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The Impacts of Loading From Acid Sulfate Soils on Boreal Estuarine Sediments

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ABSTRACT

Estuaries play a vital role in the coastal environment by filtering pollutants and nutrients from catchment runoff. In areas where acid sulfate (AS) soils are abundant, the importance of the estuary as a coastal filter is heightened as AS soils typically stress the marine environment with acidic metal-laden drainage waters. In this study, we took sediment cores from a shallow estuary in Western Finland and used geochemical and palaeoecological methods to investigate how the estuary is affected by loading from AS soils. An overall decrease in diatom species richness and diversity in the estuarine sediments was found, with a clear change from species preferring pelagic conditions to species indicative of more eutrophic conditions. The change coincides with human disturbance during the early 20th century when extensive drainage and rework of forests and peatlands into agricultural use increased. Geochemical analyses show a significant enrichment of Cd, Ni, Co, Zn and Al in the estuarine sediments which correspond to the metal loads originating from the catchment AS soils. Our calculations, however, show that in comparison to the total load of soluble metals from the catchment area, more than 80% of chalcophiles and 70% of Al are transported further out to sea. We hypothesised that a precipitation gradient driven by changes in pH and salinity due to seawater mixing would form along a transect towards the estuary outlet. Instead, we found that physical sedimentation processes are stronger drivers for element transport, as enrichment takes place only in low-energy hydrodynamic conditions at greater water depths. Glacioisostatic land uplift and significant particle transport from the catchment area are further isolating the estuary, effectively moving the saline gradient seawards and diminishing the role of the estuary as a coastal filter. We also found that the estuarine sediments are hypersulfidic and contain stores of potential acidity significantly larger than conventional AS soils. Without proper management, disturbance of the estuarine sediments can cause disastrous consequences at a local level.

1 | Introduction

Acid sulfate (AS) soils are primarily found in the coastal regions around the world, though substantial inland occurrences have also been recognised as our understanding of them has expanded (Fanning et al. 2017). These soils are estimated to cover an area of at least 500,000 km^2 with the largest occurrences found in Australia, Asia, South America and Africa. The largest occurrences in Europe are found in Finland (ca. 10,000 km^2; Edén et al. 2023), where the AS soils mainly comprise organic-rich muds that were originally deposited in the Baltic Sea during its current brackish-water phase, which began ca. 7500 years

Summary

- Acid sulfate (AS) soil impact is recorded in estuary sediments as a decline in diatom species richness and diversity.
- Hypersulfidic sediments contain high acidity potential and accumulated metal content.
- Enrichment in the estuary is primarily driven by hydrodynamic conditions.
- Estuary role as coastal filter diminished as majority of AS soil loading is driven seaward.

ago (Andriesse and van Mensvoort 2005; Boman et al. 2010; Michael 2013). In the Gulf of Bothnia, in the northern Baltic Sea, the water column was stratified during the early part of the brackish-water phase due to the inflow of saline waters via the Danish straits and the freshwater input from coastal catchment areas. Coupled with enhanced primary productivity during the coincident Holocene Thermal Maximum, this resulted in seafloor anoxia and favourable conditions for microbial reduction of sulfate and iron in the deep areas of the Gulf of Bothnia (Häusler et al. 2017). Ca. 4000 years ago, stratification in the Gulf of Bothnia gradually weakened and the seafloor oxygen conditions improved as a result of the reduced saline influx and the waning of the Holocene Thermal Maximum. Glacioisostatic rebound (today 4–9 mm/year in Western Finland; Mäkinen and Saaranen 1998) has since uplifted these organic-rich hypersulfidic muds above sea level, and intensive land use such as agriculture and urban infrastructure construction has formed well-aerated soil structures above groundwater level (Joukainen and Yli-Halla 2003; Sullivan et al. 2010). Microbially aided oxidation of iron sulfides, such as pyrite (FeS_2) and metastable iron sulfides (primarily mackinawite; FeS; and greigite; Fe_3S_4), that are found in abundance in these sediments has led to the formation of sulfuric acid (H_2SO_4) in the soil pore water, consequently lowering the pH of the soil below 4.0 (Boman et al. 2010; Högfors-Rönnholm et al. 2018). AS soils are called the 'nastiest' soils in the world as they are responsible for acidification and metal loading of water sources, leading to extensive harm for aquatic environments as well as concrete and steel corrosion on infrastructure (Dent and Pons 1995; Hudd 2000; Cook et al. 2000; Chen et al. 2021).

Estuaries play a vital role in the coastal environment. They act as natural filters for catchment areas by trapping pollutants and nutrients from coastal runoff and river systems and improving water quality at the freshwater/saline water mixing zone (Asmala et al. 2017; Nordmyr et al. 2008). In lowland coastal areas, estuaries receive large amounts of eroded sediment from the upstream catchment areas through rivers and streams. This transport is significant, especially during periods of high precipitation and snow melt typical in Boreal climates (Heikkilä 1991). As a result, these sediments are transported and deposited in the estuary, where they can create or exacerbate flooding hazards in the surrounding areas as the estuaries become bottlenecks for water flow. To mitigate this risk, excess sediment is often removed by dredging to improve the water flow. The dredged sediments can often be beneficial for agricultural purposes, as they have a high organic content, and the fine-grained sediments have an affinity to form well-structured soils. However, extensive management is always needed if the sediments are hypersulfidic (Dent and Pons 1995; Österholm et al. 2015; Johnson et al. 2022). In coastal landscapes, where AS soils are found extensively in the catchment areas, there is additionally the increased risk of potentially leached toxic metals from sulfides and silicate minerals due to the acidic soil pore water, becoming mobilised and transported to the estuaries during high flow events (Nordmyr et al. 2008; Virtasalo et al. 2020). These metals are soluble and mobile in the low pH river water typically associated with AS soils but become immobile and precipitate when the acidic river water meets the alkaline sea (Virtasalo et al. 2023). As a result, the estuarine sediments may become enriched in potentially toxic metals, which when dredged can be re-mobilised and possibly become bioavailable.

Monitoring data for the surface water quality of the Baltic Sea covers only the past several decades (e.g., Kohonen 1974). Various palaeoecological indicators, such as diatoms, dinoflagellates and molluscs, have long been used to reconstruct past water quality trends from the sediment records of lakes and oceans, including the Baltic Sea (Tuovinen et al. 2010; Weckström et al. 2017). Recently, they have increasingly been applied to estuarine studies as well (Taffs et al. 2017). Diatoms (class *Bacillariophyceae*) are microscopic, unicellular algae. They are one of the most widely used indicators because they are highly diverse, with distinct ecological tolerances for different taxa, grow in almost all aquatic environments, and their siliceous cell walls preserve well in sediments (Battarbee et al. 2001).

In this study, geochemical and palaeoecological methods were used to investigate how an estuarine system is affected by loading from AS soils in a lowland boreal environment. We investigate the metal enrichment patterns in the vicinity of the river mouths where the gradient between acidic metal-laden freshwater and alkaline seawater is strongest. The hypothesis is that a precipitation gradient will form along the transect from the river mouths towards the estuary outlet, driven by changes in pH and salinity due to seawater mixing. Elements likely to be soluble in the acidic river water are expected to start to precipitate and settle to the estuary floor. We also estimate there will be a large acidity reserve in the sediments originating from the sulfidisation processes in the anoxic sediment–water interface. The goal of this study is to pinpoint the effect of coastal AS soil loading on the sediment and water quality history and to establish the risk of future AS soils and dredge materials.

2 | Material and Methods

2.1 | Description of the Study Area

The Vaasa Southern City Bay estuary (63°4.52′ N, 21°36.89′ E) is situated south of the town of Vaasa, in Ostrobothnia, western Finland (Figure 1). The estuary is shallow (area 16 km^2, volume 19.2 M m^3) and recipient of two river catchments which drain known coastal lowland AS soils (Roos and Åström 2005). The Laihianjoki River has a flow path of ca. 77 km and a catchment area of 484 km^2, consisting mainly of forests (64%) and arable land (28%), with the main soil type being till (48%) fine-grained deposits (31%) and peat (15%). The Sulvanjoki River is

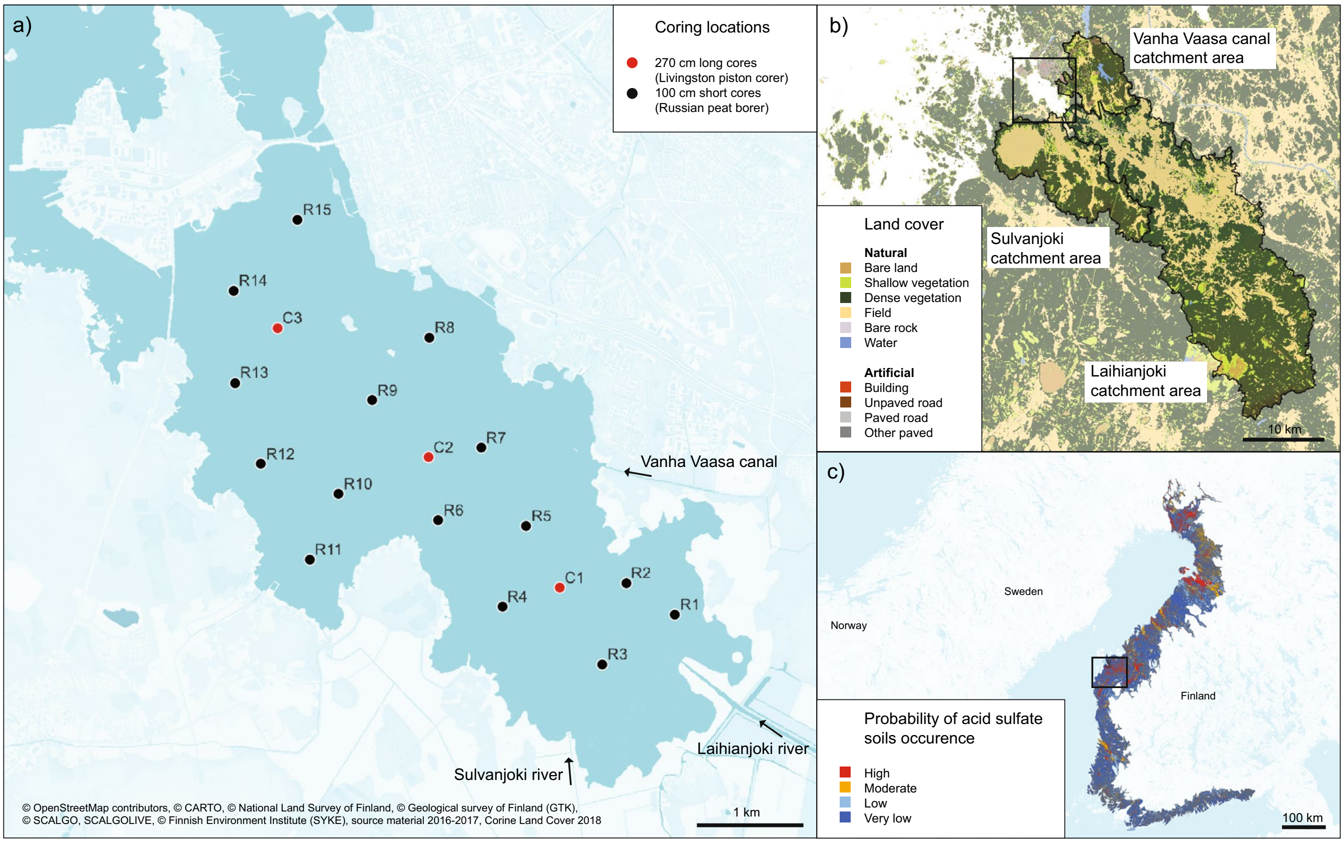

FIGURE 1 | Maps of the study area. (a) Coring sites in the Vaasa Southern City Bay estuary. (b) Map of Corine Land Cover (2018) in the Sulvanjoki, Laihianjoki and Vanha Vaasa canal catchment areas. (c) A probability map over AS soil occurrence in Finland (Geological Survey of Finland 2023).

considerably shorter, having a ca. 36 km flow path and a catchment area of 137 km^2, consisting mainly of forests (57%) and arable land (37%), with till being the main soil type (49%) followed by fine-grained deposits (35%) and peat (8%). The mean slope of the flow path is ca. 2.0% for Laihianjoki and 1.6% for Sulvanjoki, which reflects the essentially flat topography of the area. The estuary is also a recipient of a third, small catchment area, the Vanha Vaasa canal, located to the east of the estuary. The length of this flow path is approximately 22 km with a mean slope of 1.3%, and the catchment area is 61 km^2 consisting primarily of till (53%) and fine-grained deposits (36%) with 56% forests and 15% arable land, with the rest being residential or other constructed areas (Table 1; SCALGO 2023).

The bedrock in the catchment areas is mostly Precambrian mica schists, gneisses and granites. The bedrock is covered by till, glacial outwash deposits and silts and clays of the previous glaciolacustrine and post-glacial lacustrine phases of the Baltic Sea basin (Breilin et al. 2005; Virtasalo et al. 2007) The superimposed fine-grained deposits are post-glacial brackish-water muds, which are predominately hypersulfidic silty clay loams (Joukainen and Yli-Halla 2003; Nordmyr et al. 2006; Boman et al. 2008). The area was fully submerged during the early brackish-water phase of the Baltic Sea (7500–4000 years ago) but has since been uplifted above sea level due to the glacioisostatic rebound, which continues today at a rate of approximately 8 mm per year (Ekman 1996; Tikkanen and Oksanen 2002). The water in the archipelago is brackish with a surface salinity of 3–4 psu (Practical Salinity Units) and pH > 8, whereas the river water has a salinity of 0.1 psu and is often acidic, with pH measured down to 4.5 (Kautsky 1995; Dalhem et al. 2019; Virtasalo et al. 2023).

The anthropogenic impact on the estuary has been significant during the last century. A harbour was constructed during 1890–1910, with a railway crossing the northern outlet, and in 1973, a bridge was built over the northwestern outlet. Since artificial drainage and cultivation started to increase in the catchment areas in the early 1900s, the subsequent oxidation of hypersulfidic soil material in the catchment area has led to an enormous leaching of sulfate, organic matter, nitrate, phosphorus and metals (e.g., Al, Cd Co, Ni, Zn) along the drainage networks towards the estuary during high water flow conditions (Sundström et al. 2002; Roos and Åström 2005; Nystrand et al. 2016). The Söderfjärden meteorite crater in the Sulvanjoki catchment area, for instance, was reclaimed for agricultural use in 1926 initially by open ditch drainage and from 1950 with subsurface drainage (Edén 2012; Salo et al. 2023). According to an assessment of the status of Finland's waters, the quality of surface water in the estuary is classified as passable on a scale of bad to excellent (Teppo et al. 2022). Its ecological and physical–chemical state is classified as bad, and its biological state as moderate. According to the assessment, Ni and Cd have exceeded the Environmental Quality Standard (EQS) in both the Laihianjoki and Sulvanjoki rivers, as well as in the estuary (Teppo et al. 2022).

The study area is situated in the Dfb climate zone (Df: Snow climate, fully humid, b: warm summer) according to the

TABLE 1 | General information about the Laihianjoki, Sulvanjoki and Vanha Vaasa canal catchment areas.

	Laihianjoki	Sulvanjoki	Vanha Vasa canal
General information			
Catchment area (km^2)	484	137	61
Flow path lenght (km)	77	36	22
Mean slope (%)	2.0	1.6	1.3
Land use (%)			
Forests	64	57	56
Agriculture	28	37	15
Urban and industry	5	5	26
Wetlands	3	0.9	1
Water	0.4	0.1	2
Soil type (%)			
Till	48	49	53
Fine-grained deposits	31	35	37
Coarse-grained deposits	0.9	3	2
Peat	15	8	2
Bedrock outcroppings	1	5	2

Köppen–Geiger climate classification (Kottek et al. 2006). The region has a mean annual temperature of 4.4°C and experiences 5 months of below-freezing temperatures, from November to March. The mean annual precipitation is 549 mm, with August typically receiving the highest amount of rainfall, with mean precipitation of 46 mm and a 50-year maximum of 200 mm. The snow melts and ground thawing, coupled with spring rains, lead to increased runoff in April–May, while heavy rains in August–October cause autumn peak flows. Regional interpolated (10 × 10 km grid) weather data is available from Vaasa Airport weather station located 5 km from the study area (Finnish Meteorological Institute 2024).

2.2 | Sediment Sampling

Sediment coring was undertaken in March 2016 when the estuary was covered by sufficiently thick ice (> 20 cm). Three long (270 cm) cores (C1–C3) with adjacent replicates 2 m apart were collected using a tripod-operated Livingstone piston corer. The coring locations were chosen based on depth and the pH and salinity gradients that were hypothesised would affect the metal precipitation along the transect from the river mouth to the estuary outlet: one core near the river mouth where the water was shallow (ca. 0.5 m deep), one from the middle of the estuary (1–1.5 m deep) and one from the deepest part (ca. 3 m deep) near the estuary outlets. Electrical conductivity (EC) and pH were measured in the water before coring using pre-calibrated ExStick EC400 and PH100 metres (Extech, Nashua, USA) (Table 2). For a more detailed understanding of the spatial distribution, 15 short (100 cm) cores (R1–R15) were sampled at evenly distributed locations using a Russian peat corer (Jowsey 1966). Immediately after coring, the short cores were photographed and visually inspected, and cut into 20 cm samples which were thoroughly homogenised and divided into separate resealable plastic bags. The samples were frozen with dry ice at the site and, after transport, kept at −18°C in the laboratory. The long cores were sealed on both ends immediately after coring and transported to the laboratory for sampling.

2.3 | Analysis

The three long cores C1–C3 were split into two halves and promptly documented and examined visually for lithology and for correlatable features between the replicate cores. Magnetic susceptibility (κ) was measured on one half of the cores using a Bartington MS2E (Bartington, Witney, UK) point sensor at 2 mm resolution, followed by digital photography in 15 cm overlapping sections. The other core half was sampled at 10 cm intervals for ^{137}Cs-dating using gamma spectrometry (BrightSpec bMCA, Niel, Belgium) at the Geological Survey of Finland (GTK). The top 100 cm of core C3 was additionally sampled at 2.5 cm intervals for more precise ^{137}Cs-dating (GTK). Bulk density (long cores only) and loss-on-ignition (LOI) were determined from discrete samples taken in 6.9 cm^3 cubes at 5 cm intervals for 0–100 cm and at 10 cm intervals for 100–200 cm. The bulk density and weight LOI values were calculated after drying the samples at 105°C for 24 h and then ashing at 550°C for 4 h, respectively (Heiri et al. 2001). Due to a very strong correlation (Pearson $R^2 = 0.94$), bulk density for short cores was estimated from the 2nd order polynomial function generated in Excel between LOI and bulk density in C3 according to: Bulk density = 22.619(LOI)^2 − 7.6448(LOI) + 0.8365.

Subsamples ($n = 24$) from the cubes were also used for assessing diatom species assemblages, with slides prepared according to Battarbee et al. (2001). From each slide, at least 300 diatom valves were identified to the species level. Broken diatom valves were counted if more than half of the valve was intact. Chrysophyte cysts were also counted from the same microscope views as diatoms, and their ratio to diatoms was calculated. Species diversity was estimated with the Shannon index, and richness with individual rarefaction analysis using the PAST software (Hammer et al. 2001). The Shannon index takes into account the number of individuals as well as the number of taxa, with 0 meaning an assemblage with a single taxon and higher values meaning several taxa, each with few individuals. Individual rarefaction is used when comparing the number of taxa in samples of different sizes. Stratigraphically constrained cluster analysis using the unweighted pair-group average algorithm with chord distance was done with the PAST software to group taxonomically similar samples into zones. The results were plotted in a stratigraphical chart using the C2 program (Juggins 2007).

TABLE 2 | Locations of coring sites with coring dates, distance from river outlet, core lengths and water depths.

	Latitude (ETRS-TM35-FIN)	Longitude (ETRS-TM35-FIN)	Coring date	Distance from Laihianjoki outlet (km)	Core length (cm)	Water depth (cm)	pH[a]	Conductivity[a] (µS cm^{-1})	16 w incubation[b] pH	(mmol H^+ kg^{-1})
Long cores										
C1	63°03.495′	21°38.995′	8.3.2016	1.9	270	92	6.0	351	3.0	207
C2	63°04.073′	21°37.476′	8.3.2016	3.6	270	142	5.9	468	3.3	115
C3	63°04.638′	21°35.750′	9.3.2016	5.4	270	189	6.1	907	3.6	490
Short cores										
R1	63°03.413′	21°40.247′	8.3.2016	1.0	100	60	6.0	350	2.3	245
R2	63°03.544′	21°39.699′	8.3.2016	1.5	100	72	5.9	283	2.0	348
R3	63°03.142′	21°39.518′	8.3.2016	1.3	100	50	5.8	480	2.8	261
R4	63°03.381′	21°38.399′	8.3.2016	2.3	100	92	5.5	693	2.3	428
R5	63°03.781′	21°38.583′	8.3.2016	2.5	100	50	5.9	474	2.3	399
R6	63°03.774′	21°37.641′	8.3.2016	3.2	100	69	6.0	453	2.4	280
R7	63°04.141′	21°38.033′	8.3.2016	3.3	100	133	6.0	379	2.3	327
R8	63°04.653′	21°37.382′	8.3.2016	4.3	100	144	5.9	462	3.3	134
R9	63°04.327′	21°36.828′	8.3.2016	4.3	100	170	6.0	462	2.4	345
R10	63°03.862′	21°36.551′	9.3.2016	4.1	100	132	5.9	585	2.7	312
R11	63°03.530′	21°36.303′	9.3.2016	4.1	100	102	5.6	652	2.9	220
R12	63°03.973′	21°35.697′	9.3.2016	4.8	100	147	5.8	643	2.8	264
R13	63°04.356′	21°35.347′	9.3.2016	5.4	100	162	5.7	916	3.4	376
R14	63°04.800′	21°35.251′	9.3.2016	5.9	100	263	6.0	1219	2.3	452
R15	63°05.170′	21°35.869′	9.3.2016	5.9	100	172	6.0	783	3.9	275

[a]pH and EC measurements of the surface water from coring sites.
[b]16-week incubation pH and total incubation acidity (TIA) values from sediment samples taken at 40–60 cm depth.

For a spatiotemporal overview of the metal and acidity reserves of the estuary, samples were taken at selected depths from both the long and short cores for the following analyses: multi-element (Al, Fe, S, Cd, Ni Co, Zn and Ti) analysis with inductively coupled plasma optical emission spectrometry (ICP/OES) and inductively coupled plasma mass spectrometry (ICP/MS) after *aqua regia* digestion at an accredited laboratory (Activation Laboratories LTD, Canada); and for acidity characterisation using an incubation method and a titratable incubation acidity (TIA) procedure. Incubation was done according to the method by Creeper et al. (2012) with samples kept at room temperature (ca. 20°C) for 16 weeks at near field capacity moistness (moisture adjusted accordingly with deionised water). TIA was measured after the 16-week incubation period by mixing ca. 1.5 g of dry equivalent sample with 60 mL 1 M KCl in a beaker and stirring for 4 h. After settling for ca. 16 h, the mixture was stirred for 5 min and titrated to a pH of 5.5 with 0.015 M NaOH. The NaOH consumption was used to calculate the TIA (modified from Ahern et al. 2004; Österholm and Nystrand 2016). pH measurements were done with a pre-calibrated FlaTrode (Hamilton, Reno, USA) electrode.

Sulfur speciation was performed for selected samples to determine the presence of reduced inorganic sulfur (RIS) species according to the distillation-based method described in Dalhem et al. (2021). The sulfur speciation method does not quantitatively measure sediment mineral composition as it is operationally defined and dependent on analytical procedure and environmental setting, but it is used to indicate FeS_x complexes in soils and sediments (Boman et al. 2008; Rickard 2012).

2.4 | Estimation of Estuarine Element Enrichment

From data in Linnamaa (2023), the current annual input of metals into the estuary was estimated from the mouth of the main river, Laihianjoki (Figure 1), which comprises 71% of the total catchment area of the estuary. Water sampling in this river was conducted on occasions, representing the hydrological year: August 2020 (low flow), September 2020 (moderate flow in rising limb), November 2020 (peak flow) and April 2021 (falling limb, 2 weeks after the spring flow peak). Riverine 'dissolved' metals were determined from water samples filtered with a 0.45 μm filter and conserved with 2% ultrapure HNO_3. 'Acid soluble' metals, including particulate metals already precipitated in the river, were determined from aliquots filtered after 24 h treatment with 2% HNO_3 at room temperature. Metal analyses were conducted with ICP-OES (Linnamaa 2023).

To estimate the annual metal load to the estuary, the flow-weighted average concentration from the Laihianjoki River was multiplied by the long-term specific average flow ($8\,L/s/km^2 \times 60\,s \times 60\,min \times 24\,h \times 365\,d$) of the total catchment area of 682 km^2 of the estuary, which was reasonable as the other two river catchments have overall similar physical and chemical features. However, the second largest river, Sulvanjoki (20% of the catchment), has concentrations up to 60% higher than Laihianjoki (Virtasalo et al. 2023), while the remaining small fraction of the catchment (9%) is expected to have somewhat lower metal concentrations than Laihianjoki. Thus, the estimations are considered somewhat conservative, unlikely to exaggerate the element load to the estuary. The results match the less precise calculations of the known area of AS soils in the catchment (Linnamaa 2023) and the expected load per unit area of AS soils (Österholm and Åström 2004).

As a rough conservative approximation, it was assumed that multiplying the current input by 80 years (back to ca. 1936) will give an estimate of the total metal input to the estuary since the start of intensive drainage practices in the catchment area. The mean content of the two lowermost samples (60–80 and 80–100 cm) from the short cores was used as the background values, representing sediments before the intensive drainage of the hypersulfidic materials (AS soils) commenced, except for the outermost core R15 (Figure 1a). In the latter case, the background of the nearby R14 was used. Accumulation for each 20 cm layer in the cores was calculated by multiplying the difference in element content of the layer by the corresponding background value with the corresponding bulk density (ton/m^3). The sum of the enrichment for each layer in the 1 m core thus represents the enrichment in 1 m^3 sediment. For each core, the result was extrapolated to an area of 1 km^2 (1,000,000 m^3 sediment). Since the short cores are evenly distributed over the estuary, the average element enrichment multiplied by the estuary area of 14 km^2 (14,000,000 m^3 sediment) was assumed to represent the total element enrichment in the estuary. To estimate the organic matter enrichment, LOI values were converted to C by multiplying by 0.57, the ratio between organic matter and organic carbon (2.31:1) found in the nearby Kyrönjoki estuary (Heikkilä 1991).

3 | Results

3.1 | General Sediment Properties

The three long cores C1–C3 were similar upon visual inspection. The cores were composed of a fine-grained organic-rich mud that is visually nearly structureless and black, with brown/grey, intensely bioturbated and poorly laminated thin interlayers. A strong hydrogen sulfide odour was evident in all the cores, and the black colour changed to grey upon exposure to atmosphere within several hours, indicating the presence and rapid oxidation of metastable iron sulfides. The cores C1 and C2 have a stable bulk density (ca. 0.4 g/cm^3) and LOI (5%–6%) throughout the cores, whereas C3 from the deepest part of the estuary shows a sharp transition at 82.5 cm depth, where the bulk density decreased to 0.2 g/cm^3 and LOI increased to up to 20% towards the surface (Figure 2). Magnetic susceptibility measurements correlated well between core replicas, and κ values were in the same general range (mean values 64–92κ) in all three cores. However, in core C3, the susceptibility decreases noticeably (mean values 27 κ) towards the top above a larger susceptibility peak (max 750 κ) at 80–85 cm depth (Figure 2).

The short cores were visually similar to the long cores. LOI values were stable at 5%–6% in the lower part of the short cores and towards the river mouth, but increased to 10%–15% in the uppermost part of the cores and in the deeper part of the estuary. The cores closest to the river mouth (e.g., R3, LOI 45%) also had high LOI values in the surface layer due to the presence of common reed roots (Figure 3).

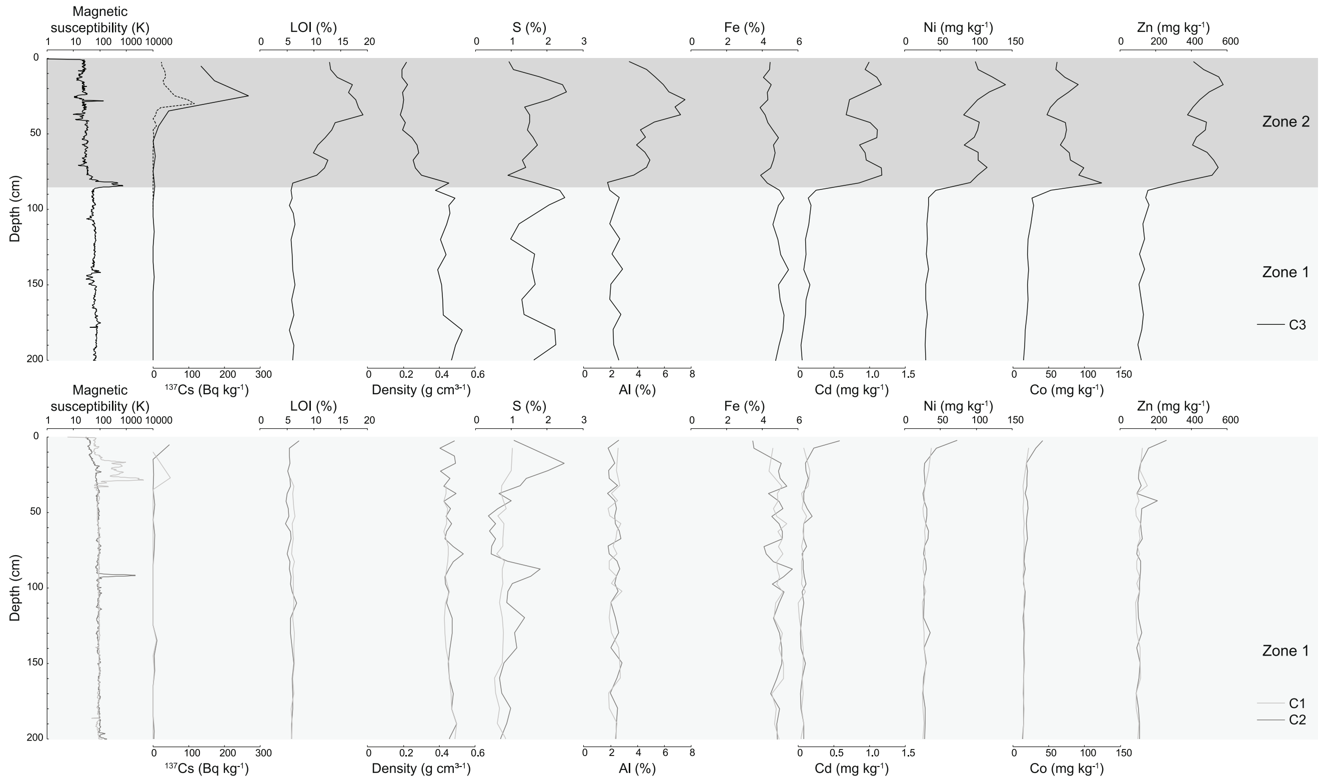

FIGURE 2 | Geochemical variables for cores C1–C3 with magnetic susceptibility (κ), ^{137}Cs, loss-on-ignition, density, S, Al, Fe, Cd, Ni, Co and Zn. Core C3 is divided into Zone 2 (above 82.5 cm; 1986 and younger) and Zone 1 (below 82.5 cm) and cores C1–C2 represent Zone 1 (deposited before 1986).

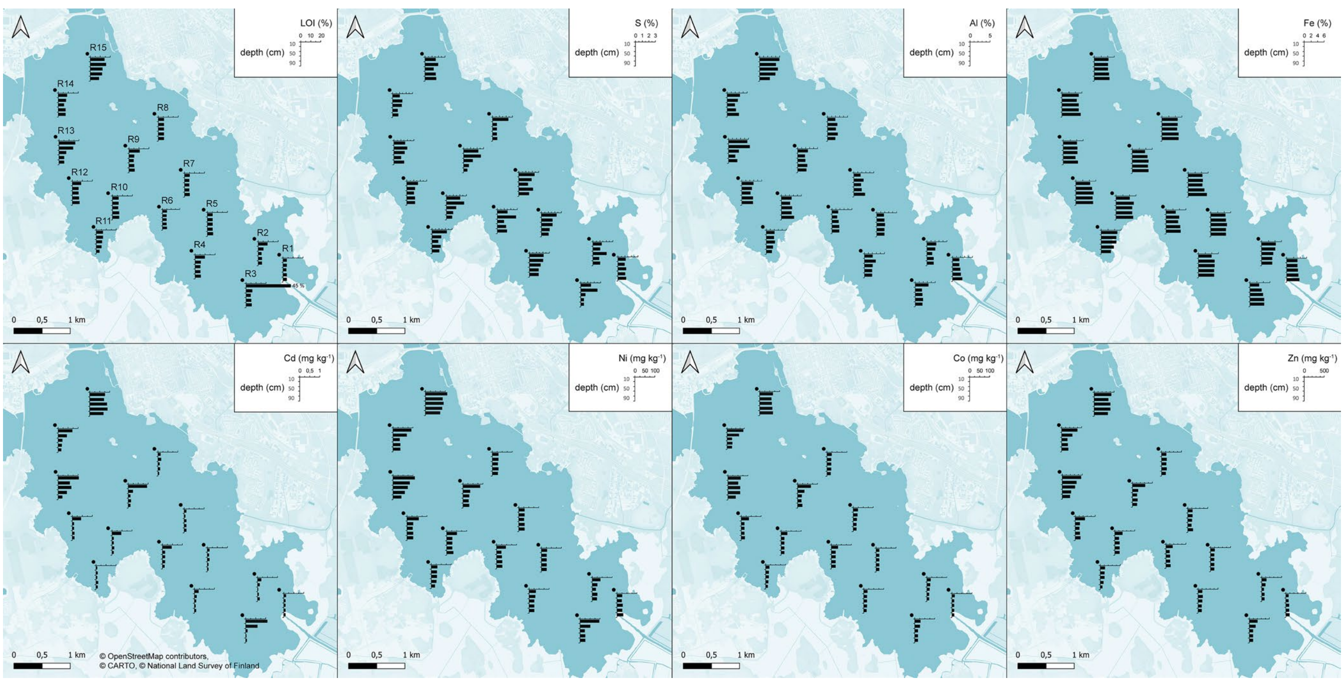

FIGURE 3 | Spatial distribution of loss-on-ignition, S, Al, Fe, Cd, Ni, Co and Zn for cores R1–R15.

3.2 | ^{137}Cs Dating

In the core C3, the main ^{137}Cs peak was at 30 cm depth according to the denser 2.5 cm sampling (Figure 2). ^{137}Cs values were elevated already at 32.5 cm, but this could be due to bioturbation and downward diffusion of Cs in the pore water. As the top of the core represents the sampling year 2016 and the main ^{137}Cs peak should represent the Chernobyl disaster of 1986, the mean sedimentation rate in the deeper part of the estuary has been ca. 1 cm/year. The cores C1 and C2 showed only low ^{137}Cs activity throughout, with no clear peaks, indicating that they were deposited before 1986.

3.3 | Diatoms

A total of 262 different diatom species were identified from the 24 samples from core C3 (Figure 2). Species diversity (Shannon index) varied from 1.13 (at 22.5 cm) to 3.65 (at 160 cm), while rarefaction-estimated species richness varied from 22 species (at 12.5 cm) to 73 species (at 110 cm). Cluster analysis identified two distinct zones in the sequence, below (Zone 1) and above (Zone 2) 82.5 cm, coinciding with the changes in density and LOI. Overall, the diatom assemblages of both zones were dominated by benthic freshwater species, with the proportion of planktonic species less than 20% throughout the core. The ratio of chrysophyte cysts to diatoms decreased towards the top part of the core. Zone 1 is characterised by the planktonic species *Pauliella taeniata* (Grunow) Round & Basson 1997, and the benthic *Planothidium delicatulum* (Kützing) Round & Bukhtiyarova 1996, and *Rhoicosphenia abbreviata* (C. Agardh) Lange-Bertalot 1980, which are virtually absent in Zone 2. Small, benthic fragilarioid species such as *Staurosira subsalina* (Hustedt) Lange-Bertalot 2004, *Staurosira venter* (Ehrenberg) Cleve & J.D. Möller 1879, *Pseudostaurosira elliptica* (Schumann) Edlund, Morales & Spaulding 2006, and *Martyana atomus* (Hustedt) Snoeijs 1991 are abundant in Zone 1. In addition, benthic species *Epithemia sorex* Kützing 1844 and other *Epithemia* species are found with an abundance of ca. 0.5%–2% in Zone 1. In Zone 2, particularly from depth 72.5 cm upwards, the benthic species *Diatoma moniliformis* (Kützing) D.M. Williams 2012 and *Fragilaria exigua* Grunow 1882 start to increase and are particularly abundant at 50–30 cm and 22.5 cm depth, respectively. Simultaneously, the other fragilarioid species start to decrease. *P. taeniata*, *P. delicatulum* and *E. sorex* decrease in Zone 2, and *R. abbreviata* disappears from the assemblages after 67.5 cm. The benthic species *Nitzschia palea* (Kützing) W. Smith 1856 increased and the benthic genus *Amphiprora* Kützing 1844 appears in Zone 2. *Eunotia paludosa* Grunow 1862 also occurs with an abundance of over 1% at a few depths in Zone 2.

3.4 | Element Patterns

Element patterns corresponded with the two zones identified with the cluster analysis of the diatom assemblages. The metal contents were relatively stable in cores C1 and C2 and in Zone 1 of C3, ranging from 1.75% to 2.89% for Al, 4.08% to 5.68% for Fe, <0.01–0.25 mg/kg for Cd, 24.6–43.1 mg/kg for Ni, 12.1–52.5 mg/kg for Co and 86.6–209 mg/kg for Zn. In Zone 2 of C3, however, the range of values for the respective elements increased significantly with maximum values up to 7.54% for Al, 1.17 mg/kg for Cd, 141 mg/kg for Ni, 124 mg/kg for Co and 577 mg/kg for Zn (Figure 2). For the short cores, metal contents in the shallower part of the estuary were relatively low, corresponding to those of the 'older' sediments of C1, C2 and Zone 1 in C3. Higher contents were found in the deeper part near the C3 coring site, with generally increasing contents towards the surface. The range of values in the short cores was 1.25%–5.67% for Al, 2.74%–5.67% for Fe, 0.02–1.08 mg/kg for Cd, 18.4–110 mg/kg for Ni, 9.8–93.2 mg/kg for Co and 48.1–474 mg/kg for Zn (Figure 3). Al and the chalcophile metals Cd, Ni, Co and Zn showed a significant positive correlation (r_s = 0.27–0.78; $p < 0.05$) with LOI in both the long and short cores (Table 3). There was a clear grouping of higher and lower LOI values, representing the two distinct zones. The chalcophiles correlated also negatively with density and depth (r_s = −0.25–0.56; $p < 0.05$). Titanium (Ti), however, was not elevated in Zone 2 and showed a positive correlation with depth and density (r_s = 0.25–0.35; $p < 0.05$) and a negative correlation ($r_s = -0.45$; $p < 0.05$) with respect to LOI.

Elevated contents in sediments corresponding to Zone 2 are recognised as representing the recent accumulation of metals related to AS soil leaching. The main part of the estimated metal accumulation, ca. 40%–70%, was in the deeper part of the estuary, in the area around cores R13–R15 (Figure 4; File S1–S6). Of the estimated dissolved (<0.45 μm) metal input from the catchment since the start of the extensive drainage, ca. 31% of Al has been precipitated and captured in the estuarine sediments. For the chalcophiles, the number is about half (14%–17%) except for Ni, for which only ca. 7% was captured. An associated significant accumulation of organic material (19%) is also evident in the corresponding sediments (Table 4; File S3).

3.5 | Sulfur and Acidity

The sediments in the estuary have high total sulfur (S) contents between 0.37% and 2.84% and a median value of 1.18% (Figure 3). The highest values (>2%) were found in the shallow to middle part of the estuary, typically above 0.6 m core depth, while the lowest values (0.4%–0.6%) were found in the shallowest and near shore parts of the estuary (Figure 4). A trend of rising S values towards the sediment surface is also evident in the shallow to middle part of the estuary. Throughout core C1 near the river outlets, the S content was stable at <1%, whereas there was more variability with core depth in the deeper part of the estuary. Two depths (22.5 and 92.5 cm) in core C3 have significantly higher S values (ca. 2.5%), and in core C2 there is a high S peak (ca. 2.5%) at 17.5 cm depth and a somewhat lower S peak (ca. 1.8%) at 87.5 cm. There was, however, no clear difference in S content between Zone 1 and Zone 2 in core C3.

Acid-generating oxidation reactions were significant during incubation due to high RIS content (up to 1.7%; File S7) in the sediments, with most samples having pH <4 after only 8 weeks, some already after 4 weeks. After a 16-week incubation period, all samples showed pH 2–4 except for the top 30 cm of core C3, which stayed at pH 4.4–4.5. A positive correlation ($r_s = 0.84$, $p < 0.05$, $n = 34$) between incubation pH and LOI was found. Likewise, the titratable incubation acidity (TIA) was very high (115–490 mmol H^+/kg) at all depths and correlated well ($r_s = 0.79$; $p < 0.05$) with total sulfur contents. No correlation was found between acidity and LOI ($r_s = -0.08$; $p > 0.5$).

4 | Discussion

4.1 | Depositional Setting and Element Accumulation and Transport

The Southern City Bay estuary has undergone several changes in the last decades. Historic orthophotography comparison between 1934 and 2021 shows a significant decrease in the estuary

TABLE 3 | Spearman's rank correlations (r_s) between geochemical variables for cores C1–C3 and R1–R15, respectively.

Spearman's rank correlation (r_s) for cores C1–C3

	Depth	LOI	Density	Al	S	Fe	Co	Ni	Zn	Cd	Ti
Depth	1.00										
LOI	−0.10	1.00									
Density	**0.45**	**−0.55**	1.00								
Al	−0.20	**0.47**	**−0.47**	1.00							
S	−0.16	**0.24**	**−0.41**	**0.26**	1.00						
Fe	**0.21**	**−0.27**	0.13	0.03	0.00	1.00					
Co	**−0.54**	**0.27**	**−0.54**	**0.41**	**0.50**	−0.16	1.00				
Ni	**−0.34**	**0.34**	**−0.51**	**0.70**	**0.51**	−0.13	**0.77**	1.00			
Zn	**−0.47**	**0.25**	**−0.56**	**0.71**	**0.52**	−0.08	**0.77**	**0.87**	1.00		
Cd	**−0.53**	**0.27**	**−0.53**	**0.44**	**0.37**	**−0.36**	**0.70**	**0.71**	**0.72**	1.00	
Ti	**0.35**	**−0.45**	**0.31**	**−0.31**	0.01	**0.47**	**−0.29**	**−0.22**	**−0.33**	**−0.33**	1.00

Spearman's rank correlation (r_s) for cores R1–R15

	Depth	LOI	Al	S	Fe	Co	Ni	Zn	Cd	Ti
Depth	1.00									
LOI	**−0.26**	1.00								
Al	−0.06	**0.77**	1.00							
S	**−0.54**	0.16	0.04	1.00						
Fe	0.19	**0.37**	**0.46**	−0.07	1.00					
Co	**−0.30**	**0.59**	**0.41**	**0.28**	0.10	1.00				
Ni	**−0.32**	**0.78**	**0.68**	**0.28**	0.17	**0.83**	1.00			
Zn	**−0.25**	**0.73**	**0.67**	0.23	**0.25**	**0.91**	**0.93**	1.00		
Cd	**−0.31**	**0.52**	**0.38**	**0.34**	−0.11	**0.82**	**0.77**	**0.79**	1.00	
Ti	**0.25**	**−0.45**	**−0.25**	−0.10	**0.31**	**−0.62**	**−0.53**	**−0.56**	**−0.63**	1.00

Note: Values in bold denote statistically significant results at $p < 0.05$ ($n = 74$). Bolded Indicated significant at p-values under 0.05.

area (Figure 5) due to the strong isostatic uplift of the area (ca. 8 mm/year; Mäkinen and Saaranen 1998), sedimentation and overgrowth of reeds. The C1 coring area in the shallow part of the estuary was noticeably deeper and not as overgrown with reeds in 1934. The extensive drainage and reworking of forests and peatlands into agricultural use since the early 1900s that has severely enhanced soil erosion in the catchment areas (Åström et al. 2005) and led to increased transport of particulate matter into the basin. A narrowing of the estuary outlet due to bridge constructions and the expansion of the harbour area may also have restricted water exchange with the sea, potentially enhancing sediment trapping in the estuary on one hand and, on the other hand, decreasing metal precipitation due to a lower proportion of alkaline seawater. Changing conditions over time are apparent from the diatom species assemblages in the sediments, which show a clear change (at 82.5 cm depth in core C3) from species preferring more saline, pelagic conditions to species indicative of shallower and more eutrophic conditions. This was supported by a notable overall decrease in the chrysophyte cysts to diatoms – ratio in the sediment profile. Chrysophytes are a diverse group of mostly planktonic algae, which have been shown to be more competitive in more oligotrophic conditions (Smol 1985). The shift from oligotrophic saline conditions to more eutrophic freshwater conditions coincides with the changes in catchment land use and geochemistry of the estuarine sediments.

Low ^{137}Cs activity in cores C1 and C2 indicates no net sediment deposition in the shallow parts of the estuary during the recent decades. In contrast, the ^{137}Cs peak at the 30 cm depth in core C3 shows recent sediment deposition at a mean rate of 1 cm/year in the deeper part of the estuary, ca 5.4 km from the Laihianjoki outlet. Assuming the constant deposition rate of 1 cm/year, the Zone 1 and 2 boundary at the depth of 82.5 cm in C3 would correspond to the year 1934. The lower magnetic susceptibility of the upper Zone 2 (above 82.5 cm in C3) is likely due to the dilution of the minerogenic material with organic matter originating from discharge from forested areas and the associated low bulk density of these recent sediments. The older sediment (Zone 1) has a lower organic content and is more compacted,

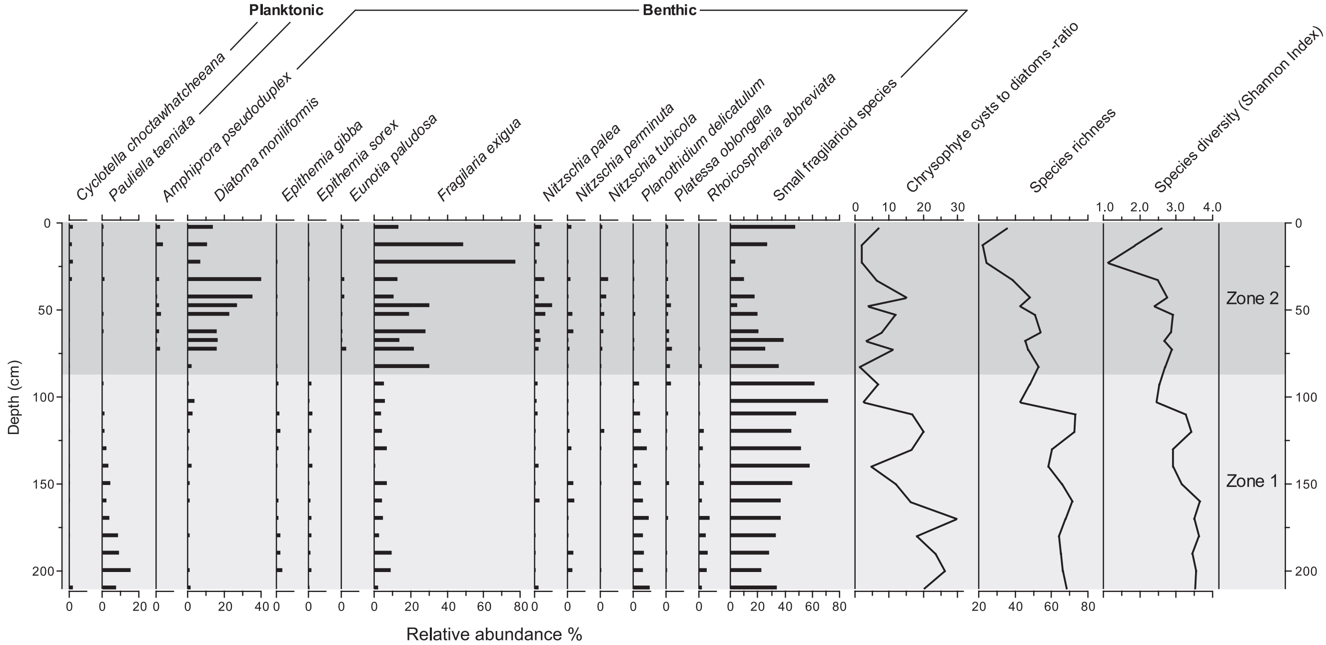

FIGURE 4 | Diatom assemblages identified in core C3 with relative abundance, species richness and species diversity (Shannon Index).

TABLE 4 | The estimated total load of C and AS soil-related metals (Al, Cd, Ni Co and Zn) from the catchment (682 km²) during the last century and the accumulation (total and relative) of these elements in the Vaasa Southern City Bay estuary.

	Catchment load (ton)	Estuarine enrichment (ton)	Estuarine enrichment (%)
Al	24,901	7765	31
C	147,542	28,097	19
Cd	3.8	0.56	15
Ni	594	42	7
Co	229	33	14
Zn	972	155	16

likely accumulated before intensive land use in the area. The planktonic *P. taeniata* and benthic *R. abbreviata* are relatively abundant in Zone 1 (deeper than 82.5 cm). They exhibit a salinity optimum of approximately 6 psu according to Weckström and Juggins (2005), who also associate *P. taeniata* and *R. abbreviata* with relatively unimpacted, deeper and slightly more saline sites in the Gulf of Finland. In Zone 1, the presence of *P. delicatulum*, with a salinity range of 1.8–9.0 psu, and *E. sorex* occurring exclusively at pH > 7 (Van Dam et al. 1994) further supports the more saline alkaline conditions in Zone 1.

Based on ^{137}Cs activity, Virtasalo et al. (2020) established sedimentation rates of 0.2–1.3 cm/year in the archipelago area, outside the inner estuary, 8–26 km out from the Laihianjoki River mouth. In contrast, Yu et al. (2015) found large spatial and temporal variability in deposition rates (0.5–5 cm/year) from a deeper and narrower estuary 50 km northeast from the study area. Both studies, however, found distinct changes in the sediment metal profiles corresponding to changes in catchment land use in the early and middle 1900s. Heikkilä (1999) found that sediment deposition in the nearby Kyrönjoki River estuary was highest in the 1950s, when land reclamation for agricultural purposes was intense, and decreased after subsurface drainage became the norm in the 1960s. The changes in the metal enrichment patterns in the estuary sediments are also apparent in the diatom assemblages. Zone 2 is characterised by the increase of *D. moniliformis* and *F. exigua*. *D. moniliformis* has been found to be a typical species in Finnish streams that are primarily affected by agriculture and have a high electrolyte concentration (Soininen et al. 2004), and in low salinity conditions (< 4.5 psu) in the coastal waters of the Gulf of Finland (Weckström and Juggins 2005). *F. exigua* dominates the assemblage towards the top of the sediment bed in Zone 2. *F. exigua* and *D. moniliformis* have a similar tolerance to saline conditions according to Weckström and Juggins (2005). However, the decreasing abundance of *D. moniliformis* towards the top of the core indicates that it is less tolerant to the corresponding high contents of S and metals and/or to the changes in surface water, i.e., loading of nutrients, metals, organic material and acidity from the catchment area. *N. palea*, which Soininen et al. (2004) link to eutrophic, polluted conditions in Finnish stream waters, also increases slightly towards the top of the core. Acidophilous *E. paludosa* occurs at a few depths in Zone 2. However, other acidophilous freshwater species from genera such as *Eunotia*, *Neidium* and *Pinnularia* (Van Dam et al. 1994) are otherwise largely absent throughout the sediment profile.

Similar major changes in species compositions and decreases in diversity linked to anthropogenic impacts have been shown in several studies from the Baltic Sea, though the species composition shifts are usually from assemblages dominated by benthic taxa to assemblages dominated by small centric planktonic taxa (e.g., Weckström 2006; Andrén et al. 2017; Ning et al. 2018; Norbäck Ivarsson et al. 2019). The amount of planktonic species

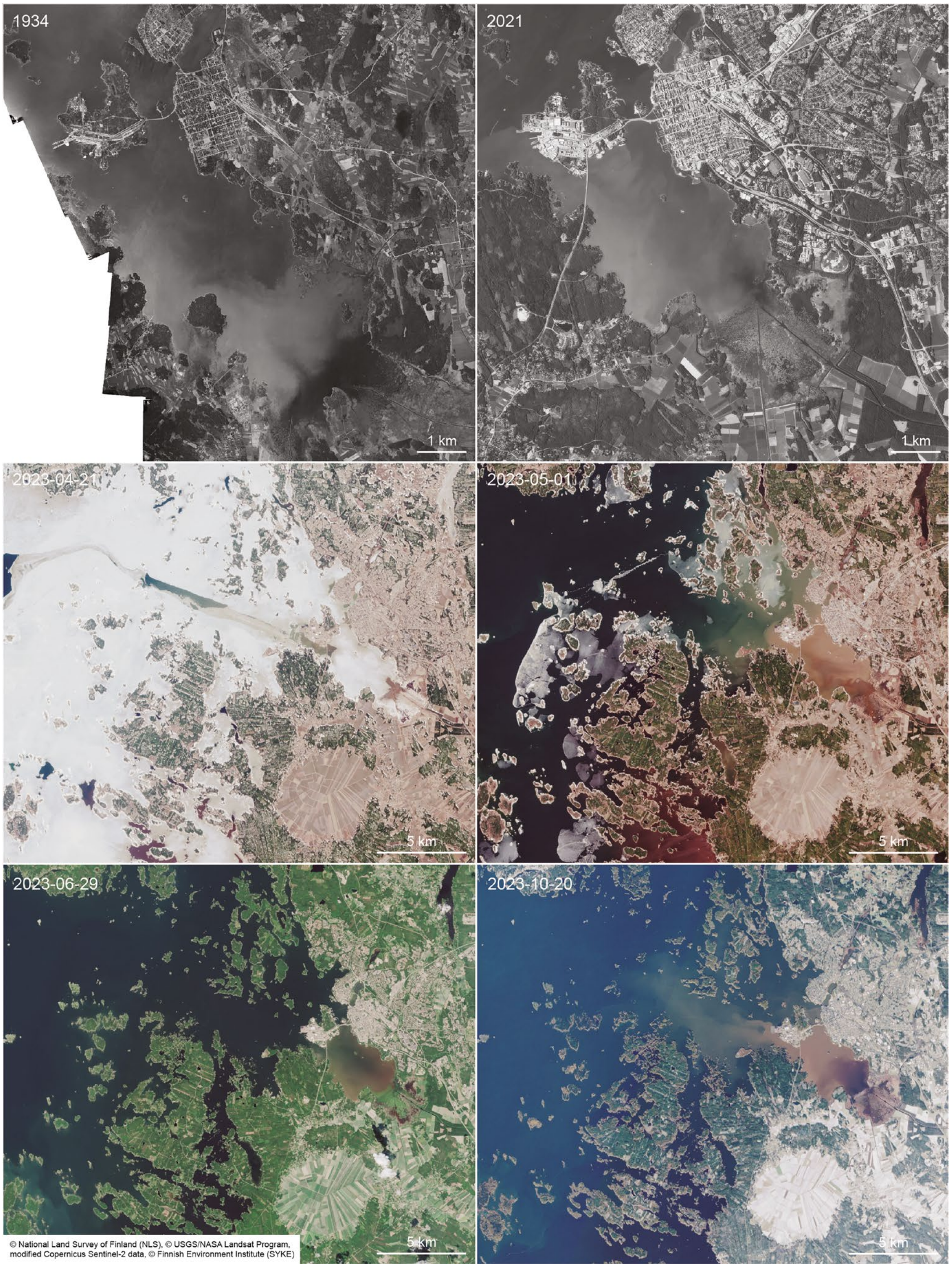

FIGURE 5 | Orthographic photos from 1934 and 2021 and satellite imagery from April, May, June and October of 2023 of the Vaasa Southern City Bay estuary.

is consistently very low, probably due to the influence of river inflow and the shallowness of the estuary. The only small centric planktonic species to increase is *Cyclotella choctawhatcheeana* (Prasad 1990), with abundances of 1.5%–2% in the top of the sediment bed. This small, summer-blooming centric diatom has been linked to eutrophication and anthropogenic disturbance of brackish waters (e.g., Andrén et al. 1999; Norbäck Ivarsson et al. 2019). Small fragilarioid species are abundant throughout the core, though they decrease somewhat in Zone 2 as *D. moniliformis* and *F. exigua* increase. These species are characterised by their opportunistic nature and rapid reproduction, and exhibit remarkable adaptability to diverse environmental conditions. Their abundance aligns with a broader pattern observed in the transition from embayments to coastal lakes within the Baltic Sea region (Weckström and Juggins 2005). The overall increasing trend in the abundance of small fragilarioid species in Zone 1 might therefore be related to the increasing isolation of the estuary due to isostatic land uplift, as well as the increasing human disturbance during the early 20th century.

Previous studies have documented significant metal loads from AS soils, particularly during autumn flow events (e.g., Nyberg et al. 2012; Nystrand et al. 2016). Elements that are found to be extensively released by AS soils (such as Al, Cd, Ni Co and Zn) are mainly transported from the catchment areas as free inorganic cations or sulfate complexes in the acidic river water. Complexation and flocculation with organic carbon are likely in waters with high TOC concentrations, which typically originate from forests and peatlands. Eroded particulates, mainly phyllosilicates, are also associated with colloidal and/or particulate elements (Åström and Corin 2000; Nystrand and Österholm 2013). Organic matter likely does play an important role in this precipitation–transport mechanism. The intensive drainage of peatlands and forests in the early 1960s has increased the leaching of organic matter in the catchment areas (Peltomaa 2007). Increased temperature and precipitation, with more varying temporal dynamics in flow patterns due to climate change, have also led to an increase in riverine total organic carbon in the past few decades (Asmala et al. 2019; Räike et al. 2024). Humic acids abundant in river water facilitate flocculation and settling in the estuary. Virtasalo et al. (2023) demonstrated in laboratory experiments that especially Al is strongly transferred to organic flocs already at low salinity values. In the estuary sediments, these findings are further corroborated as especially Al strongly correlates with the higher LOI values in Zone 2.

The hypothesis was that a precipitation gradient driven by seawater mixing would form along the transect towards the estuary outlet. The diatom assemblages of coring site C3 also revealed that freshwater conditions in the estuary have become more widespread and the saline gradient narrower, thus extending the precipitation and accumulation zone further out into the archipelago. However, from enrichment patterns, it is evident that precipitation occurred, but the most important factor determining the fate of the leached elements in the estuary was the hydrodynamic variables controlling the sedimentation. Consequently, of the AS soil related elements, 40%–70% were deposited in up to 1 m thick low-density sediments at the deepest and outermost coring sites (e.g., R13 and R14) where active sedimentation occurs to this day, representing less than 15% of the estuary area. In addition, as compared to the load of soluble metals from the catchment, more than 80% of the chalcophiles and 70% of Al were transported further out to the sea. It is also notable that roughly half of the total Al (51% in Laihianjoki) input was already in a particulate form when entering the catchment (< 10% for other metals), that is, far exceeding the amount deposited in the estuary and, thus, clearly showing that Al accumulation is not dependent on precipitation. Considering the total Al input (including the particulate fraction), only 15% was trapped in the estuary.

The sediment transport is generally directed outwards to the sea due to an excess water input from the rivers. The shallow parts of the estuary are thus affected by high hydrodynamic energy conditions such as the water input, as well as currents and wind wave action. These conditions keep the particulate matter in suspension and rework sediment from the basin floor towards lower hydrodynamic energy conditions in the deeper part of the estuary. This is also apparent from recent satellite imagery (as seen in Figure 5). During spring (late April) suspended sediment from rivers concentrated within the estuary, and as the sea ice melts, the sediment plume spread further out. Near the river mouths, the water exhibited a dark red-brown colour, indicative of humic-rich water from forests and peatlands, as well as iron-rich drainage water from farmlands (Räike et al. 2024). During the spring high-flow event (early May), the brown water extended further out in the estuary before eventually receding closer to the river mouths. The sediment plume dispersed and settled only after the end of June. During autumn high-flow events (October) there was again a noticeable increase in suspended concentration within the estuary, spreading far out into the archipelago. The relatively low proportion of metals trapped in the inner estuary and widespread plumes to the outer estuary is in strong accordance with Virtasalo et al. (2020) who demonstrated that the metal loading from AS soils extends more than 20 km seaward from the river mouths in the archipelago. This may be due to the decoupling of C and AS soil-derived elements, whereby C is deposited in the estuary while the elements are transported farther and accumulate without dilution by the organic matter. High flood events also change the water chemistry in the estuary by tipping the balance between seawater and freshwater towards the freshwater input from the rivers, thereby extending the flocculation zone for organic matter seawards. In addition to the sedimentation conditions, this may be another explanation why such a large proportion of metals are transported further out to the sea. Consequently, the estuary's capacity to function as an effective coastal filter (Asmala et al. 2019) has notably declined.

4.2 | Future AS Soils and Consequences of Sediment Uplift and Redeposition

Several natural and anthropogenic factors will lead to lowland coastal estuary systems in boreal post-glacial environments becoming narrower and shallower. In addition to the strong glacioisostatic land uplift, erosion is enhanced in the catchment areas due to intensified land use. Precipitation is likely to increase due to climate change, leading to increased sediment and nutrient transport as well as increased risk of washouts (Trenberth 2011). This can, however, be balanced by more sustainable drainage practices and soil conditioning. A larger variation in snow cover, with earlier onset of snowmelt and decreased availability of water in summer, will affect both the quantity and quality of water (Puustinen et al. 2007). Climate change will also lead to a rise in sea level; however, it will be balanced by glacioisostatic rebound in certain areas, such as the northern Baltic Sea region (Meier et al. 2004). As a result of continuing land uplift, additional land area will be uncovered and made available for land use. As the estuaries in Boreal climates are highly dynamic, there are several circumstances that can affect the future of the metal-enriched sediments. Continued sedimentation in the estuary could eventually compact and bury the sediments, while simultaneously moving the sedimentation and precipitation gradient further out as the water depth becomes shallower. As the organic-rich sediments are much less compacted and of lower density, they may also be, depending on the bottom topography, naturally eroded and redeposited further out as the water depth decreases and physical forces have a stronger effect on the bottoms.

The estuary sediments have significantly higher sulfur contents compared to previously studied sulfidic soils and sediments in Finland and the Bothnia Bay area (Åström and Rönnback 2005, Boman et al. 2023). In contrast to the diatom assemblages and other geochemical variables, there was no clear distinction in S content between Zone 1 and recent sediments in Zone 2. The decreasing water depth could lead to more oxic conditions and subsequent lower sulfate-reducing bacteria activity, which, on the other hand, can be expected to be counterweighed by the increased organic and nutrient input that has been observed. As the sulfur is mainly present as RIS, the estuarine sediments contain large reserves of stored acidity with a high reactivity in the presence of oxygen. The generation of acidity was, as expected, strongly dependent on S content, although the low-density sediments of Zone 2 showed some buffering capacity because of the higher organic content. AS soils in Finland typically have significantly lower acidity values than those found in these sediments, apart from some organic and fine-grained deposits in peatlands in northern Finland (Hadzic et al. 2014; Boman et al. 2023). In addition to very high acidity, the recent sediments are strongly enriched in easily soluble precipitated metals that will be mobilised together with acidity if oxidised. With time, there will be an increasing demand by local authorities or stakeholders to dredge these sediments to enable free flow of water at the river mouth and prevent flooding of catchment infrastructure. At a local level, these sediments can cause disastrous consequences, much larger than conventional sulfidic sediments and, thus, disturbance should be minimised. As evident in this study, however, the metal-enriched sediments will not be uplifted by natural causes in the next few centuries.

5 | Conclusions

In this study, we have determined that the loading from AS soils in the past 100 years is reflected in estuarine sediments as large enrichments of Al, Cd, Ni, Co and Zn, as well as organic matter. The loading has been captured in organic-rich mud at water depths with low hydrodynamic energy conditions. Most of the catchment load from AS soils is, however, transported further out into the archipelago, with an estimation of 30% or less captured by the estuary. Diatom assemblages in the sediments show a significant change from saline, pelagic conditions to species indicative of eutrophication and anthropogenic disturbance of surface waters. As the estuary is decreasing in size due to glacioisostatic land uplift and particulate transport from the catchment areas, its role as a coastal filter is clearly weakening, with the seawater mixing zone moving seawards. The sediments were hypersulfidic with very high amounts of potential acidity and recent sediments enriched in easily soluble metals that will be released together with acidity if oxidised. Future disturbances such as dredging operations should be well planned to minimise the environmental consequences. However, it is likely that some of the low-density metal-enriched sediments will be eroded and gradually transported further out as they are uplifted to higher hydrodynamic energy conditions with further shallowing of the estuary.

Author Contributions

Krister Dalhem: conceptualization, investigation, visualization, writing – original draft, writing – review and editing, formal analysis. **Karoliina Kehusmaa:** investigation, writing – original draft, writing – review and editing, formal analysis. **Joonas J. Virtasalo:** writing – review and editing, investigation, formal analysis. **Mats Åström:** writing – review and editing, project administration, funding acquisition, conceptualization. **Peter Österholm:** conceptualization, funding acquisition, writing – review and editing, project administration, supervision, formal analysis.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Data will be made available on request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.