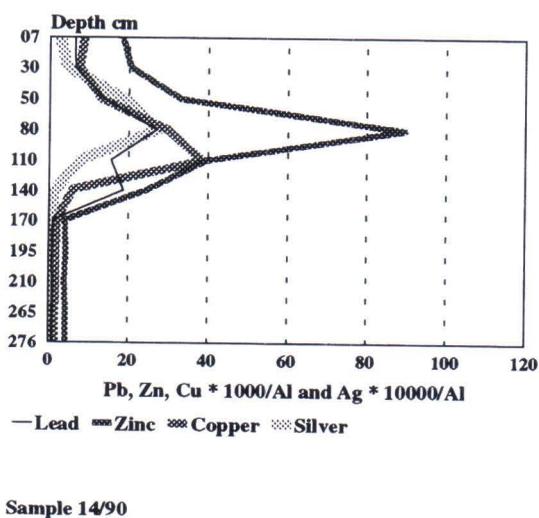


Fig. 30. Human impact on the geochemistry of recent sediment at Jätkäsaari was clearly shown after minimizing the "geological" variations in lead, zinc, copper and silver concentrations with metal/Fe and metal/Al ratios. All concentrations obtained by aqua regia extraction.

tions. The method makes it difficult to unravel the elements components bound to fractions of different solubility and to assess the long-term effects of different element concentrations. However, such

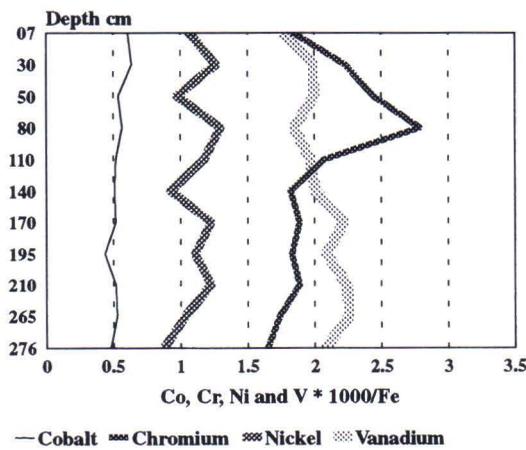
an approach attempted to avoid the formation of new compounds (minerals) during the analysis's progress.

5.2 Effect of grain-size and its compensation

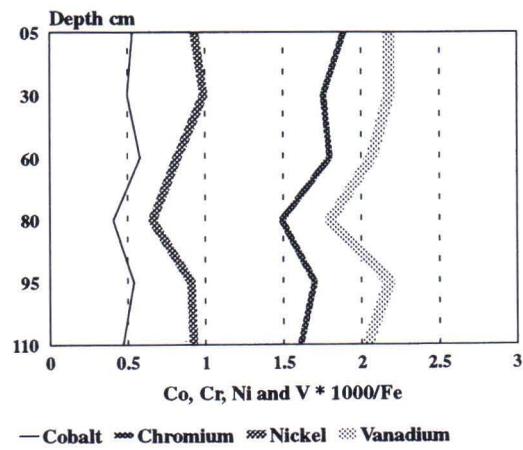
Most human-derived heavy metals are bound to fine-grained material (grain size < 0.63 μm) and transported in suspension. In such material, heavy metal concentrations correspond to the concentrations of fine-grained component of bottom sediment (Biksham et al. 1991). Anthropogenic impact

on the element concentrations in a sediment is shown more clearly in analyses of the element concentrations of fine-grained sediments than in those of bulk samples (Helmke et al. 1977, Castaing et al. 1986, Moore et al. 1989, Biksham et al. 1991, Leoni et al. 1991, Erlström and Sivhed 1992).

Element/Fe ratios

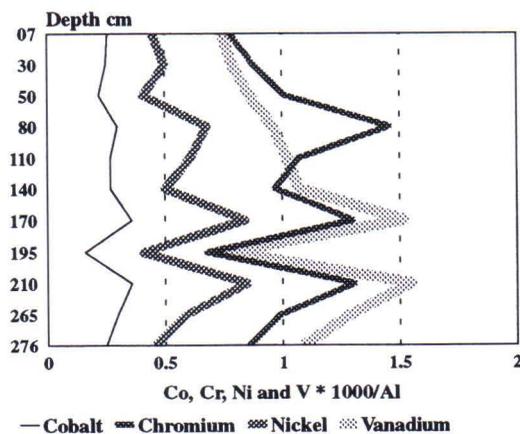


Sample 14/90

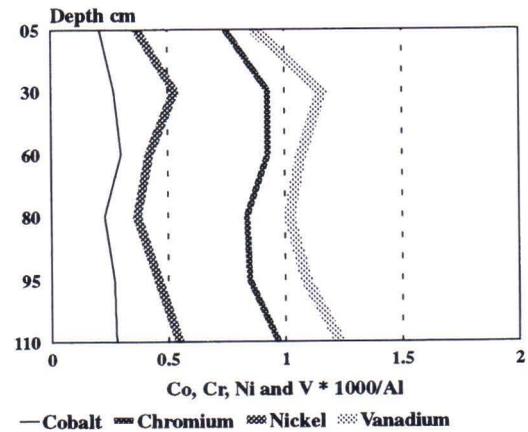


Sample 15/90

Element/Al ratios



Sample 14/90



Sample 15/90

Fig. 31. Element_{tot}/Fe_{tot} and element_{tot}/Al_{tot} ratios for cobalt, chromium, nickel and vanadium. Human impact on element concentrations was clear in chromium.

In coarse recent sediment at Jätkäsaari, there were higher heavy metal concentrations than in glacial clay, especially with weak extractions.

Grain size variation in the sedimentation basin caused a change in the sediments' element concentration levels (Biksham et al. 1991). The sediment's heavy metal concentrations are generally reduced when the grain size becomes coarser (e.g. Paetzel and Schrader 1991). A mutual comparison of heavy metal concentrations in sediments with dissimilar grain-size distribution requires correction for the grain-size effect (de Groot et al. 1982, Förstner and Wittman 1981, Helmke et al. 1977). However, grain-size compensation for originally coarse human-derived material can lead to completely wrong interpretation (Moore et al. 1989). Therefore, account should be taken of total element concentrations and their relationships to unpollut-

ed background material.

Figures 30 and 31 give the proportion to aluminium and iron concentrations of lead, zinc, copper, silver, cobalt, chromium, nickel and vanadium in recent and glacial sediments. Compensation for the effect of grain-size variation (see Fig. 6) from element concentrations led to similar results.

Chrome was enriched in relationship to aluminium both in the Salpausselkä stage clay and in the lower unit of the recent sediment. However, it was only enriched relative to iron in recent sediment (Fig. 31). Lead, zinc, copper and silver were enriched in recent sediment, especially its lower unit (Fig. 30). The proportion of heavy metal concentrations to aluminium and iron concentrations highlighted the human-derived component of heavy metals in comparison to unpolluted background concentrations.

5.3 Main geochemical features of the Jätkäsaari samples and evaluation of anthropogenic component

Comparison of element concentrations, established with different extraction methods, revealed the geochemical characteristics of the various units of the Jätkäsaari samples. Four dissimilar units were distinguished in the eastern sample (14/90). The sample's surface layer was the 30 cm thick upper unit of the recent clay. Concentrations of heavy metals, phosphorus, carbon and sulphur were remarkably high, between 30 cm and 144 cm in the recent clay's lower unit. The third geochemically dissimilar unit (between 157 cm and 275 cm) consisted of sediment that belongs to the lower part of Ancyclus-age clay or to the upper sequence of glacial clay, together with the Salpausselkä stage varved glacial clay (between 208 cm and 275 cm) and an overlying thin sand-layer (subsample from 195 cm). In the lower part of sample 14/90, between 275 cm and 300 cm, there was geochemically distinct and nearly homogeneous Yoldia stage glacial clay.

In the western sample (15/90) three sedimentary units were distinguished based on dissimilar geochemical characteristics. The recent clay unit (thickness between 10 to 20 cm) in the upper part of sequence was clearly distinguishable. Between the recent sediment and clearly glacial clay there was a unit (between 20 cm and 92 cm) with complex geochemical characteristics. In the lower part of sample 15/90, there was a clay unit between 92 cm and 117 cm. In this arsenic and sulphur concentrations (between 92 cm and 106 cm) corresponded to concentrations in the overlying mixed unit. The rest of the elements, however, behaved in the same

way as in the glacial clay between 106 cm and 117 cm.

In recent sediment, the ratios of aqua regia extracted component vs. total concentrations of elements (later given as aqua regia vs. total ratios and other extraction ratios) were lower than in glacial clay. Thus the aqua regia soluble components of elements, compared with total concentration, increased in older sediment. The aqua regia vs. total ratio was generally highest in the upper part of glacial clay, i.e. in the Salpausselkä stage's sediments (Fig. 32). Zirconium's aqua regia vs. total ratio in the glacial clay differed distinctly from the recent sediment's ratio (Fig. 32). The elements' aqua regia vs. total ratio varied between the separate units of one sedimentation cycle. The elements' solubilities in the glacial clay's sandy interlayer corresponded to the solubilities of coarse-grained (see Fig. 6) recent sediment.

The ratio of aqua regia vs. total concentrations was proportional to each others for iron, magnesium, cobalt, chromium, nickel and vanadium. The ratio had similar variation in different sedimentary units (Fig. 32). Aluminium and calcium also behaved similarly to each other (Fig. 32). The anthropogenic impact on the solubilities of zinc, silver and to some extent also of copper, was clearly shown in the ratio of ammonium chloride vs. aqua regia extractable element concentrations (Fig. 33). This ratio could be determined in recent sediments, but in the unpolluted glacial clays there were no ammonium chloride extractable zinc, silver and copper.

Aqua regia extracted part of element

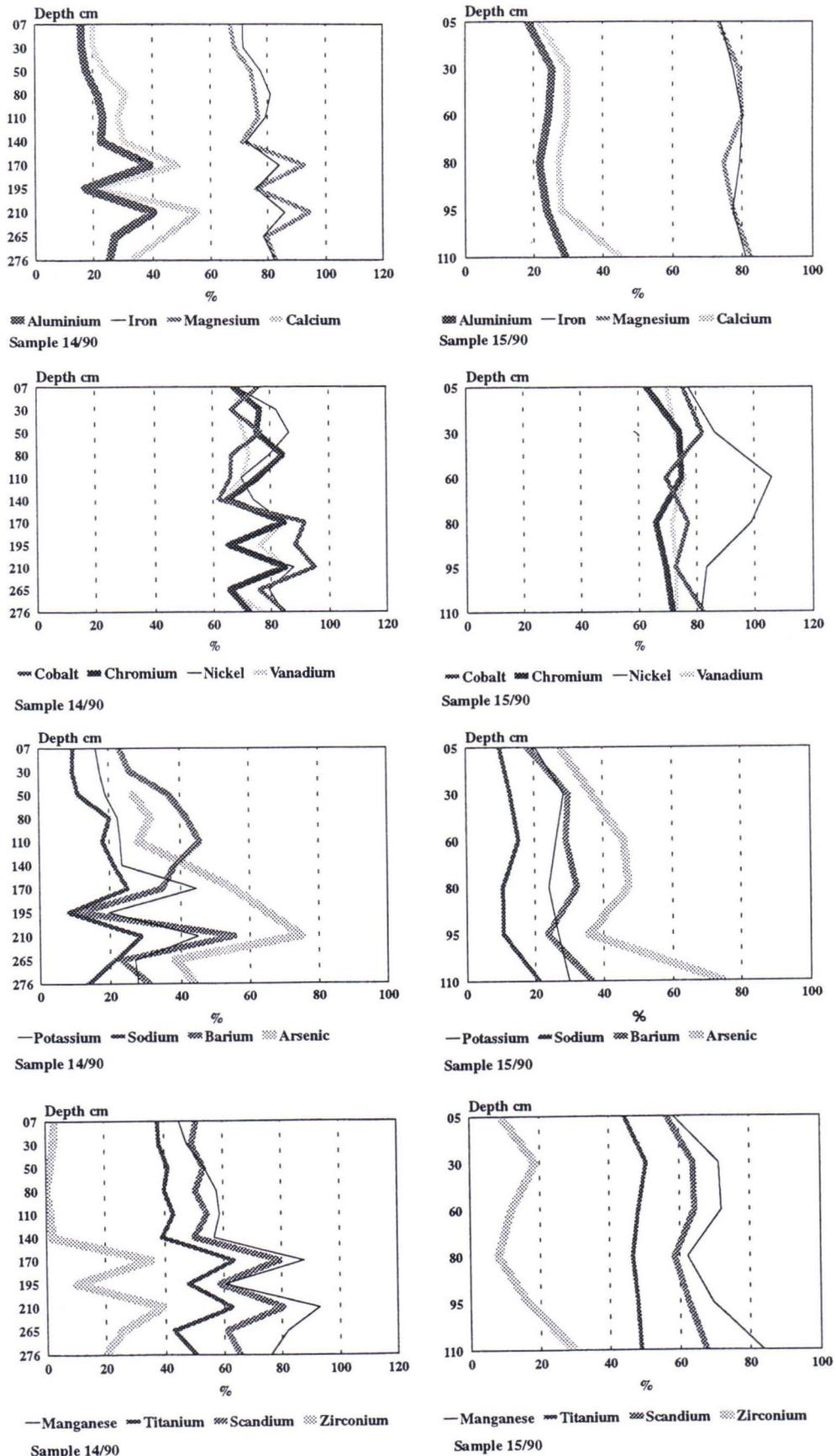


Fig. 32. Ratios of aqua regia extracted component vs. total concentrations of elements. These depend on the element species, mineral composition, grain-size distribution and age of sediments. Heavy metals were more easily extractable by aqua regia than other elements.

The ammonium chloride vs. total ratio of the elements changed only slightly for potassium, barium and vanadium in different sedimentary units. The ammonium chloride vs. total ratio for magnesium, cobalt and nickel was higher in recent sediment than in glacial clay (Fig. 34). Sodium and potassium behaved similarly to each other (Fig. 34). Manganese behaved differently to other elements because the ammonium chloride vs. total ratio was quite even except in the upper unit of recent sediment. Manganese solubility increased towards the surface where, in the surface layer of recent sediment, there was more easily soluble manganese in proportion to total concentrations (Figs 34 and 35).

Based on the results obtained by weak extractions, elements generally leached more easily from the recent sediment than from the glacial clay. This was shown especially well by the ratios of elements leached with acid rain vs. ammonium chloride extracted concentration. In the sedimentary sequence, these ratios decreased with depth. The most remarkable change occurred at the boundary between recent sediment and glacial clay (Fig. 35). In the Jätkäsaari samples the acid rain vs. ammonium chloride ratios of vanadium increased with depth in recent sediment, which was atypical behaviour. Acid rain vs. ammonium chloride ratio revealed that the human-derived components of elements were bound weaker to the sediment than elements' components that had originated from natural processes.

The recent sediment's element concentrations were mostly natural if the amounts of elements

corresponded to the area's background concentrations (Leoni et al. 1991). In the lower unit of the Jätkäsaari recent sediment, human-derived lead, zinc, copper, silver, cadmium, chrome and barium exceeded the background concentrations in glacial clay. These elements derived from atmospheric deposition and from waste water (cf. Niskavaara and Äyräs 1991). In the recent sediment at Jätkäsaari, concentrations of lead (33.8-391 ppm), copper (41.3-672 ppm) and zinc (102-1300 ppm) corresponded to, or were slightly higher than, proven heavy metal concentrations in contaminated fine-grained sediments elsewhere (esim. Leoni et al. 1991: Pb 51-97 ppm, Cu 34-50 ppm, Zn 111-194 ppm and As 24-38 ppm; see also Niemistö and Voipio 1981). The heavy metal concentrations in the Jätkäsaari recent sediment were as high as the concentrations found in intensively industrialized Central-Europe (cf. Salomons and Förstner 1984).

Phosphorus, sulphur and organic carbon concentrations exceeded background concentrations in the recent clay's lower unit at the sampling site 14/90. A granary and mill, situated close to the harbour basin at Hernesaari island, influenced the amount of organic material in recent sediment. The upper unit of recent sediment contains fewer concentrations of heavy metals than the lower unit, so that, because of diminished contamination, concentration levels were lower. A similar decrease in the concentration of heavy metals has been reported in the sediments at the northern part of the Gulf of Bothnia (Enckell-Sarkola et al. 1989).

The sedimentation rate of the Jätkäsaari recent sediment was assessed by division of the total

Ammonium chloride extracted part of element

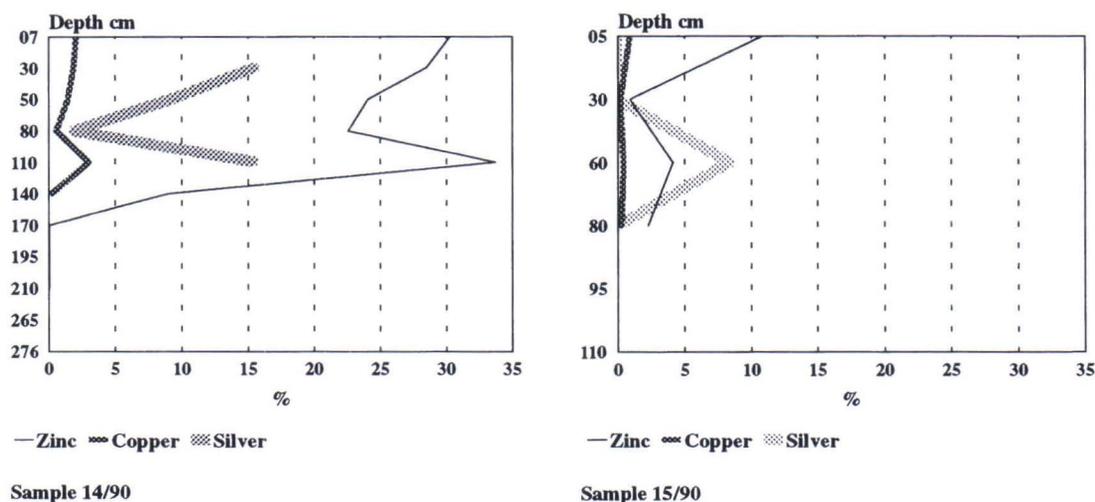


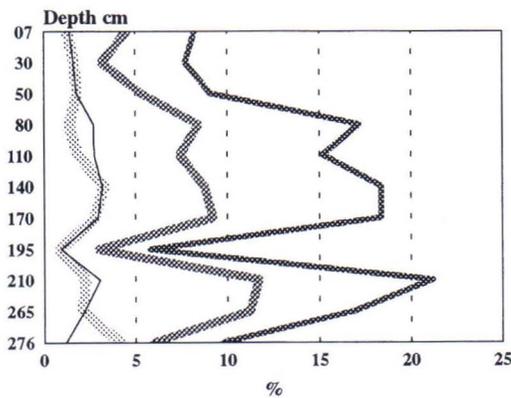
Fig. 33. Ratio of ammonium chloride vs. aqua regia extractable element concentrations for human-derived heavy metals in sediments from Jätkäsaari harbour.

thickness of the recent unit with the amount of time after dredging. This calculation did not take account all probable environmental processes (e.g. strong storm) that may have removed some previously deposited recent material. However, it gave an estimate that was clearly of the correct size. At the eastern sampling site, 14/90, the sedimentation rate was about 3 cm/year and at the more dynamic western sampling site 15/90 about 0.5 cm/year. Thus, the sedimentation rate in the Jätkäsaari harbour basin was higher than the Baltic Sea's average deposition rate of 0.1-0.7 cm/year (Boström et al. 1981, Niemistö and Voipio 1981). At the western sampling site, 15/90, exactly dated element concentrations could not be obtained from recent sed-

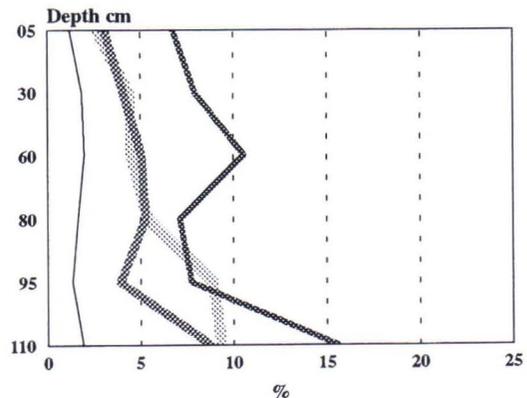
iments because this was a dynamic sea-floor area. Here, material may continuously mix, move back and forward in many directions and be transported from the basin.

The evolution of the Jätkäsaari harbour basin was primarily assessed from the eastern sample 14/90. This revealed very well changes in the element concentrations of recent sediment from the 1940s to until the present. Sample site 14/90 was dredged in the middle of the 1940s. The amount of organic material in clay deposited after this showed up in the analysis as high carbon concentrations. The highest carbon concentrations, which corresponded to the middle of 1960s, were 80 cm below the sediment surface. The present carbon concentra-

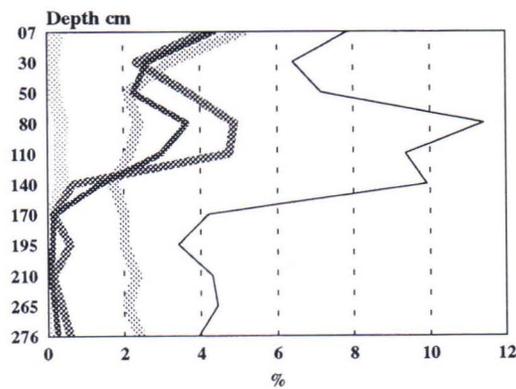
Ammonium chloride extracted part of element



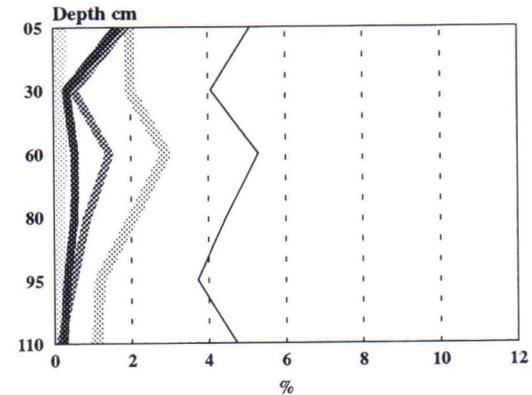
Sample 14/90



Sample 15/90



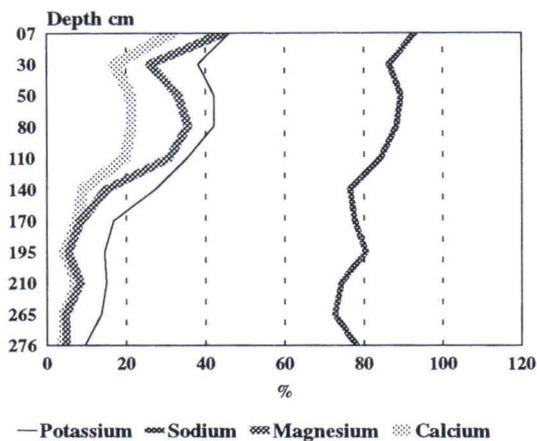
Sample 14/90



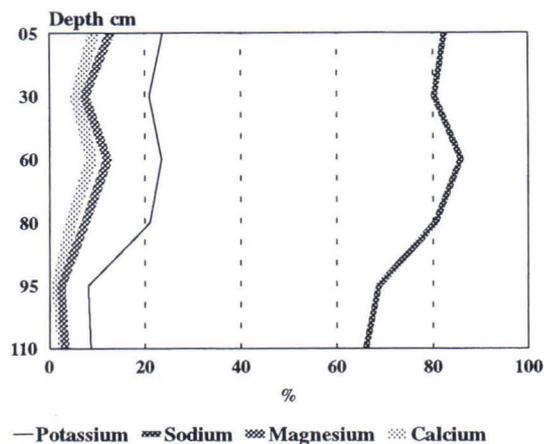
Sample 15/90

Fig. 34. Elements' ammonium chloride extracted vs. total concentration ratio in sediments from Jätkäsaari harbour.

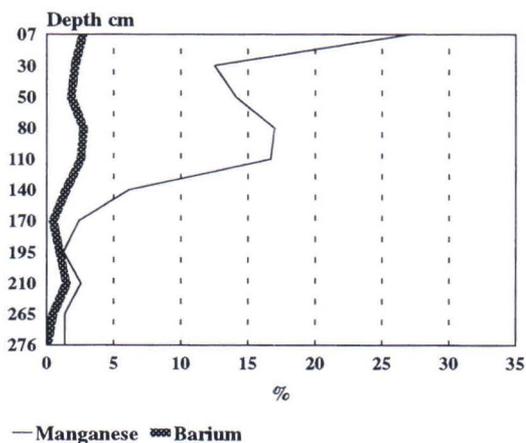
Acid rain extracted part of element



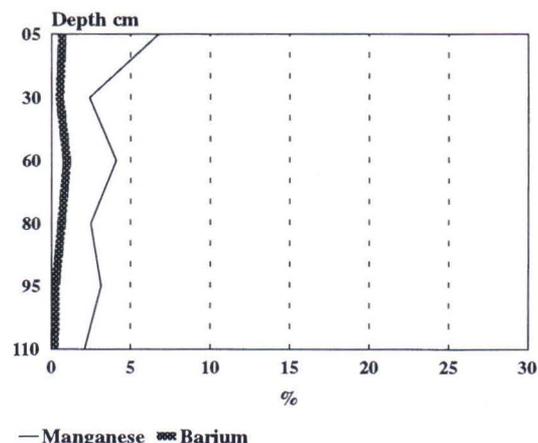
Sample 14/90



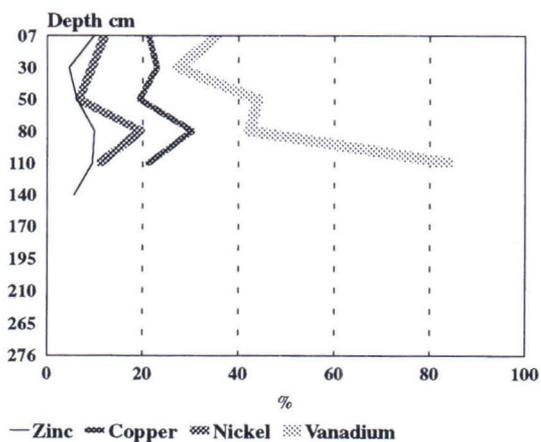
Sample 15/90



Sample 14/90



Sample 15/90



Sample 14/90

Fig. 35. Ratio of elements leached with acid rain vs. ammonium chloride extracted concentration in sediments from Jätkäsaari harbour. Elements leached more easily in recent sediment than in glacial clay.

tion is only 20 % of the earlier amount, but still four times higher than carbon concentrations in the glacial clays. The change in the concentrations of phosphorus and sulphur has been similar. Sulphur concentrations were up to 3 to 4 times higher than the concentrations determined in glacial clay, but the amount of phosphorus had decreased to the same concentration levels as in glacial clay. Carbon, phosphorus and sulphur concentrations decreased in the upper unit of recent sediment after the development of sewerage (at the beginning of 1980s) and conversion of the flour mill to a granary.

It could be concluded that the increased concentrations of lead, zinc, copper, silver and cadmium in the recent sediment are derived from the human sources. Since the beginning of the 20th century the surroundings of Jätkäsaari basin have been industrialized and the resultant emissions have increased heavy metal concentrations in the harbour basin's recent sediment. Lead, zinc and cadmium concentrations, unlike those of copper and silver, markedly increased immediately after dredging. At Jätkäsaari, copper concentration was highest 110 cm below the sediment surface. This concentration corresponded to deposition in the mid-1950s, after when the concentration decreased (at the turn of the 1970s and 1980s) to a near natural state level 30 cm below the sediment's surface. The decrease in copper concentration in the upper part of the recent sediment was a consequence of changes over the years in industrial activity and raw materials and of the construction of modern sewerage during the 1970s and 1980s. High lead, cadmium and copper concentrations had been typically derived from waste water effluents.

The highest amounts of zinc, lead, chromium, silver and cadmium, deposited in the mid-1960s, occurred at a depth of 80 cm below sediment's top surface. This result accorded with the view that most industrial emissions of heavy metals to the environment were in the 1960s (Enckell-Sarkola et al. 1989). A clear decrease in the sediment's heavy metal concentrations between 80 cm and 50 cm corresponds to the turn of the 1960s and 1970s when the use of lead-bearing paints in the shipyard ceased (Masa Yards, pers. comm. 1993). Heavy metal concentrations further rapidly decreased to a depth of 30 cm, corresponding to the turn of the 1970s and 1980s, and remained after that period at a level about twice as high as in the glacial clay. The lead concentration was different from that of other heavy metals since it had already increased during dredging in the middle 1940s. The decrease in heavy metal concentrations in the upper part of the recent sediment were a consequence of changes

over the years in industrial activity, in production and raw materials. Further, the lead concentration in the upper part of recent sediment reflects decreased lead from car exhausts.

A rubbish dump sited in the middle part of Hernesaari island to the southeast of sampling site 14/90, until the beginning of 1960s, did not affect the element concentrations of presently deposited material (cf. Assmuth et al. 1991). Instead, heavy metals leached from a dump in use (Assmuth et al. 1991) may have entered sediment deposited then. In recent sediment at Jätkäsaari, in samples of 1950s and 1960s age, the soluble component of heavy metal concentrations were influenced by dumping of, for example, zinc, copper, chromium and lead. The amounts of heavy metal leached from the dump were generally low compared to industrial emissions, but the effect may have been significant near the dump (Assmuth et al. 1991).

Weak extraction vs. total dissolution ratios for chromium, nickel and cobalt concentrations showed that metal concentrations in the lower unit of the recent sediment contained a small additional human-derived component. Chromium, nickel and cobalt concentrations correspond to those in glacial clay in sediment deposited at present. The arsenic concentration has increased in the lower unit of recent sediment. Based on the Jätkäsaari samples, zinc, copper, lead, barium, cobalt, magnesium and sulphur were enriched in clays. In the recent sediment there was an "acid rain" extractable component of anthropogenic zinc, which could have easily mobilized if the sedimentary environment had changed, e.g. during the dredging or dumping.

Carbon and phosphorus concentrations from the western sample, 15/90, showed that it was a sedimentary unit, below the recent surface layer, composed of mixed recent sediment and glacial clay. This interpretation was supported by, e.g., Ag, Al, Ni, Mn and Zn concentrations determined with weak extractions. In the mixed sedimentary unit of the western sample, the human-derived influence was greatest 60 cm below the sediment's surface. In this mixed unit, element concentrations were generally between those of recent sediment and glacial clay while being closer to the glacial clay's concentrations.

In the surface part of sample 15/90, the aqua regia extracted zirconium concentration was 9.2 % of total amount, which inferred that in this area there was regular mixing of glacial clay (solubility 10.4-39.3 %) and recent material (solubility 0.1-3.0 %). A side scan sonar image (Fig. 2) revealed the difference in dynamic conditions between the western (15/90) and eastern (14/90) sampling sites.

The sea-floor of the western sample's area undulated (due to ships propeller current) while the sea-floor of the eastern sample's area was smooth. Maximum enrichments of heavy metals is typical of low energy basins (Leoni et al. 1991). Thus, the low anthropogenic component of the western sample's elements was a consequence of dilution caused by mixing of glacial clay and recent sediment.

In the Salpausselkä stage clay, there were more potassium, sodium, aluminium, iron, titanium and magnesium than in the homogeneous glacial clay. Further, trace elements indicated higher amounts of manganese, copper, chromium, cobalt, lead, silver, vanadium, zinc, nickel, scandium and phosphorus than in the homogeneous glacial clay. During the Salpausselkä stage, saline marine water possibly transgressed the coast of southern Finland (cf. Kotilainen 1991). There were higher chromium, cobalt, nickel and zinc concentrations in the Salpausselkä stage clay than in the homogeneous glacial clay. These differences support the idea of a marine transgression since average concentrations in marine clays correspond to those in the Salpausselkä stage clay and lower concentrations in homogeneous glacial clay correspond to those of fresh water clays (cf. Wedepohl 1969, 1970, 1972, 1974, 1978).

Trace element concentrations in the Jätkäsaari glacial clay were comparable to background concentrations in the Gulf of Bothnia and central Baltic Sea sediments (see Niemistö and Voipio 1981, Boström et al. 1978, Enckell-Sarkola et al. 1989). In material being presently deposited at Jätkäsaari, the total concentrations of lead, zinc, copper, silver and cadmium were near to those of natural state glacial clay. However, especially in the recent sediment's lower unit, these element concentrations distinctly exceeded the geological background concentration. Good correlations of major and trace elements suggests that both were incorporated in mica and clay mineral lattices (Räisänen et al. 1992b). At Jätkäsaari, major elements and heavy metals in recent sediment behaved differently from each other so that the heavy metal concentrations of the sediment also affected by human sources.

According to Verta et al. (1989), the magnesium-, potassium- and sodium concentrations of sediments increased in southern Finland because of atmospheric transportation. There was no evidence for this phenomenon in the Jätkäsaari sediments, but depositing material contained even less of these elements than natural state glacial clay. The variation in magnesium, potassium and sodium concentrations in the Jätkäsaari sediments arise from geological factors. This is because these elements

belong to the sediments' major elements, in which the natural variation of concentrations was quite wide compared to the amount of atmospheric deposition.

In southern and central Finland, lead, zinc, cadmium and mercury from human sources make over 50 % of the heavy metal load that accumulates in sediments (Verta et al. 1989). Further, the lead, zinc, copper, carbon and sulphur concentrations in the Jätkäsaari surface sediment exceeded glacial clay's natural concentration level and variations caused by geological factors. According to Verta et al. (1989), the greatest part of lead, zinc, cadmium and mercury concentrations derive from atmospheric long-range transport. At Jätkäsaari long-range transport has not been an important factor because local emissions have greatly affected the concentrations of elements. This fact is shown by the distinct change in element concentrations over time that happened at nearly the same time as changes in industrial activity, production and raw materials.

A maximum in zinc concentration below the surface layer may be caused by the downwards transportation of element in oxygenous sediment and subsequent precipitation in anaerobic sediments (e.g. Carignan and Tessier 1985, Tenhola 1988, Verta et al. 1989). This type of diffusive maximum for zinc was not found with the subsampling interval used at Jätkäsaari. Instead, the lower concentration of zinc in the upper unit of recent sediment was explained to be a consequence of decreased human-derived deposition (cf. Rühling et al. 1987). In an environment, where conditions varied between aerobic and anaerobic, interpretation of element concentration based only on analysis of surface sediments must take account of the diffusive movement of elements (e.g. manganese in the Jätkäsaari's recent sediment).

Aqua regia extracted element concentrations were too high for estimating the bioavailability of elements (cf. Koljonen and Malisa 1991) since some minerals dissolved completely in aqua regia (Räisänen et al. 1992b). Element concentrations obtained with weak extraction show better which portion of the total concentration of elements is bioavailable (e.g. Hickey and Kittrick 1984). Elemental mobility and bioavailability fall in nearly direct relation to decreases in solubility (Harrison et al. 1981). Based on element mobility, bioavailability decreases in the order $Cd > Zn > Cu = Ni$ (Hickey and Kittrick 1984). From chemical character and biological effectiveness, the elements most hazardous to the environment were As, Cd, Hg, Co, Cr, Cu, Pb, V, Mn, Zn, Ni, Sn, Sb and Se. Of these, the most important are arsenic, cadmium and mer-

cury since these are easily mobile elements and very toxic for organisms (Koljonen and Malisa 1991, Kubin 1991, Erlström and Sivhed 1992). Low water salinity promotes the uptake of metals and makes them more toxic for organisms (Enckell-Sarkola et al. 1991).

Based on element mobilities recent sediment and glacial clay in the Jätkäsaari samples differed significantly from each other. In the glacial clay, high total concentrations of metals caused by geological factors were not hazardous for the environment because the elements were bound tightly to the sediment. Elements remobilized more easily from the recent sediment and mobilities decreased in the order zinc → magnesium → silver → manganese → copper → nickel → cobalt. The mobilization of lead could not be assessed from the Jätkäsaari sediments. A relatively low concentration of an element's human-derived components could be hazardous for the environment since this part of elements are easily soluble (e.g. Förstner 1987, Räisänen and Hämäläinen 1991). The behaviour of zinc and cadmium was an exception to this since these have varying mobility even in a natural state environment (Sandström 1984, Enckell-Sarkola et al. 1989, Räisänen and Hämäläinen 1991). Lead and chromium are tightly bound in the sediments and copper only slight weaker (e.g. Salomons and Förstner 1984, Enckell-Sarkola et al. 1989). This was also the case at Jätkäsaari.

Copper, nickel and zinc generally occur in ion

exchangable form, but only in minor concentrations, and thus are easily introduced to vegetation (Hickey and Kittrick 1984, Elsokkary and Lång 1978, Tessier et al. 1980, Harrison et al. 1981, Miller and McFee 1983, Kuo et al. 1983). At Jätkäsaari, there were only zinc and minor amounts of silver, nickel, magnesium and cadmium in moderately easily mobile forms (ammonium chloride and/or acid rain extractable). In recent sediment there was a component of copper and zinc either absorbed onto the surface of grains, or bound to organic substances. There was also clearly some lead, zinc, copper, cobalt, nickel and iron in sulphides and Fe-Mn (hydr)oxides, all which were generally easily soluble in aqua regia.

Comparison of the geochemical composition of samples collected from the Jätkäsaari harbour basin to the geochemical composition of surface samples collected from nearby marine bay areas (tables 5 and 6) revealed similarities and differences. Lead concentration in the upper unit of the harbour basin's recent sediment corresponded to lead concentration in the surface sediment of nearby bays. However, in the lower unit of recent sediment lead concentration was considerably higher. Lead concentrations in the natural state glacial clay were only half of the concentration determined from depositing material. Zinc concentrations in the surface sediment in the nearby marine bay areas were of the same level or slightly lower than zinc concentrations in the harbour basin's sediments.

Table 5. Sampling sites (HWWA) near Jätkäsaari harbour, and the matter type of samples (Varmo 1988). L.O.I. = loss of ignition.

Sample station	Depth m	Coordinates	Matter	L.O.I. %	Location
38	28.5	6668.60-554.60	(clay)	4.2	Vallis. S
44	22.0	6670.52-553.85	mud/clay	9.3	Harakka SW
54	14.0	6669.52-550.60	mud/clay	3.0	Pi/Melk vä
55	20.0	6668.31-550.50	(sand)	2.0	Melkki SE
61	8.0	6667.72-561.50	(clay/mud)	6.2	Lauttas. E
62	10.5	6671.25-550.18	clay/sand	3.3	Lauttas. E
63	10.5	6672.15-550.00	mud/clay	5.8	Lauttas. E

() = FeMn concretions in the sample

Table 6. Sampling sites (HWWA) near Jätkäsaari harbour and heavy metal concentrations in surface sediments (Varmo 1988). TS= dry weight.

Sample station	Pb ppm mg/kg (TS)	Zn ppm	Cd ppm	Co ppm	Cu ppm	Cr ppm	Mn ppm	Fe ppt g/kg(TS)
38	82	96	1.4	10	41	21	140	15
44	76	190	2.9	21	58	69	380	37
54	40	83	1.3	10	41	30	120	16
55 sand	23	49	1.0	9.3	16	20	110	13
61	97	200	2.5	19	220	58	220	33
62	43	97	1.7	13	46	34	140	18
63	73	170	2.0	19	76	59	210	31

Cadmium amounts in the surface sediments of the nearby marine bay areas were higher than concentrations in the natural state glacial clay, but lower than concentrations in the Jätkäsaari recent sediment. At Jätkäsaari, the highest amounts of cadmium were in the lower unit of recent sediment, but cadmium concentrations decreased towards the sediment's surface. Copper concentrations in the eastern sampling site were higher, especially in the lower unit of recent sediment, than in the surface sediments of nearby bay areas. Copper concentrations in the sediments of the western sample and nearby marine bays were only slightly higher than

the natural state concentration.

The cobalt and chromium concentrations of surface sediments near Jätkäsaari harbour correspond to those of the Jätkäsaari sediments, which infers that the most of the concentrations were derived from natural sources. Manganese concentrations in the surface sediments of nearby marine bays were significantly low compared to the concentrations in Jätkäsaari sediments. This difference was a consequence of the dissimilar extraction methods used by GSF and HWWA. Iron concentrations correspond to each other in the surface sediments of nearby bays and in the Jätkäsaari harbour basin samples.

6. CONCLUSIONS

Geosciences can significantly contribute to research on environmental changes. Environmental studies from unpolluted and older sediments correctly shown the condition that prevailed in an area before impact by human activities. The latter may have changed environmental conditions and been hazardous for nature (Salminen 1991). Emissions to the environment caused by human activity were usually short-lived and peaked in character (e.g. sea dumping, occasional peak-load of waste water). It is difficult to assess the environmental impact of such emissions only by monitoring element concentrations in water because changes in that medium are rapid (Paetzel and Schrader 1991).

Natural geological factors concentrate heavy metal amounts and can result as high deposition rates usually considered to be human-derived (cf. Salminen 1991, Paetzel and Schrader 1991). Therefore, the study of surface samples alone can lead to erroneous conclusion if results was not compared with conditions in the natural state. Following definition of natural background processes, it is possible to assess human impact on geological processes and compare their intensity to natural events.

At Jätkäsaari, by comparison with natural state glacial clay, changes within the recent sediment after the construction of the harbour basin were examined. The grain-size distribution and element concentrations of recent sediment differed from those of glacial clay. Variations in element concentrations in the recent sediment were explained by changes to anthropogenic sources during deposition, changes in the amount of the human-derived component of elements, the varied distance of sampling site from emission sources and by chemical processes operative at the water/sediment interface (affecting manganese).

This study showed that the concentrations of elements and their form of binding to the sediment could be easier examined with separated extractions than with the selective sequential extraction method. This approach avoided changes, during extraction, in the way elements were bound to sediment. A useful selection of separated extractions is as follows: HF-H₃BO₄ total dissolution, aqua regia partial extraction, nitric acid partial extraction, hydroxylamine hydrochloride or ammonium oxalate extraction and ammonium acetate extraction. The subsamples from the sedimentary core had to be a little larger in volume because they were split to numerous separated initial samples for every extraction. However, this larger subsample (by volume) was not too large to take, compared to ordinary subsample, because modern analysis methods permit use of small initial samples. In environmental research, in the routine analysis of sediments aqua regia extraction and ammonium chloride extraction, or an equivalent, may represent applicable strong and weak leaches respectively.

In the Jätkäsaari samples, separate units were clearly distinguished from each other based on applied extraction methods (hydrogen fluoride-boric acid total dissolution, aqua regia partial leaching, ammonium chloride weak extraction and "acid rain" weak extraction). The impact of human activity was distinct in recent sediment compared to natural state glacial clay. The method detected changes in the human-derived element concentrations during the deposition of recent sediment and the effect of dynamics on element concentrations in the sedimentation basin. In the glacial clay sequence, different units were discernible based on the concentrations and solubilities of elements.

In recent sediment, using total dissolution or aqua regia extraction, there were usually more

lead, zinc, copper, silver, (cadmium), phosphorus, carbon and sulphur than in glacial clay. The natural state glacial clay, and especially the Salpausselkä stage unit that belongs to upper part of the glacial sequence, usually contain more aluminium, iron, magnesium, cobalt, chromium, nickel, manganese, titanium, vanadium and scandium, obtained by total dissolution, than recent sediment. Based on total dissolution, calcium, sodium, potassium, barium, arsenic and zirconium were distributed evenly between the different sedimentary units.

The ammonium chloride vs. aqua regia extracted concentration ratio was determined for only zinc, copper and silver since the ammonium chloride vs. total concentration ratio could not be calculated for these elements. Based on ammonium chloride vs. aqua regia ratios, recent sediment was distinguished from glacial clay, in which this ratio could not be determined because its ammonium chloride solubilities were below the detection limit. The differences between recent and glacial sediment were emphasized by zinc since, with ammonium chloride solvent, even 34 % of the aqua regia soluble amount of zinc could be extracted from the recent sediment.

Recent and glacial sediments were clearly different based on the ratio of ammonium chloride extracted vs. total concentration. Ammonium chloride vs. total concentration ratios for potassium and

vanadium behaved quite evenly throughout various sediment units. The ammonium chloride vs. total concentration ratio for manganese was the same except in the surface layer of recent sediment. One cause of the exceptional behaviour of manganese compared to other elements was its solubility in a reducing environment and its consequent mobility in the direction of chemical potential towards the oxidizing surface of the reducing sediment.

The ratios of ammonium chloride extracted vs. total concentration for manganese, cobalt and nickel clearly decreased from recent sediment to glacial clay. The ratio of "acid rain" vs. ammonium chloride extractable concentrations proved that there were more easily soluble elements in recent sediment than in natural state glacial clay.

The effect of different grain-size distribution in recent sediment and glacial clay on the heavy metal concentrations of sediments were compensated by normalization of these concentrations in proportion to the sediments' iron and aluminium concentrations. This treatment emphasized differences in heavy metal concentrations between recent and glacial sediments. Human emissions most clearly affected the lead, zinc, copper and silver concentrations of recent sediment. Besides, slight human impact was shown in the recent sediments' chromium and barium concentrations.

7. SUMMARY

In environmental assessment it is essential to conduct a comprehensive geochemical survey of the sediments, which reveals all chemical changes in the sedimentary sequence that took place even before human activity affected the sediments' elemental concentrations. The survey must include methods with which it is possible to determine accurately chemical features of elements in the sediment. This is because the elements' chemical character and their form of binding to the sediment are crucial when assessing the importance of elements for environment. Accurate examination of the trace element geochemistry of sediments can also help us in interpretation of the original natural state deposition conditions of the sediments. Such a study must take account of differences in the grain-size distribution between and within sediments since those may cause variation in element concentrations. However, they can be compensated for by, for example, normalization of heavy metals concentrations in proportion to aluminium and/or iron concentrations.

The present study suggests that the natural con-

centrations of heavy metals may be higher than elements' concentrations derived from human emissions. Thus, it is very important to know the natural background concentration of an element in the area under investigation and not only carry out a routine analysis using total concentrations.

High, but natural, concentrations of heavy metals in the sediments were not generally hazardous for environment since the greater parts of natural element concentration were tightly bound in the sediments. However, the human-derived component of heavy metals was usually in an easily mobile form and thus moderate total concentration of elements may be environmentally hazardous, if the elements' chemical state was dangerous to organisms.

In Jätkäsaari's recent sediment and glacial clay, the analysis methods used showed clear differences between the concentrations and binding forms of elements. In the recent sediment there were more lead, zinc, copper, silver and cadmium. From comparison with background concentrations in natural state glacial clay, these are clear consequence of

human impact. Further, there were some nickel, cobalt and magnesium in easily mobile forms in the recent sediment, unlike in glacial clay.

In recent sediment, the easily soluble part of heavy metal concentrations could remobilize if there was a change in the sediments' geochemical environment (e.g. caused by dredging). This is because the human-derived part of the concentrations of elements remobilized more easily than

those of elements in natural state glacial clays. The decreased concentrations of harmful elements in depositing materials, compared to material deposited in the 1960s and 1970s, reflect changes in industry, its working methods, in sewerage and in raw materials (paints and unleaded fuel). Thus, all improvements in the control of effluents from industry, traffic and human activity have led to an amelioration of pollution problems in a short period of time.

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Appendix 1. Element concentrations in sediments from Jätkäsaari harbour. 312P = total dissolution, 511P = aqua regia extraction, 202P = ammonium chloride extraction, 206P = acid rain extraction, 810L = Leco-sulphur analyser and 811L = Leco-carbon analyser. ! = concentration of element is below reliable detection limit.

Sample index	Pb	Zn	Cu				Ag			C		S
	ppm 511P	ppm 511P	202P	206P	ppm 511P	202P	206P	ppm 511P	202P	206P	% 811L	% 810L
14/90/07	70.2	203	61.5	6.17	96.2	1.97	0.42	2.82!	0.71	0.02!	1.37	0.50
14/90/30	74.8	234	66.8	3.14	87.5	1.61	0.37	5.17	0.80	0.02!	1.41	0.41
14/90/50	168	408	98.3	6.13	161	2.28	0.44	23.2	2.14	0.02!	1.93	0.64
14/90/80	391	1300	294.0	29.3	433	2.37	0.72	39.6	0.75	0.03	6.12	1.59
14/90/110	270	683	244.0	23.4	672	20.4	4.32	13.9	2.14	0.02!	3.74	1.41
14/90/140	324	424	38.1	2.20	106	0.25	0.47	2.94!	0.08	0.02!	4.76	1.39
14/90/170	39.3	158	0.03	0.01!	76.0	0.04!	0.04!	2.19!	0.13	0.02!	0.35	0.13
14/90/195	10.7	56.8	0.02	0.01!	23.9	0.04!	0.04!	0.94!	0.07	0.02!	0.09	0.08
14/90/210	39.3	168	0.02	0.01!	77.9	0.04!	0.04!	2.99!	0.08	0.02!	0.36	0.16
14/90/265	27.4	120	0.01!	0.01!	46.9	0.04!	0.04!	1.76!	0.08	0.02!	0.30	0.14
14/90/276	20.7	97.4	0.01!	0.01!	34.5	0.04!	0.04!	1.41!	0.09	0.02!	0.16	0.09
15/90/05	33.8	102	11.1	0.03	41.3	0.37	0.04	1.57!	0.37	0.02!	0.42	0.13
15/90/30	40.3	153	1.40	0.01!	56.1	0.09	0.09	2.71!	0.19	0.02	0.52	0.35
15/90/60	148	255	10.6	0.02	79.2	0.33	0.20	5.24	0.44	0.02!	1.12	0.24
15/90/80	81.5	215	4.85	0.01!	62.7	0.18	0.16	2.07!	0.11	0.02!	0.91	0.56
15/90/95	18.9	94.0	0.01	0.01!	36.2	0.04!	0.06	1.39!	0.02!	0.02!	0.15	0.80
15/90/110	28.9	130	0.01!	0.01!	42.0	0.04!	0.05	1.73!	0.10	0.02!	0.20	0.09

Sample index	Cd	P		Ba	As		Co					
	ppm 312P	ppm 511P	ppm 511P	ppm 312P	ppm 511P	202P	206P	ppm 312P	ppm 511P	202P	206P	
14/90/07	5.82!	0.00!	682	570	131	7.34	0.20	18.9!	18.0	13.7	0.79	0.10
14/90/30	2.73!	2.28!	853	592	154	9.86	0.21	19.6!	17.9	11.9	0.47	0.02!
14/90/50	10.7	1.64!	865	675	248	12.4	0.23	27.2!	15.5	11.9	0.35	0.02!
14/90/80	3.91!	3.79!	1390	942	393	13.0	0.36	31.8!	20.0	13.3	0.73	0.10
14/90/110	3.40!	2.66!	1090	959	436	18.0	0.46	32.6!	20.1	13.3	0.60	0.08
14/90/140	5.72!	1.38!	959	741	284	24.5	0.35	33.1!	20.8	12.9	0.29	0.02!
14/90/170	3.86!	0.03!	810	703	243	19.4	0.09	61.9	34.9	32.0	0.06	0.02!
14/90/195	4.61!	0.00!	488	542	62.7	4.67	0.02!	16.0!	12.1	10.7	0.02!	0.02!
14/90/210	2.33!	0.00!	887	995	551	22.6	0.34	82.5	36.6	34.8	0.03	0.02!
14/90/265	0.69!	0.00!	808	599	139	12.6	0.06	49.3	29.9	22.7	0.02!	0.02!
14/90/276	0.00!	0.00!	751	688	212	28.7	0.03	35.0!	21.8	18.4	0.06	0.02!
15/90/05	0.00!	0.00!	586	589	107	15.9	0.11	30.1!	16.7	12.6	0.28	0.02!
15/90/30	0.00!	0.00!	662	679	204	29.9	0.16	34.4!	23.5	19.3	0.08	0.02!
15/90/60	1.35!	0.33!	792	681	198	30.8	0.30	38.5!	25.5	17.7	0.14	0.02!
15/90/80	0.00!	0.00!	619	681	220	36.8	0.24	31.6!	18.7	14.4	0.10	0.02!
15/90/95	5.62!	0.00!	652	656	155	58.5	0.21	40.0	23.7	17.2	0.08	0.02!
15/90/110	1.23!	0.00!	793	767	280	71.8	0.19	47.9	28.7	23.6	0.07	0.02!

Sample index	Cr		Ni		V							
	ppm 312P	ppm 511P	ppm 312P	ppm 511P	ppm 312P	ppm 511P	202P	206P	ppm 312P	ppm 511P	202P	206P
14/90/07	54.2	36.5	31.5	21.4	1.31	0.16	52.1	36.5	0.14	0.05		
14/90/30	62.2	43.8	35.5	29.1	0.83	0.07!	55.6	37.8	0.09	0.03!		
14/90/50	70.1	52.7	28.2	24.4	1.04	0.07	57.5	40.8	0.11	0.03		
14/90/80	98.1	82.6	45.8	36.5	2.24	0.44	65.0	47.2	0.25	0.11		
14/90/110	79.4	60.0	45.2	31.6	2.15	0.24	75.4	53.0	0.26	0.11		
14/90/140	73.6	47.9	37.8	28.0	0.25	0.07!	81.3	52.1	0.31	0.26		
14/90/170	127	82.7	82.7	69.7	0.13	0.07	149	127	0.24	0.03!		
14/90/195	50.5	33.1	30.5	19.6	0.18	0.07!	57.6	43.7	0.03	0.03!		
14/90/210	132	112	86.1	75.6	0.11	0.07!	157	134	0.24	0.03!		
14/90/265	97.6	64.1	58.6	46.5	0.07!	0.07!	127	82.9	0.16	0.03!		
14/90/276	74.7	54.1	40.1	33.6	0.24	0.07!	94.3	72.3	0.12	0.03!		
15/90/05	60.0	37.7	29.5	22.8	0.55	0.07!	69.4	48.5	0.14	0.03!		
15/90/30	82.1	60.9	46.3	40.1	0.25	0.07!	102	74.5	0.14	0.03!		
15/90/60	78.9	59.0	35.8	37.9	0.52	0.07!	90.6	68.8	0.17	0.03!		
15/90/80	68.1	44.9	30.1	29.8	0.26	0.15	82.6	59.1	0.10	0.03!		
15/90/95	75.0	52.0	40.4	33.7	0.07!	0.07!	96.4	70.3	0.11	0.06		
15/90/110	98.8	70.6	56.5	46.0	0.08	0.07!	125	91.3	0.22	0.03!		

Appendix 1. (Continued)

Sample index	Al		ppm 206P	Fe		Mg		ppm 202P	206P	Ca		ppm 202P	206P
	% 312P	% 511P		% 312P	% 511P	% 312P	% 511P			% 312P	% 511P		
14/90/07	6.97	1.10	2.00!	2.95	2.11	0.85	0.57	669	299	1.46	0.29	622	197
14/90/30	7.07	1.14	2.00!	2.79	2.00	0.86	0.59	552	144	1.49	0.30	474	80.5
14/90/50	6.97	1.23	2.00!	2.87	2.23	0.89	0.66	637	211	1.43	0.34	760	161
14/90/80	6.74	1.45	2.00!	3.51	2.85	0.99	0.75	1130	404	1.30	0.40	1100	236
14/90/110	7.42	1.73	2.00!	3.83	3.04	1.12	0.86	1050	325	1.34	0.38	995	198
14/90/140	7.61	1.73	2.00!	4.05	2.94	1.22	0.87	1210	182	1.29	0.39	1130	102
14/90/170	9.80	3.82	2.00!	6.71	5.64	2.40	2.22	1010	86.5	1.32	0.64	1220	93.7
14/90/195	7.39	1.26	3.18	2.76	2.10	0.92	0.70	316	16.7	1.43	0.29	426	18.7
14/90/210	10.1	4.07	2.00!	7.00	6.01	2.50	2.36	1080	91.3	1.22	0.68	1430	108
14/90/265	9.87	2.69	3.10	5.62	4.41	1.81	1.44	804	37.3	1.06	0.47	1190	50.1
14/90/276	8.66	2.20	2.99	4.54	3.74	1.44	1.19	571	27.9	1.39	0.45	837	34.5
15/90/05	7.98	1.46	2.00!	3.18	2.35	1.08	0.79	553	71.0	1.42	0.31	437	40.9
15/90/30	8.81	2.24	4.62	4.67	3.62	1.58	1.25	646	48.3	1.31	0.39	537	29.8
15/90/60	8.50	2.07	2.10	4.38	3.51	1.41	1.13	747	91.8	1.31	0.39	665	58.9
15/90/80	8.09	1.76	6.33	4.58	3.64	1.23	0.92	551	41.2	1.47	0.40	775	35.3
15/90/95	8.83	2.10	27.6	4.42	3.42	1.47	1.14	547	13.4	1.39	0.39	547	8.85
15/90/110	10.2	2.99	9.93	6.14	4.98	1.94	1.60	919	29.7	1.11	0.50	973	29.4

Sample index	K				Na			
	% 312P	% 511P	ppm 202P	206P	% 312P	% 511P	ppm 202P	206P
14/90/07	2.14	0.35	301	139	1.92	0.19	1580	1470
14/90/30	2.13	0.37	347	133	1.99	0.19	1540	1330
14/90/50	2.15	0.41	384	162	1.87	0.21	1700	1520
14/90/80	2.04	0.46	552	233	1.74	0.35	2990	2640
14/90/110	2.29	0.53	630	224	1.77	0.32	2690	2270
14/90/140	2.33	0.55	748	205	1.74	0.37	3200	2450
14/90/170	3.21	1.43	946	159	1.91	0.48	3520	2740
14/90/195	2.33	0.46	222	32.3	2.02	0.17	1170	942
14/90/210	3.36	1.51	1030	155	1.74	0.50	3690	2740
14/90/265	3.43	0.93	752	103	1.49	0.32	2520	1830
14/90/276	2.88	0.80	352	34.0	1.82	0.25	1780	1390
15/90/05	2.61	0.53	322	76.6	2.01	0.20	1360	1120
15/90/30	2.87	0.82	535	112	1.85	0.24	1470	1180
15/90/60	2.85	0.75	566	133	1.83	0.28	1970	1690
15/90/80	2.49	0.60	417	87.6	1.88	0.20	1340	1080
15/90/95	2.91	0.78	397	32.2	1.85	0.20	1430	982
15/90/110	3.60	1.08	694	60.6	1.65	0.35	2570	1700

Sample index	Mn				Ti		Sc		Zr	
	ppm 312P	511P	202P	206P	ppm 312P	511P	ppm 312P	511P	ppm 312P	511P
14/90/07	424	191	21.7	5.90	2450	926	7.40	3.76	175	5.28
14/90/30	402	192	13.0	1.62	2520	964	8.13	4.00	212	5.48
14/90/50	377	202	8.04	1.13	2500	1030	8.07	4.29	170	2.61!
14/90/80	382	221	9.12	1.55	2640	1050	8.92	4.29	165	0.18!
14/90/110	422	248	9.02	1.51	3000	1290	10.6	5.77	174	2.76!
14/90/140	433	246	7.44	0.46	3170	1240	11.4	5.70	164	3.42
14/90/170	823	722	16.6	0.40	5340	3390	18.0	14.3	152	53.6
14/90/195	400	243	8.04	0.10	2590	1240	8.13	4.77	154	16.0
14/90/210	839	781	19.5	0.50	5510	3470	19.0	15.3	146	57.4
14/90/265	627	515	13.1	0.18	4610	1980	16.5	10.1	171	44.1
14/90/276	582	444	14.1	0.19	3940	1980	12.9	8.46	158	31.5
15/90/05	432	252	8.56	0.58	2950	1310	9.59	5.41	171	15.7
15/90/30	559	398	11.1	0.27	3860	1950	13.3	8.50	145	27.2
15/90/60	510	367	14.9	0.61	3590	1730	12.2	7.83	161	19.1
15/90/80	487	303	10.0	0.25	3240	1510	11.2	6.55	185	14.8
15/90/95	561	390	6.68	0.21	3960	1900	13.0	8.14	174	28.8
15/90/110	680	570	7.51	0.16	4890	2380	17.0	11.5	137	40.6



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