Discharge of potentially toxic elements from acid sulfate soils in western Finland: Conflict between water protection and land use?

Toivonen, Janne; Boman, Anton

Published in:
Regional Studies in Marine Science

DOI:
10.1016/j.rsma.2024.103426

Published: 01/04/2024

Document Version
Final published version

Document License
CC BY

Link to publication

Please cite the original version:
Toivonen, J., & Boman, A. (2024). Discharge of potentially toxic elements from acid sulfate soils in western Finland: Conflict between water protection and land use? *Regional Studies in Marine Science*, *71*, Article 103426. https://doi.org/10.1016/j.rsma.2024.103426

Regional Studies in Marine Science 71 (2024) 103426

Contents lists available at ScienceDirect

Regional Studies in Marine Science

journal homepage: www.elsevier.com/locate/rsma

Discharge of potentially toxic elements from acid sulfate soils in western Finland: Conflict between water protection and land use?

Janne Toivonen [a,*], Anton Boman [b]

[a] Geology and Mineralogy, Åbo Akademi University, Akademigatan 1, Åbo 20500, Finland
[b] Geological Survey of Finland, Teknologiakatu 7, Kokkola 67101, Finland

ARTICLE INFO

Keywords:
Acid sulfate soils
Metal pollution
Protection of waters
Environmental protection legislation

ABSTRACT

Acid sulfate soils (ASS) are commonly found in many coastal areas worldwide and typically develop from artificial draining of sulfidic sediments, which release acidity and metals, causing unfavuorable effects on recipient watercourses. This study estimates the actual amounts of metals and elements carried to the Gulf of Bothnia and the Baltic Sea by stream water yearly. The combined load from the many small streams and ditches was found to be proportionally high related to the size of their catchment, emphasizing the importance of including numerous small streams in the understanding of pollution in fresh water and marine environments. This study shows that Cd concentrations in the majority of the studied rivers exceed the Environmental Quality Standard set by the European Union (EU). This causes lowered ecological and chemical status according to the European classification system. Many potentially toxic elements discharge yearly to the Baltic Sea in large quantities from the study area: Thousands of tons of Al and Mn, tens of tons of Co, Cu and Ni, and hundreds of kg of Cd. A challenge for the estimation was irregular, or even missing, data for many rivers, which highlights careful planning of monitoring programs. While the current land use on ASS requires efficient drainage, the national and European strategies and legislation aim towards improved status in water bodies and forbid pollution of the environment. Therefore, the land use and water protection policy conflict.

1. Introduction

Acid sulfate soils (ASS) develop on fine-grained sulfidic sediments in many coastal areas worldwide. Due to land reclamation for agriculture and forestry, building of infrastructure, dredging watercourses etc., the sediments are drained and the sulfides are exposed to oxygen. Aided by microbes, the sulfides oxidize to sulfuric acid, causing the soil pH to drop below 4.0, which is a diagnostic criterion for an ASS consisting of mineral soil materials (for organic soil materials, the pH limit is < 3.0; Boman et al., 2023). Upon the oxidation and drop in pH, many minerals dissolve, and acidity and potentially harmful elements are released in large quantities (Peltola and Åström, 2002; Haraguchi, 2007; Sukitprapanon et al., 2018; Mattbäck et al., 2022). This does not only cause problems for agriculture (Palko, 1994), but also for the recipient water courses where the acid metal discharge drains to; the water courses draining ASS often suffer from lowered water quality (Åström and Björklund, 1995; Green et al., 2006; Enio et al., 2020). A visible and spectacular result from poor water quality is seen as occasional large fish kills (Sammut et al., 1995; Sutela et al., 2012) but the main effect is seen as overall negative impact on the ecology and ecosystems (Hudd and Leskelä, 1998; Russell and Helmke, 2002; Amaral et al., 2012; Toivonen et al., 2020). The metals are transported to river estuaries, which are important reproduction sites of many fish species in boreal environments (Lehtonen and Hudd, 1990), and precipitate in the brackish water (Nystrand et al., 2016). Enrichment of potentially toxic metals is visible in the sediments with potential detrimental effects on marine biota (Wallin et al., 2015; Virtasalo et al., 2020). These metal-enriched sediments also form new threats in dredging operations (Johnson et al., 2022), as well as in future drainage operations as the land uplift (about 8 mm/year in coastal areas of western Finland) reveals new areas in the shallow archipelago. For these reasons, ASS are commonly referred to as "the nastiest soils in the world" (Dent and Pons, 1995).

International water frameworks, agreements and legislation regarding the study area include the Water Framework Directive (2000/60/EC), the Marine Strategy Framework Directive (2008/56/EC) and the HELCOM (Helsinki-Commission). These policies and agreements commit countries to achieve good ecological and chemical status of all water bodies in the European Union (EU) and to protect the Baltic Sea

* Corresponding author.
E-mail address: jatoivon@abo.fi (J. Toivonen).

https://doi.org/10.1016/j.rsma.2024.103426
Received 18 September 2023; Received in revised form 19 January 2024; Accepted 6 February 2024

from pollution. The drainage of sulfidic sediments and subsequent development of active ASS with a potential high load of acidity and hazardous substances is regarded as the main hindrance from achieving the goals regarding water protection in the study area (Teppo et al., 2022). Therefore, knowledge of the amount of pollution that is released from ASS is of great importance in understanding environmental challenges.

The aim of this study is to examine the total yearly load, calculated using different approaches, of selected elements carried to the Baltic Sea from a drainage area of rivers and streams in a region in western Finland; this area is known for the high occurrence of ASS (Geological Survey of Finland, 2023). Furthermore, studies on streams draining catchments between the rivers are also included because the numerous and difficult monitored small streams have in previous studies shown to contribute with a relatively large load (Toivonen et al., 2019). The studied suite of elements both include those that are highly mobilized from ASS and some elements that are not.

2. Materials and methods

2.1. Study area

The study area consists of the drainage areas of 17 rivers (total drainage area 17 614 km^2), as well as the numerous smaller drainage areas (including some larger islands) between the rivers draining to the Baltic Sea (total drainage area 2408 km^2, Fig. 1). The study area roughly corresponds to the administrative regions of Ostrobothnia and South Ostrobothnia in western Finland, which are known for the occurrence of ASS (Palko, 1994; Geological Survey of Finland, 2023). Part of the study area is located within the so-called maximum extent of the Littorina Sea, which has been mapped for ASS occurrence by the Geological Survey of Finland (GTK, Edén et al., 2023; Geological Survey of Finland, 2023) and where the majority of ASS in Finland are present (Edén et al., 2023). The mapped area and calculated probability of ASS is visualized in Fig. 1. The parent material of the ASS in Finland are typically fine-grained sediments deposited during the Littorina and post-Littorina Sea-stages (8000 – 0 BP) that have been uplifted up to 100 m above current sea level due to post-glacial isostatic uplift (up to 8 mm/year in the study area). The majority of ASS are, however, commonly present below c. 60 m above current sea level (Geological Survey of Finland, 2023). Due to microbial reduction of sulfate to sulfide during sedimentation, these sediments have an S-content of 0.54% on average (Åström and Björklund, 1997), mainly in the form of iron sulfides (Boman et al., 2010). Especially during the latter half of the 20th century, intensive land use in the form of drainage for agriculture and forestry has lowered the ground water table in the water-logged sediments. As a result, the sulfides in the drained part of the soil have oxidized into sulfuric acid, creating active ASS with detrimental effects on the water quality in the area (Åström and Björklund, 1995, Saarinen et al., 2010). About one-fifth of the study area within the mapped area by GTK (within the Littorina and post-Littorina area, Fig. 1) consists of ASS (cf. Edén et al., 2023).

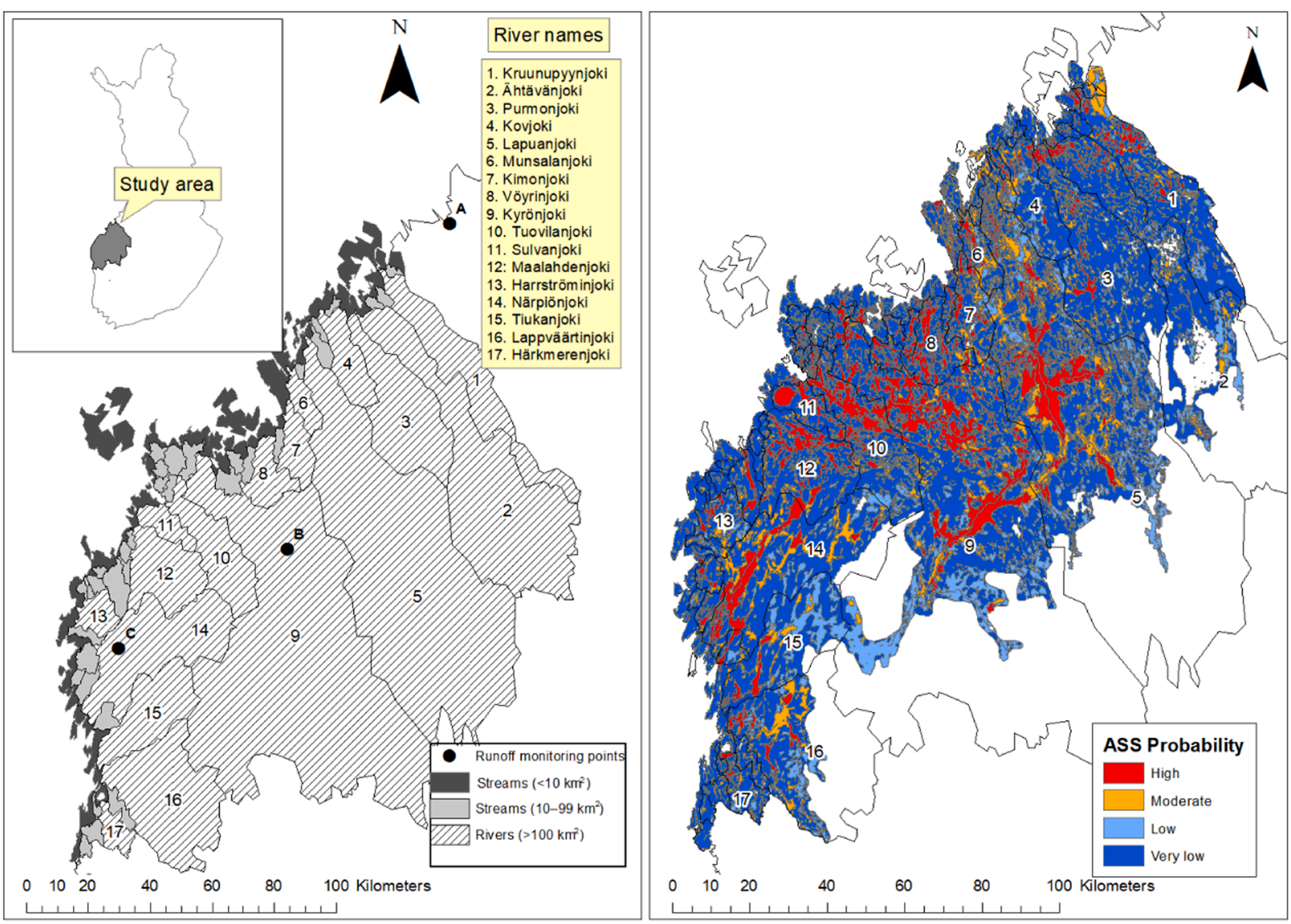

Fig. 1. Left: The location of the study area, locations of the drainage areas and sampled streams and rivers, and the locations of the runoff monitoring points (A, B and C). Right: The mapped area and results of the calculated probability of acid sulfate soils (ASS) related to the study area.

2.2. National monitoring data

National monitoring data for the period 2010 – 2019 (Finnish Environment Institute, 2022) on water quality in rivers (drainage area > 100 km^2) was used. This data set is referred to "data set 1" in the text. Aluminum, Cd, Co, Cu, Mn, Ni, and U are good indicators on the impact from ASS due to the high rates of mobilization and release from these soils (Åström and Björklund, 1995; Sundström et al., 2002; Nystrand and Österholm, 2013). Even though some elements may occur in small-size particulate fractions in some areas (Nystrand et al., 2012), element concentrations analysed on filtered (0.45 μm) water samples are widely used in water research and is operationally defined as "dissolved" and potentially harmful for biota. However, the availability of data on dissolved fractions varies in the national monitoring data. Therefore, data on both total and dissolved element content was chosen due to the often sparse information on dissolved fractions. The mentioned elements prevail mainly in dissolved form if the pH is low (Nystrand and Österholm, 2013). During sampling events when both total and dissolved fractions have been analysed, the sample showing the lower content was chosen (usually the dissolved fraction). Data on some additional potentially harmful elements (As, Cr, and Pb) was also collected, even though these are not considered to leach from ASS in any larger extent compared with other soils (Åström and Björklund, 1997; Peltola and Åström, 2002; Sundström et al., 2002; Roos and Åström, 2006; Nystrand and Österholm, 2013). For these elements, results only from unfiltered samples were used due to the generally meagre availability of results from filtered samples, as well as because the dissolved fraction of the mentioned elements does not reflect well the total concentrations (Nystrand and Österholm, 2013).

2.3. Water sampling and analysis

To obtain data that is more comparable between the rivers, additional water sampling from the same sites as in the national monitoring program was performed by the authors for three years (spring 2016 and 2019, and autumn 2017) from each river. This water sampling was performed during a short period (2 days) each year so that the hydrological conditions would be as similar as possible, and the results between rivers more comparable. This data is referred to "data set 2" in the text. pH and electric conductivity (EC) were measured *in situ*, and samples for element analysis (Al, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and U with ICP-OES/MS) were filtered (0.45 μm) and acidified with ultrapure HNO_3. For five rivers, unfiltered samples were also analysed during spring 2016 and autumn 2017 (n=10) for the comparison of dissolved vs. total fractions. A selection of streams (n=29, drainage area < 100 km^2, also "data set 2") found in the near-field (draining catchments between the rivers) were also sampled during the same time as the rivers. The choice of which streams to sample was strived to be representative for the area in terms of soil types, land use and geography, but with the requirement of easy accessibility by car close to the mouth of the stream.

2.4. River discharge and calculation of element load

Data on river discharge, available for nine of the studied rivers, was collected from the national monitoring data. For those rivers where discharge is not monitored (n=8), estimated river discharge for the period was acquired from the Finnish Environment Institute based on watershed simulation and forecasting system (Vehviläinen and Huttunen, 2001; Vehviläinen et al., 2005). The national monitoring data also includes runoff measurements in smaller catchments, which is better suited to fit the hydrological behaviour of the streams draining the catchments between the rivers. Three monitoring points, measuring the daily runoff in catchments with a size of 6.1, 8.1, and 11.6 km^2 (A, B, and C, respectively, in Fig. 1), were chosen to represent the runoff in the streams. The monitoring point closest to each sampled stream was chosen to represent the runoff for the stream. The rivers (n=17) represent a total drainage area of 17 614 km^2. A runoff-weighted average for each river and element was calculated separately for data set 1 and 2. The yearly mean quantity for each river and element was estimated by multiplying the runoff-weighted average with the mean discharge for the study period. For the streams draining the catchments between the rivers in data set 2, a runoff-weighted average was calculated separately for the small streams (drainage area <10 km^2, n=15, represents a drainage area of 1453 km^2) and large streams (drainage area 10 – 99 km^2, n=14, represents a drainage area of 955 km^2). Estimating the exact drainage area of the sampled small streams is difficult. However, based on the data on runoff at the closest monitoring point (A, B, and C in Fig. 1) and the discharge measured *in situ*, the sampled small streams have a drainage area of approximately 7.7 km^2. The sampled large streams have a drainage area of 506 km^2. The calculated loads from the small and large streams are combined and represent the load from the catchments between the rivers (2408 km^2).

3. Results

3.1. Availability of national monitoring data

The availability of data on water quality in the national monitoring data is irregular; for some elements in the rivers with larger catchment sizes, sampling and analysis have been performed about 13 times/year, evenly spread throughout the seasons (Fig. 2), which gives promise of representative results. On the other hand, the sparse data often found for the rivers with smaller catchments foreshadows a risk of less representative results for these rivers (e.g., Figs. 3 and 4); the timing and frequency of sampling are irregular throughout the study period and the choice of analysing total or dissolved contents varies, thus amplifying the risk of biased results. For one river, # 6 (Munsalanjoki River, Fig. 1), there is complete lack of information on water quality in the national monitoring data for the study period.

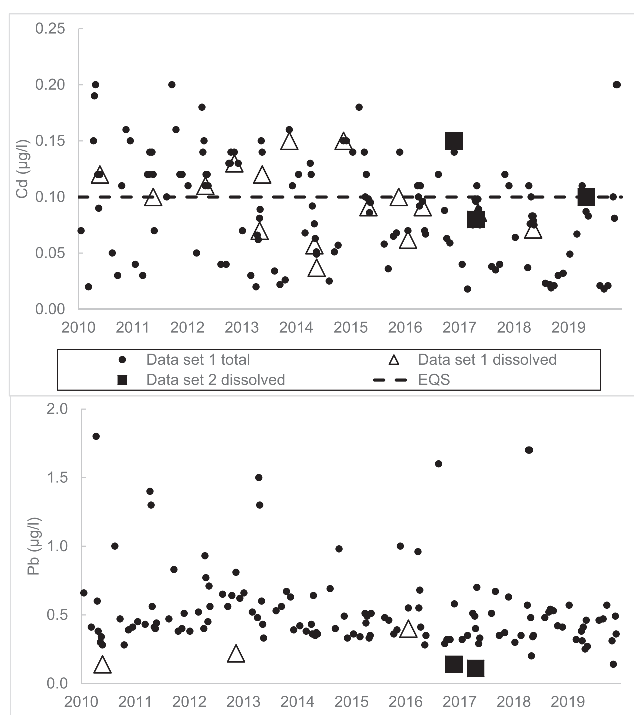

Fig. 2. Total and dissolved (0.45 μm) Cd and Pb levels and sampling events in Kyrönjoki River, and environmental quality standard (EQS) for Cd (0.1 μg/l). Data set 1 denotes the national monitoring data and data set 2 denotes the authors' data.

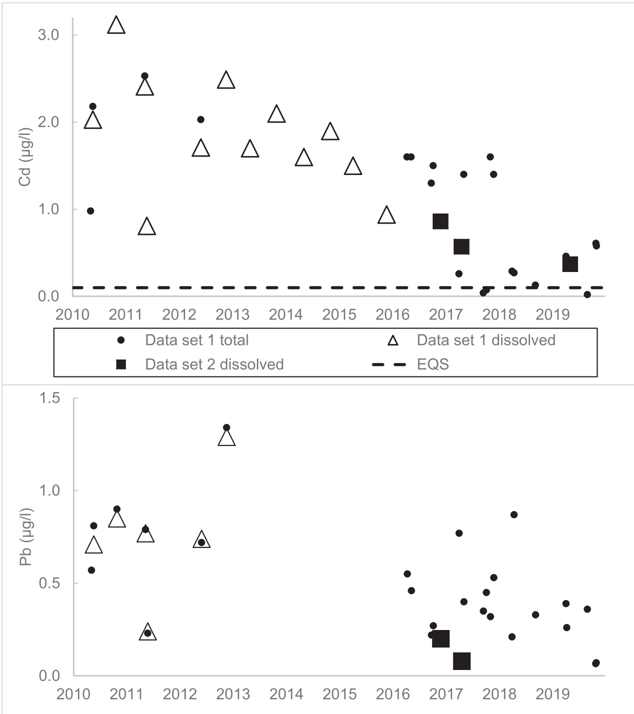

Fig. 3. Total and dissolved (0.45 µm) Cd and Pb levels and sampling events in Sulvanjoki River, and environmental quality standard (EQS) for Cd (0.1 µg/l). Data set 1 denotes the national monitoring data and data set 2 denotes the authors' data.

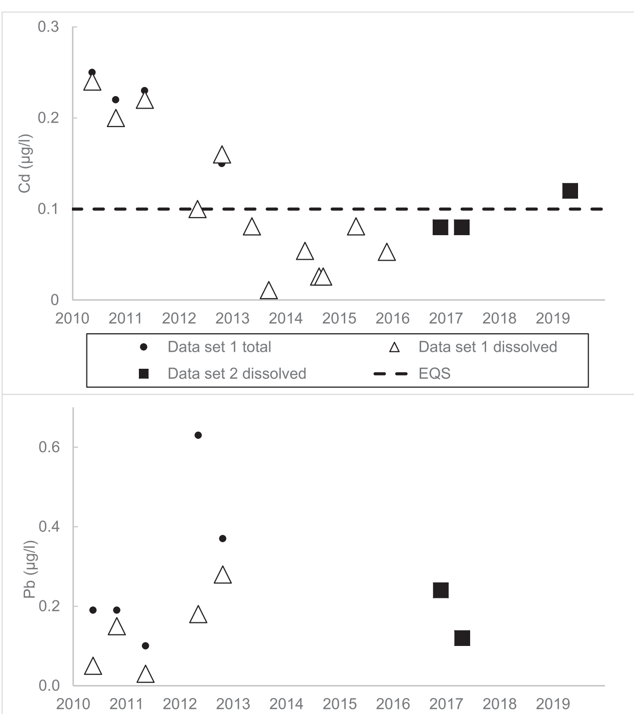

Fig. 4. Total and dissolved (0.45 µm) Cd and Pb levels and sampling events in Kovjoki River, and environmental quality standard (EQS) for Cd (0.1 µg/l). Data set 1 denotes the national monitoring data and data set 2 denotes the authors' data.

3.2. pH and concentrations of potentially toxic elements in the studied streams and rivers (data set 2)

The sampled small streams (drainage area <10 km^2, n=15) showed a pH-range of 3.5 to 6.7 (median 5.7). The large streams (drainage area 10 – 99 km^2, n=14) showed a pH-range of 4.4 to 6.8 (median 5.8). 37% of the sampling events in the small and large streams displayed pH 5.5 or below. The rivers showed a pH-range of 4.5 to 6.6 (median 5.8). 33% of the sampling events in the rivers displayed a pH 5.5 or below. The calculated runoff-weighted averages of Cd in 12 of the 17 rivers in data set 1 (Table 1) and in 10 of the 17 rivers in data set 2 (Table 2) exceed the Environmental Quality Standard (EQS). The runoff-weighted average of the streams also exceeds the EQS (Table 3). The calculated runoff-weighted averages of Al exceed 500 µg/l in all but one of the studied rivers (Table 2). Since the load related to stream size is directly dependent of the runoff-weighted average, the differences in the concentrations between rivers and the near-field is visualized in Fig. 6.

3.3. Yearly load of elements (Al, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and U)

The yearly load (t) of elements carried from the study area to the Baltic Sea during 2010 – 2019 based on data set 1 is as follows: Al 7975, Mn 1657, Ni 70, Co 35, Cu 25, Cr 9.2, As 4.9, Pb 3.3, U 1.0, and Cd 0.6 (Table 1). Because data from river # 6 is missing, results from data set 2 are used for this river. The load (t) calculated from data set 2 compared with the results above is generally lower; 25 – 100% compared with data set 1: Al 4197, Mn 1280, Ni 63, Co 23, Cu 16, As 4.9, Cr 3.9, Pb 0.82, U 0.64, and Cd 0.51 (Table 2).

For the rivers where the dissolved fraction was compared with the total fraction (data set 2), the share of the mean dissolved fraction (0.45 µm) for each element was as following (%): Ni (96), Mn (90), Cd (89), Co (88), Cu (84), As (83), Al (62), U (62), Cr (50), and Pb (36). The minimum and maximum pH in these sampled rivers was 4.5 and 6.4, respectively.

The combined load from the near-field, i.e., the areas between the rivers drained by numerous streams, is for many elements equal to, or even larger than, the load from the largest river (Fig. 5, Table 3). The load of the ASS-related elements Al and Cd carried by the streams is about 25% of the total load, and about 20% for Cu, Mn, Ni, and U. A remarkable result regarding the rivers is that the small rivers do not contribute with a high share of the total loads but instead, contribute with the largest loads per km^2 (Fig. 6 and Table 2).

For part of the study area, rivers # 1 – 4, the yearly load of some ASS-related elements has previously been calculated (Toivonen et al., 2019) using the same methods of sampling, analyses, and runoff-weighted averages as described in Sections 2.3 and 2.4. The results in Toivonen et al. (2019) describes the situation during 2007, a period characterized by extremely poor water quality and fish kills (Sutela et al., 2012; Toivonen et al., 2013). The load carried by the four rivers was 2.1 – 4.8 times greater for Cd during 2007 compared with data set 2 (Fig. 7), and 2.5 – 4.4 times greater for Ni (data not shown).

4. Discussion

4.1. Suitability and reliability of the data and comparability between data sets

Effects of discharge from ASS are known to show great short- and long-term variations due to changes in the hydrological conditions, changes in land use, element depletion in soil, climate change etc. (Österholm and Åström, 2008; Toivonen et al., 2013). This is also obvious in the rivers in the current study (Figs. 2 – 4). Therefore, a variation in the frequency or timing of sampling may cause problems in the comparability between rivers and between data sets when calculating the load. For a river with analysis results evenly spread throughout the study period (e.g., river # 9, data set 1, Fig. 2), the

Table 1
River number (River names in Fig. 1), drainage area, average runoff, number of samples (n), runoff-weighted average and yearly total load for analysed elements for each river based on data set 1.

Data set 1 (2010-2019)

River info			Al			Mn			Ni			Co			Cu		
River number	Drainage area km^2	Average runoff l/s/km^2	n	Runoff-weighted average µg/l	Load t/y	n	Runoff-weighted average µg/l	Load t/y	n	Runoff-weighted average µg/l	Load t/y	n	Runoff-weighted average µg/l	Load t/y	n	Runoff-weighted average µg/l	Load t/y
1	788	9.4	19	764	178	5	178	41	33	6.9	1.6	10	3.2	0.75	22	2.4	0.56
2	2054	8.6	71	358	200	56	95	53	34	4.3	2.4	11	1.5	0.81	23	2.0	1.1
3	864	8.9	60	1009	245	43	184	45	24	7.2	1.7	8	4.3	1.1	13	2.4	0.58
4	292	6.2	12	1260	72	5	266	15	12	9.2	0.52	5	6.8	0.39	5	2.6	0.15
5	4122	8.8	131	1556	1784	133	391	449	132	14	16	18	7.3	8.4	130	4.4	5.1
6*	120	7.1	3	1592	35	3	317	7.4	3	14	0.32	2	5.8	0.14	3	3.7	0.09
7	196	9.9	21	1855	113	7	201	12	22	14	0.86	6	8.2	0.50	12	6.5	0.40
8	223	10	42	4880	341	19	687	48	33	43	3.0	11	25	1.7	23	9.1	0.64
9	4923	8.9	135	1706	2367	134	423	587	142	15	21	18	6.9	9.6	131	6.1	8.4
10	504	8.0	26	2470	314	15	479	61	34	36	4.6	10	19	2.5	24	9.1	1.2
11	144	8.7	30	10,355	410	15	2501	99	31	146	5.8	13	91	3.6	24	14	0.57
12	500	9.0	54	3039	429	49	400	56	68	25	3.6	52	14	1.9	29	8.5	1.2
13	140	13	20	943	53	5	146	8.2	6	14	0.79	7	4.0	0.22	15	5.2	0.29
14	992	9.6	134	1963	592	132	275	83	61	15	4.4	21	5.8	1.7	53	6.8	2.1
15	542	10	25	1597	279	7	136	24	26	5.9	1.0	6	4.5	0.79	15	3.8	0.66
16	1098	13	148	1133	491	148	146	63	148	3.8	1.7	20	1.4	0.61	144	3.1	1.4
17	113	12	11	1633	72	5	110	4.8	11	11	0.47	5	3.6	0.16	5	4.6	0.20
Total	17,614				7975			1657			70			35			25

	As			Cr			Pb			U			Cd		
River number	n	Runoff-weighted average µg/l	Load t/y	n	Runoff-weighted average µg/l	Load t/y	n	Runoff-weighted average µg/l	Load t/y	n	Runoff-weighted average µg/l	Load t/y	n	Runoff-weighted average µg/l	Load t/y
1	24	0.81	0.19	24	1.1	0.25	23	0.38	0.09	10	0.12	0.03	33	0.05	0.01
2	25	0.88	0.49	25	0.65	0.36	25	0.22	0.12	10	0.09	0.05	35	0.03	0.02
3	14	0.65	0.16	14	1.3	0.32	14	0.47	0.11	7	0.13	0.03	24	0.08	0.02
4	5	0.68	0.04	5	2.2	0.12	5	0.42	0.02	5	0.21	0.01	12	0.11	0.01
5	131	0.89	1.0	132	1.6	1.8	132	0.59	0.67	16	0.21	0.24	131	0.10	0.12
6*	2	1.0	0.02	2	1.20	0.03	2	0.14	0.003	2	0.20	0.005	3	0.17	0.004
7	13	0.68	0.04	13	1.5	0.09	13	0.7	0.04	6	0.29	0.02	20	0.15	0.01
8	24	1.3	0.09	24	1.9	0.14	24	0.97	0.07	10	0.47	0.03	33	0.33	0.02
9	133	1.19	1.7	133	2.3	3.3	133	0.84	1.2	18	0.24	0.33	142	0.12	0.16
10	24	0.92	0.12	24	2.0	0.25	24	0.90	0.11	9	0.31	0.04	34	0.22	0.03
11	24	1.0	0.04	25	1.9	0.08	25	0.66	0.03	12	1.1	0.04	31	1.3	0.05
12	55	0.94	0.13	55	3.0	0.42	55	0.69	0.10	16	0.35	0.05	68	0.23	0.03
13	15	0.62	0.03	15	1.4	0.08	15	0.64	0.04	7	0.19	0.01	21	0.14	0.01
14	53	0.93	0.28	53	2.0	0.59	53	0.85	0.26	19	0.21	0.06	61	0.11	0.03
15	13	1.1	0.20	13	2.5	0.44	13	0.79	0.14	6	0.16	0.03	26	0.06	0.01
16	145	0.74	0.32	145	2.0	0.86	145	0.69	0.30	20	0.13	0.06	148	0.05	0.02
17	4	0.76	0.03	4	1.7	0.08	4	0.84	0.04	5	0.21	0.01	11	0.16	0.01
Total			4.9			9.2			3.3			1.0			0.6

* data from data set 2

Table 2
River number, drainage area, average runoff, runoff-weighted average, yearly total load and load/km^2 for analysed elements for each river based on data set 2. The number of samples is n=3 for each river and element except for Co, U, As, Cr, and Pb where n=2.

Data set 2 (authors'data 2016-2019)

Rivers

River info			Al			Mn			Ni			Co			Cu		
River number	Drainage area km2	Average runoff l/s/km2	Runoff-weighted average µg/l	Load t/y	Load t/km2	Runoff-weighted average µg/l	Load t/y	Load t/km2	Runoff-weighted average µg/l	Load t/y	Load kg/km2	Runoff-weighted average µg/l	Load t/y	Load kg/km2	Runoff-weighted average µg/l	Load t/y	Load kg/km2
1	788	9.4	526	122	0.16	174	40	0.05	4.3	1.00	1.3	1.6	0.36	0.46	1.8	0.41	0.53
2	2054	8.0	319	166	0.08	99	52	0.03	3.3	1.7	0.83	0.91	0.47	0.23	1.8	0.94	0.46
3	864	8.3	778	175	0.20	214	48	0.06	6.2	1.4	1.6	1.7	0.39	0.45	3.3	0.73	0.85
4	292	5.7	823	43	0.15	212	11	0.04	7.8	0.41	1.4	3.4	0.18	0.61	2.8	0.15	0.51
5	4122	8.3	699	758	0.18	293	318	0.08	9.3	10	2.4	3.7	4.1	0.98	2.2	2.4	0.58
6	120	6.2	1502	35	0.29	317	7.4	0.06	14	0.32	2.7	5.8	0.14	1.1	3.7	0.09	0.73
7	196	9.0	1394	78	0.40	285	16	0.08	13	0.75	3.8	4.6	0.25	1.3	3.3	0.18	0.93
8	223	9.2	2892	187	0.84	684	44	0.20	42	2.7	12	15	0.97	4.4	5.7	0.37	1.7
9	4923	8.6	831	1112	0.23	339	454	0.09	18	24	4.8	6.0	8.1	1.6	4.5	6.0	1.2
10	504	8.2	1751	229	0.45	600	79	0.16	43	5.7	11	16	2.1	4.1	6.5	0.85	1.7
11	144	8.8	3540	141	0.98	778	31	0.22	64	2.6	18	33	1.3	9.1	7.6	0.30	2.1
12	500	10	1823	274	0.55	289	43	0.09	21	3.2	6.4	8.6	1.3	2.6	6.1	0.92	1.8
13	140	13	680	38	0.27	125	7.0	0.05	13	0.71	5.1	3.3	0.18	1.3	5.2	0.29	2.1
14	992	10	1220	376	0.38	254	78	0.08	18	5.4	5.5	6.3	1.9	1.9	4.8	1.5	1.5
15	542	10	828	142	0.26	87	15	0.03	6.4	1.1	2.0	1.8	0.31	0.57	3.1	0.53	0.97
16	1098	12	661	275	0.25	77	32	0.03	3.9	1.6	1.5	1.2	0.51	0.46	1.7	0.69	0.63
17	113	12	1082	45	0.40	92	3.8	0.03	7.5	0.31	2.7	2.4	0.10	0.88	2.7	0.11	0.99
Total (rivers)	17,614			4197			1280			63			23			16	
Load compared to data set 1 (%)				52			77			89			64			67	

	As			Cr			Pb			U			Cd		
River number	Runoff-weighted average µg/l	Load t/y	Load kg/km2	Runoff-weighted average µg/l	Load t/y	Load kg/km2	Runoff-weighted average µg/l	Load t/y	Load kg/km2	Runoff-weighted average µg/l	Load t/y	Load kg/km2	Runoff-weighted average µg/l	Load t/y	Load kg/km2
1	0.74	0.17	0.22	0.64	0.15	0.19	0.17	0.04	0.05	0.08	0.02	0.02	0.05	0.01	0.02
2	0.83	0.43	0.21	0.5	0.26	0.13	0.09	0.05	0.02	0.08	0.04	0.02	0.02	0.01	0.01
3	0.60	0.14	0.16	0.7	0.16	0.18	0.37	0.08	0.10	0.09	0.02	0.02	0.08	0.02	0.02
4	0.82	0.04	0.15	1.1	0.06	0.21	0.17	0.01	0.03	0.19	0.01	0.04	0.09	0.005	0.02
5	0.77	0.84	0.20	0.8	0.87	0.21	0.14	0.15	0.04	0.14	0.15	0.04	0.08	0.08	0.02
6	1.0	0.02	0.20	1.2	0.03	0.23	0.14	0.003	0.03	0.20	0.005	0.04	0.17	0.004	0.03
7	0.89	0.05	0.25	0.8	0.04	0.23	0.22	0.01	0.06	0.15	0.01	0.04	0.15	0.01	0.04
8	1.4	0.09	0.40	0.70	0.05	0.20	0.09	0.01	0.03	0.22	0.01	0.06	0.33	0.02	0.10
9	1.2	1.7	0.34	0.75	1.0	0.20	0.13	0.18	0.04	0.15	0.20	0.04	0.13	0.17	0.03
10	1.4	0.19	0.38	0.80	0.10	0.21	0.11	0.01	0.03	0.20	0.03	0.05	0.26	0.03	0.07
11	2.4	0.09	0.66	0.91	0.04	0.25	0.12	0.005	0.03	0.37	0.01	0.10	0.62	0.02	0.17
12	1.4	0.21	0.42	1.3	0.20	0.39	0.26	0.04	0.08	0.18	0.03	0.06	0.21	0.03	0.06
13	0.69	0.04	0.28	0.88	0.05	0.35	0.31	0.02	0.12	0.13	0.01	0.05	0.14	0.01	0.06
14	1.3	0.40	0.40	1.3	0.39	0.40	0.24	0.07	0.07	0.16	0.05	0.05	0.14	0.04	0.04
15	1.0	0.17	0.32	1.0	0.18	0.33	0.23	0.04	0.07	0.09	0.02	0.03	0.06	0.01	0.02
16	0.71	0.30	0.27	0.66	0.27	0.25	0.21	0.09	0.08	0.07	0.03	0.03	0.04	0.02	0.02
17	0.84	0.03	0.31	1.1	0.05	0.40	0.26	0.01	0.10	0.12	0.01	0.05	0.11	0.004	0.04
Total (rivers)		4.9			3.9			0.82			0.64			0.51	
Load compared to data set 1 (%)		100			42			25			60			90	

Table 3
Runoff-weighted average, yearly total load and load/km^2 for analysed elements for near-field streams based on data set 2. The number of samples is n=3 for each stream and element except for Co, U, As, Cr, and Pb where n=2.

Data set 2 (authors' data 2016-2019)

Near-field streams

	Drainage area km^2	Al Runoff-weighted average µg/l	Al Load t/y	Al Load t/km^2	Mn Runoff-weighted average µg/l	Mn Load t/y	Mn Load t/km^2	Ni Runoff-weighted average µg/l	Ni Load t/y	Ni Load kg/km^2	Co Runoff-weighted average µg/l	Co Load t/y	Co Load kg/km^2	Cu Runoff-weighted average µg/l	Cu Load t/y	Cu Load kg/km^2
Near-field streams (<10 km2)	1453	2652	1131	0.78	425	181	0.12	25	11	7.6	4.0	1.7	1.2	6	2.6	1.8
Near-field streams (15-92 km2)	955	1319	370	0.39	278	78	0.08	19	5.4	5.7	7.5	2.1	2.2	5.08	1.4	1.5
Near-field stream total	2408		1501	0.62		259	0.11		16	6.7		3.8	1.6		4.0	1.7
Total (rivers and near-field streams)	20,021		5698			1540			79			26			20	
Share of near-field streams (%)	12		26			17			21			14			19	

	As Runoff-weighted average µg/l	As Load t/y	As Load kg/km^2	Cr Runoff-weighted average µg/l	Cr Load t/y	Cr Load kg/km^2	Pb Runoff-weighted average µg/l	Pb Load t/y	Pb Load kg/km^2	U Runoff-weighted average µg/l	U Load t/y	U Load kg/km^2	Cd Runoff-weighted average µg/l	Cd Load t/y	Cd Load kg/km^2
Near-field streams (<10 km2)	0.51	0.22	0.15	0.54	0.23	0.16	0.09	0.04	0.03	0.15	0.06	0.04	0.30	0.13	0.09
Near-field streams (15-92 km2)	1.1	0.31	0.32	1.1	0.32	0.34	0.20	0.06	0.06	0.24	0.07	0.07	0.20	0.06	0.06
Near-field stream total		0.53	0.22		0.55	0.23		0.09	0.04		0.13	0.05		0.19	0.08
Total (rivers and near-field streams)		5.4			4.5			0.91			0.76			0.70	
Share of the load carried by the near-field streams (%)		9.8			12			10			17			27	

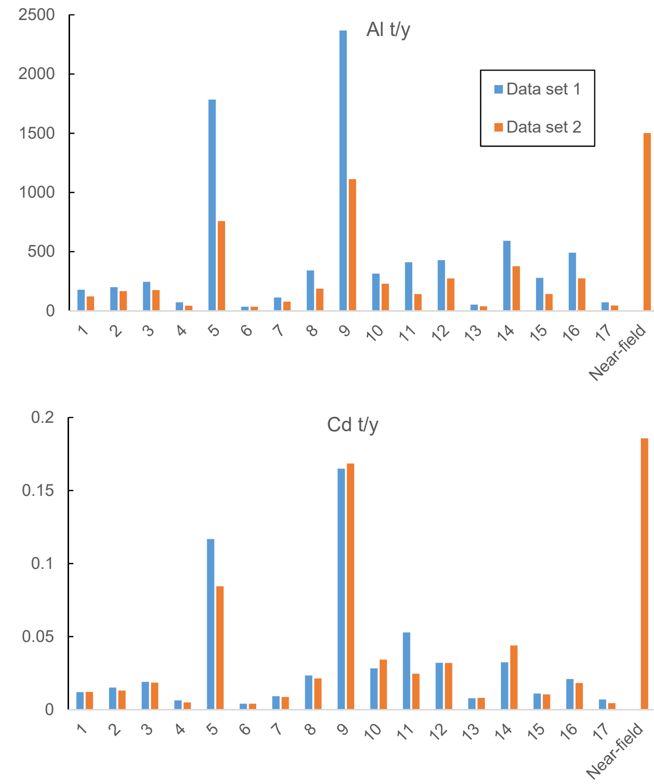

Fig. 5. Comparison of yearly load (t) carried by the rivers (river names are found in Fig. 1) between data sets for Al (above) and Cd (below).

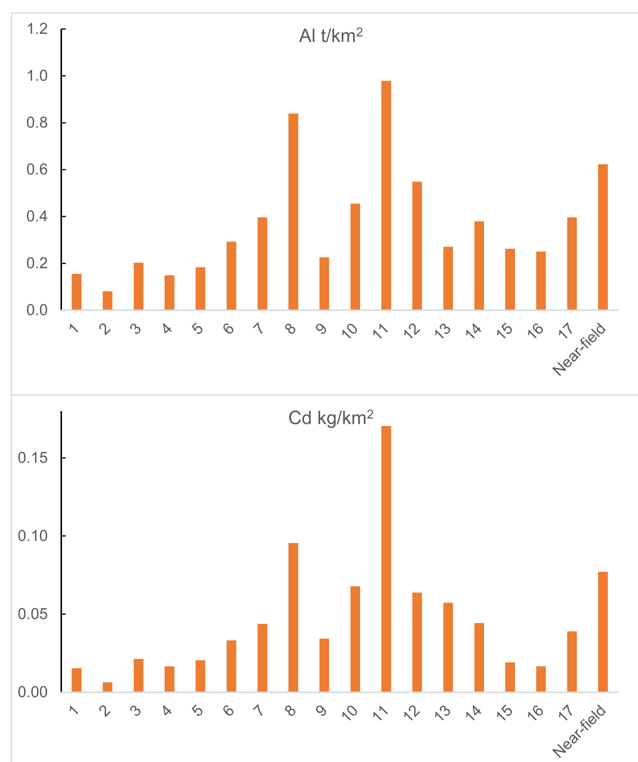

Fig. 6. Comparison of yearly load of Al (above) and Cd (below) in relation to the drainage areas (based only on data set 2).

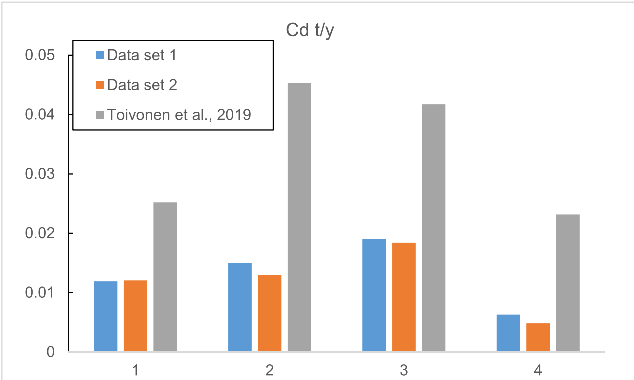

Fig. 7. The yearly load of Cd in the current study (data set 1 and 2) compared with the load during 2007 (Toivonen et al., 2019) in rivers # 1 – 4.

calculations can be considered to represent the yearly load well. However, for river # 11 and # 4 (Figs. 3 and 4), the relatively few sampling events may cause lower or higher results by coincidence depending on if sampling has been performed at the beginning of the study period, late in the study period, during periods of high/low flow, choice of analysing filtered or unfiltered samples, etc. The strategy in monitoring programs has also been to identify and study periods with poor water quality. Therefore, more frequent sampling and preference of filtering samples have occurred during periods with acidic water compared with periods with better water quality, causing an overrepresentation of data with poor water quality. An example of discrepancy in the results between the data sets can be seen in river # 11, where total Cd has been analysed a few times (once/year) at the beginning of the study period (2010 – 2012), and with increased frequency (3 – 6 times/year) 2016 – 2019, while dissolved Cd has been analysed 1 – 2 times/year only during 2010 – 2016. The results in data set 2 are based only on a few sampling occasions 2016 – 2019, a period when Cd-levels appears to have been generally lower for river # 11 (Fig. 3). This explains the difference in the results between the data sets for Cd for the river in question in Fig. 5. For elements mainly occurring in dissolved form in the study area, e.g., Cd, Co, Mn, and Ni where the dissolved fraction is close to, or more than 90% of, the total fraction, the choice of using data on both total and dissolved concentrations plays a minor role in the outcome of the results. For Al, As, Cu, and U, the dissolved fraction is lower (62 – 84%) and may cause a greater margin of error when both fractions are used in the calculations. The use of both total and dissolved fractions in the calculations was motivated by the benefit of a large data pool (minimizing coincidental factors) outweighing the disadvantage of lack of comparability. For Cr and Pb, the dissolved fraction is considered too low (50 and 35%, respectively) for allowing the use of both dissolved and total fractions. In addition, analysis results on the dissolved fraction are scarce, as with the situation with As. Therefore, only total concentrations were used for As, Cr, and Pb in data set 1, while only the dissolved fraction was available in data set 2. The reasons above explain to a great part why there is greater difference between the results from data set 1 and 2 for e.g., Al, Cr, Pb, and U (25 – 60%) than for Cd, Co, Mn, and Ni (88 – 96%).

Comparing the load between rivers gives a greater margin of error when using data set 1 due to the variability in the timing and frequency of sampling between the rivers. Data set 2 is based on consequent timing of sampling and amount of data for each river, which increases the overall comparability between the rivers. The disadvantage in data set 2 is the small number of samples, which increases the risk of coincidental factors, e.g., local rain events affecting one river but not the other etc. For many elements, the calculated load according to data set 2 is lower compared with the results from data set 1. This is mainly because data set 2 is based on sampling late during the study period (2016 – 2019), and concentrations of several elements in many rivers show a declining trend towards the end of the study period (e.g., Fig. 3). To summarize, when taking into consideration the factors mentioned above, both data set 1 and 2 give comparable and representative results on the yearly load of elements transported to the Baltic Sea from the study area.

4.2. *Acid sulfate soils: effects on pH and a source of pollution*

Acid sulfate soils have in many studied been identified as the main cause of water acidification, metal pollution and subsequent detrimental effects on biota in western Finland (Åström and Björklund, 1995; Hudd and Leskelä, 1998). Even though it is impossible to give an exact threshold to water quality with detrimental effects, pH 5.5 or below can be regarded as a crude threshold to harmful water quality. In the current study, 37% of the sampling events in the streams and 33% in the rivers performed by the authors 2016 – 2019 (data set 2), displayed a pH 5.5 or below. Combined with Al concentrations commonly exceeding 500 μg/l, a crude threshold for harmful water quality in acidic environments (Earle and Callaghan, 1998), this study confirms that discharge from ASS frequently causes unfavourable conditions in water courses and estuaries.

Quantification of elements released from ASS in the study area has been studied previously in Sundström et al. (2002). The area in the mentioned study was somewhat larger than the current study area, the sampled ditches were scattered throughout the study area and drained exclusively ASS, and the load represents the amounts released to higher order streams. The water samples used were unfiltered and collected during various hydrological conditions 1990 – 2000. The result in the current study agrees well with Sundström et al. (2002) regarding the load of Cd, Mn, and Ni, but lower amounts of Al, Co, and Cu are found in this study. This may be due to the use of both filtered and unfiltered water samples in the current study (see Section 4.1), causing lower results. For As, Pb, and Cr, the results in the current study are significantly higher, probably reflecting the fact that the streams and rivers sampled in this study represents all soil types and other pollution sources found in the study area instead of exclusively ASS (focus on fine-grained ASS), which was the case in Sundström et al. (2002). Even though the study area and approach differ between the current study and the study by Sundström et al. (2002), this study confirms that ASS are the main source of several potentially toxic elements (Cd, Ni etc.) found in streams, while elements (As, Cr, and Pb) not associated with ASS are not released in any significant amounts. Most of the elements found in high concentrations are also transported in large quantities all the way to estuaries in the Baltic Sea.

The severity of the pollution may vary greatly between years, depending on the hydrological conditions. Even though there is great short-term variation in water quality, there are signs that the water quality is slowly improving since the latest large fish kills that occurred 2006 and 2007; some metals in many of the studied rivers indicate decreasing levels with time (Figs. 2 – 4). Toivonen et al. (2013) also found a rising trend in pH in river # 2 (Ähtävänjoki) 1970 – 2010, indicating an ongoing depletion of the acidity in ASS. Focus in this study lies on the total load of potentially harmful elements from ASS to the Baltic Sea, and the trends in water quality that follows possible depletion of acidity, climate change etc. was not in the scope of this study. However, long-term trends in water quality may be important in the understanding of the total effects of ASS on the environment and should be addressed in future studies.

4.3. *Significance of small streams*

The areas between rivers that are drained by numerous small streams were found to contribute with 17 – 27% of the total load to the Baltic Sea regarding the ASS-related elements Al, Cd, Cu, Mn, Ni, and U, even though the drainage area is only 12% of the total drainage area. Some of the rivers with small catchments also contribute with a relatively large load when taking the size of the drainage area into account (Fig. 6). This is a result of the different distribution of ASS, which occur mainly in areas below the highest coastline of the Littorina Sea (90 m above current sea level in the study area). This cause a higher occurrence of ASS in near-coastal drainage areas, thus affecting more the streams and rivers with a higher proportion of such drainage areas. The share of the load of As, Cr, and Pb (10 – 12%), elements leached from ASS to a lesser extent, is closer associated to the size of the drainage area. These findings confirm the importance of understanding the total load carried by small unmonitored streams.

4.4. Protection of waters

The Environmental Quality Standard (EQS) according to the Environmental Quality Standards Directive (EQSD, 2013/39/EU) for the studied streams and rivers is 0.1 μg/l for Cd (dissolved fraction, Figs. 2 – 4) and 4.0 μg/l for Ni (bio-available fraction), for annual averages. When considering the calculated runoff-weighted averages (Tables 1 and 2), Cd-levels exceed the EQS in 12 of the 17 studied rivers in data set 1 and in 10 of the rivers in data set 2. Cadmium levels also exceed the EQS in most of the studied small streams between the river catchments, which exhibits a runoff-weighted average of 0.3 μg/l (catchments < 10 km^2) and 0.2 μg/l (catchments 10 – 99 km^2, Table 3), respectively. For Ni, the EQS is modelled as a bio-available fraction, which has not been performed on the samples used for this study. However, according to the latest classification of the chemical status in Finnish water courses (Teppo et al., 2022), Ni-levels in the area commonly exceeds the EQS. An EQS is also set for Pb according to the mentioned legislation and is similarly calculated as a bio-available fraction. Because Pb is not an element that is typically leached from ASS in any greater amounts, the total and dissolved concentrations in the study area are usually below the EQS (1.2 μg/l). No EQS is set for Al, even though Al is abundantly leached from ASS (Tables 1, 2 and 3, Sundström et al., 2002, Nordmyr et al., 2006) and is considered the main toxic element in acidic environments (Gensemer and Playle, 1999). The lack of an EQS may be because EQS are usually set for harmful substances directly created by human activities (pesticides, industry etc.) and not for elements occurring in naturally high concentrations. Also, Al exists in a variety of chemical forms, and is not necessarily toxic in certain circumstances even if found in high concentrations (Nystrand et al., 2012). The toxicity of Al is, consequently, something that needs to be addressed in future strategies and legislation regarding protection of waters.

Protection of waters is governed by national programs, strategies, and legislation, which are based on, among other things, the Water Framework Directive (2000/60/EC). The aim is to prevent environmental pollution and to achieve at least a good status for surface and ground waters. Pollution of waters is prohibited according to the Finnish national legislation. Activities that may cause changes in the aquatic environment, risk of pollution of ground water, deterioration in the ecological status of a water body or damage to fish stocks are subject to a permit according to national legal acts (Environmental Protection Act, 527/2014 and Water Act, 587/2011). Many water courses in the study area have a lowered status mainly due to the acidity and harmful substances released from ASS, and one of the most important goals in water protection in the study area is to reduce the environmental impact from ASS (Teppo et al., 2022). These soils are easily cultivated once they have been limed and are highly valued for their excellent crop yields. Therefore, there is a strong social, economic, and political pressure to maintain the productivity of these soils, which requires efficient drainage. However, no permits are usually required for drainage operations in areas with sulfidic sediments or ASS in e.g., agriculture or forestry, while permits are required only in larger dredging-operations (>500 m^3). Therefore, there is a conflict between land use policy on ASS and water protection policy.

Attempts to reduce the harmful consequences of the draining and land use on ASS while maintaining high productivity have been made. Since Finland joined the EU in 1995, farmers have been able to obtain economic support for various mitigation methods, including surface liming, lime-filter drainage and controlled subsurface pipe-drainage (Åström et al., 2007). The present strategy for water protection includes several measures to attempt to reduce the impact from ASS, but the achievement to improve the ecological and chemical status in water bodies is challenging due to high costs (Teppo et al., 2022). Also, the lack of cost-effective mitigation methods is obvious because no method has so far proven to be able to counteract the environmental risks associated with drainage operations, nor to reduce the existing load from ASS to any greater extent at reasonable costs. It is therefore likely that the water quality in the study area will continue to be strongly affected by discharge from ASS for a long time, and changes in water quality will be more dependent on meteorological factors, long-term natural depletion of acidity in ASS and changes in land use rather than on applied mitigation methods (Österholm and Åström, 2004; Österholm and Åström, 2008; Toivonen et al., 2013; Salo et al., 2021). If the status of water bodies is to be improved in a reasonable near future, new measures or mitigation methods that are cost effective enough to be applied on large enough areas are needed, as well as avoiding activities that cause oxidation of new sulfidic materials and creation of active ASS.

5. Conclusions

It is well known that the rivers in coastal areas in ASS landscapes carry large amounts of potentially toxic elements. This study calculates the yearly amounts reaching the Gulf of Bothnia in the Baltic Sea to tens, hundreds or even thousands of tons, depending on the element. Due to the low pH, large proportions of the elements occur in toxic small-sized fractions. This study further points out the significance of the combined load from the numerous small streams, which contribute up to one fourth of the total load, even though they drain only 12% of the area. For many of the studied streams and rivers, the concentrations of the potentially harmful elements Cd and Ni exceed the Environmental Quality Standard (EQS) set by the European Union. Interests between land use policy and water protection policy diverge, and the load caused by land use and drainage operations on ASS in the study area conflicts with National legislation as well as the goals in the Water Framework Directive set by the European Union. The timing of sampling, choice of analysed elements and choice of analysing filtered or unfiltered samples play a major role in the outcome of the study. Therefore, careful planning and consistent sampling of water courses is crucial in the understanding of the impact from ASS.

Funding

This work was supported by the Finnish Society of Sciences and Letters and the Centre for Economic Development, Transport and the Environment.

CRediT authorship contribution statement

Toivonen Janne: Conceptualization, Formal analysis, Funding acquisition, Investigation, Project administration, Resources, Visualization, Writing – original draft, Writing – review & editing. **Boman Anton:** Investigation, Resources, Visualization, Writing – original draft, Writing – review & editing.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work, no generative AI or AI-assisted technologies have been used.

Declaration of Competing Interest

The authors declare the following financial interests/personal

relationships which may be considered as potential competing interests. Anton Boman reports financial support, equipment, drugs, or supplies, and travel were provided by Geological Survey of Finland. Janne Toivonen reports financial support was provided by The Finnish Society of Sciences and Letters. Janne Toivonen reports financial support was provided by Centre for Economic Development, Transport end the Environment.

Data availability

Data will be made available on request.

Acknowledgements

We thank Peter Österholm at Åbo Akademi University for valuable help in the planning process and Anssi Teppo at the Centre for Economic Development, Transport and the Environment, South Ostrobothnia, for valuable help in the writing process. Two anonymous reviewers are thanked for the constructive comments that helped improve the paper.

Role of the funding source

The funding source was not involved in the study design, collection, analysis, interpretation of data, writing of the report or decision to submit the article for publication.

References

Amaral, V., Thomson, E.L., Bishop, M.J., Raftos, D.A., 2012. The proteomes of Sydney rock oysters vary spatially according to exposure to acid sulfate runoff. Mar. Freshwat. Res. 63 (4), 361–369. https://doi.org/10.1071/MF11213.
Åström, M., Björklund, A., 1995. Impact of acid sulfate soils on stream water geochemistry in western Finland. J. Geochem. Explor. 55, 163–170. https://doi.org/10.1016/0375-6742(95)00018-6.
Åström, M., Björklund, A., 1997. Geochemistry and acidity of sulphide-bearing postglacial sediments of western Finland. Environ. Geochem. Health 19, 155–164. https://doi.org/10.1023/A:1018462824486.
Åström, M., Österholm, P., Bärlund, I., Tattari, S., 2007. Hydrochemical effects of surface liming, controlled drainage and lime-filter drainage on boreal acid sulfate soils. Water, Air, Soil Pollut. 179, 107–116. https://doi.org/10.1007/s11270-006-9217-8.
Boman, A., Fröjdö, S., Backlund, K., Åström, M.E., 2010. Impact of isostatic land uplift and artificial drainage on oxidation of brackish-water sediments rich in metastable iron sulfide. Geochim. Cosmochim. Acta 74, 1268–1281. https://doi.org/10.1016/j.gca.2009.11.026.
Boman, A., Mattbäck, S., Becher, M., Yli-Halla, M., Sohlenius, G., Auri, J., Öhrling, J., Liwata-Kenttälä, P., Edén, P., 2023. Classification of acid sulfate soils and soil materials in Finland and Sweden: Re-introduction of para-acid sulfate soils. Bull. Geolog. Soc. Finland 95 (2), 161–186. https://doi.org/10.17741/bgsf/95.2.004.
Dent, D.L., Pons, L.J., 1995. A world perspective on acid sulphate soils. Geoderma 67, 263–276. https://doi.org/10.1016/0016-7061(95)00013-E.
Earle, J., Callaghan, T., 1998. Impacts of mine drainage on aquatic life, water uses, and man-made structures. Chapter 4 in Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania. Edited by: K.B.C. Brady, M.W. Smith and J. Schueck, Department of Environmental Protection, Harrisburg, PA.
Edén, P., Boman, A., Mattbäck, S., Auri, J., Yli-Halla, M., Österholm, P., 2023. Mapping, impacts, characterization and extent of acid sulfate soils in Finland. Bull. Geol. Soc. Finland 95 (2), 135–160. https://doi.org/10.17741/bgsf/95.2.003.
Enio, M.S.K., Shamshuddin, J., Fauziah, C.I., Husni, M.H.A., Qurban, A.P., 2020. Quantifying the release of acidity and metals arising from drainage of acid sulfate soils in the Kelantan Plains, Malaysia. Min. Miner. Depos. 14 (3), 50–60. https://doi.org/10.33271/mining14.03.050.
Gensemer, R.W., Playle, R.C., 1999. The bioavailability and toxicity of aluminum in aquatic environments. Crit. Rev. Environ. Sci. Technol. 29 (4), 315–450. https://doi.org/10.1080/10643389991259245.
Green, R., MacDonald, B.C.T., Melville, M.D., Waite, T.D., 2006. Hydrogeochemistry of episodic drainage waters discharge from an acid sulfate soil affected catchment. J. Hydrol. 325, 356–375. https://doi.org/10.1016/j.jhydrol.2005.10.022.
Haraguchi, A., 2007. Effect of sulfuric acid discharge on river water chemistry in peat swamp forests in central Kalimantan, Indonesia. Limnology 8, 175–182. https://doi.org/10.1007/s10201-007-0206-4.
Hudd, R., Leskelä, A., 1998. Acidification-induced species shifts in coastal fisheries off the River Kyrönjoki, Finland. A Case Study. Ambio. 27, 535–538 https://www.jstor.org/stable/i399327.
Johnson, A., Högfors-Rönnholm, E., Engblom, S., Österholm, P., Åström, M., Dopson, M., 2022. Dredging and deposition of metal sulfide rich river sediments results in rapid conversion to acid sulfate soil materials. Sci. Total Environ. 813, 151864 https://doi.org/10.1016/j.scitotenv.2021.151864.
Lehtonen, H., Hudd, R., 1990. The importance of estuaries for the reproduction of freshwater fish in the Gulf of Bothnia. In: W.L.T. van Densen, B. Steinmetz, R.H. Hughes (Eds.), Management of freshwater fisheries. Proceedings of a symposium organized by the European Inland Fisheries Advisory Commission, Goeteborg, Sweden, 31 May – 3 June 1988. Pudoc Wageningen, 82 – 89.
Mattbäck, S., Boman, A., Sandfält, A., Österholm, P., 2022. Leaching of acid generating materials and elements from coarse- and fine-grained acid sulfate soil materials. J. Geochem. Explor. 232, 106880 https://doi.org/10.1016/j.gexplo.2021.106880.
Nordmyr, L., Boman, A., Åström, M., Österholm, P., 2006. Estimation of leakage of chemical elements from boreal acid sulphate soils. Boreal Environ. Res. 11, 261–273 https://www.diva-portal.org/smash/get/diva2:986141/FULLTEXT01.pdf.
Nystrand, M.I., Österholm, P., Nyberg, M.E., Gustafsson, J.P., 2012. Metal speciation in rivers affected by enhanced soil erosion and acidity. Appl. Geochem. 27, 906–916. https://doi.org/10.1016/j.apgeochem.2012.01.009.
Nystrand, M.I., Österholm, P., 2013. Metal species in a Boreal river system affected by acid sulfate soils. Appl. Geochem. 31, 133–141. https://doi.org/10.1016/j.apgeochem.2012.12.015.
Nystrand, M.I., Österholm, P., Yu, C., Åström, M., 2016. Distribution and speciation of metals, phosphorus, sulfate and organic material in brackish estuary water affected by acid sulfate soils. Appl. Geochem. 66, 264–274. https://doi.org/10.1016/j.apgeochem.2016.01.003.
Österholm, P., Åström, M., 2004. Quantification of current and future leaching of sulfur and metals from Boreal acid sulfate soils, Western Finland. Aus. J. Res. 42, 547–551. https://doi.org/10.1071/SR03088.
Österholm, P., Åström, M., 2008. Meteorological impacts on the water quality in the Pajuluoma acid sulphate area, W. Finland. Appl. Geochem. 23, 1594–1606. https://doi.org/10.1016/j.apgeochem.2008.01.011.
Palko, J., 1994. Acid sulphate soils and their agricultural and environmental problems in Finland. Acta University Oulu, C75. University of Oulu, Academic dissertation.
Peltola, P., Åström, M., 2002. Concentrations and leachability of chemical elements in estuarine sulfur-rich sediments, W. Finland. Sci. Total Environ. 284, 109–122. https://doi.org/10.1016/S0048-9697(01)00872-5.
Roos, M., Åström, M., 2006. Gulf of Bothnia receives high concentrations of potentially toxic metals from acid sulphate soils. Boreal Environ. Res. 11, 383–388.
Russell, D.J., Helmke, S.A., 2002. Impacts of acid leachate on water quality and fisheries resources of a coastal creek in northern Australia. Mar. Freshwater Res. 53 (1), 19–33. https://doi.org/10.1071/MF00100.
Saarinen, T., Vuori, K.-M., Alasaarela, E., Kløve, B., 2010. Long-term trends and variation of acidity, COD_{Mn} and colour in coastal rivers of Western Finland in relation to climate and hydrology. Sci. Total Environ. 408, 5019–5027. https://doi.org/10.1016/j.scitotenv.2010.07.009.
Salo, H., Salla, A., Koivusalo, H., 2021. Seasonal effects of controlled drainage on field water balance and ground water levels. Hydrol. Res. 52 (6), 1633–1647. https://doi.org/10.2166/nh.2021.056.
Sammut, J., Melville, M.D., Callinan, R.B., Fraser, G.C., 1995. Estuarine Acidification: Impacts on Aquatic Biota of Draining Acid Sulphate Soils. Aus. Geograph. Stud. Volume 33 (Issue 1), 89–100. https://doi.org/10.1111/j.1467-8470.1995.tb00687.x.
Sukitprapanon, T., Suddhiprakarn, A., Kheoruenromne, I., Gilkes, R.J., 2018. Partitioning and potential mobilization of aluminum, arsenic, iron, and heavy metals in tropical active and post-active acid sulfate soils: Influence of long-term paddy rice cultivation. Chemosphere 197, 691–702. https://doi.org/10.1016/j.chemosphere.2018.01.099.
Sundström, R., Åström, M., Österholm, P., 2002. Comparison of the metal content in acid sulfate soil runoff and industrial effluents in Finland. Environ. Sci. Technol. 36 (20), 4269–4272. https://doi.org/10.1021/es020022g.
Sutela, T., Vuori, K.-M., Louhi, P., Hovila, K., Jokela, S., Karjalainen, S.M., Keinänen, M., Rask, M., Teppo, A., Urho, L., Vehanen, T., Vuorinen, P.J., Österholm, P., 2012. Happamien sulfaattimaiden aiheuttamat vesistövaikutukset ja kalakuolemat Suomessa. Suomen ympäristö. 14. Suomen ympäristökeskus (in Finnish). http://hdl.handle.net/10138/38771.
Teppo, A., Bonde, A., Koivisto, A.-M., Nikolajev-Wikström., Petäjä-Ronkainen, A., Westberg, V., Dalhem, K., Eklund, L., Könönen, O., Mäenpää, E., Pakkala, J., Rantataro, T., Saarenpää, E., Seppälä, T., Tolonen, M., Vainio, A., Viitaniemi, K., 2022. Vesienhoidon toimenpideohjelma 2022 – 2027 (Programme for Implementation of River Basin Management Plans 2022 – 2027, in Finnish).
Toivonen, J., Österholm, P., Fröjdö, S., 2013. Hydrological processes behind annual and decadal-scale variations in the water quality of runoff in Finnish catchments with acid sulfate soils. J. Hydrol. 487, 60–69. https://doi.org/10.1016/j.jhydrol.2013.02.034.
Toivonen, J., Fröjdö, S., Österholm, P., 2019. Impact of acid sulfate soil catchments on water quality in a lake in western Finland; trends and total metal load. Boreal Environ. Res. 24, 79–99 http://urn.fi/URN:NBN:fi-fe2020100882925.
Toivonen, J., Hudd, R., Nystrand, M., Österholm, P., 2020. Climatic effects on water quality in areas with acid sulfate soils with commensurable consequences on the reproduction of burbot (*Lota lota* L.). Environ. Geochem. Health Volume 42, 3141–3156. https://doi.org/10.1007/s10653-020-00550-1.
Vehviläinen, B., Huttunen, M., 2001. Hydrological forecasting and real time monitoring in Finland: The Watershed Simulation and Forecasting System (WSFS) (pdf) 2001. Helsingin yliopisto, helsinki.fi. http://hdl.handle.net/10138/170125.
Vehviläinen, B., Huttunen, M., Huttunen, I. 2005. Hydrological forecasting and real time monitoring in Finland: the watershed simulation and forecasting system (WSFS). In:

Innovation, advances and implementation of flood forecasting technology, conference papers, 17–19 October 2005, Tromsø, Norway.

Virtasalo, J.J., Österholm, P., Kotilainen, A.T., Åström, M.E., 2020. Enrichment of trace metals from acid sulfate soils in sediments of the Kvarken Archipelago, eastern Gulf of Bothnia, Baltic Sea. Biogeosciences 17, 6097–6113. https://doi.org/10.5194/bg-17-6097-2020.

Wallin, J., Karjalainen, A.K., Schultz, E., Järvistö, J., Leppänen, M., Vuori, K.-M., 2015. Weight-of-evidence approach in assessment of ecotoxicological risks of acid sulphate soils in the Baltic Sea river estuaries. Sci. Total Environ. 508, 452–461. https://doi.org/10.1016/j.scitotenv.2014.11.073.

Web references

Finnish Environment Institute. https://www.syke.fi/fi-FI/Avoin_tieto/Ymparistotietojarjestelmat (accessed August 17th, 2022).

Geological Survey of Finland, 2023. https://gtkdata.gtk.fi/hasu/index.html (accessed August 21th, 2023).