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Diffuse sources dominate the sulfate load into Finnish surface waters

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Abstract

Sulfate (SO$_4^{2-}$) affects the cycling of ecologically important substances, such as carbon, nutrients and metals, but the contribution of anthropogenic activities in sulfate load entering aquatic systems is poorly known. We calculate specific sulfate loads for land cover types, atmospheric deposition and point sources, and then estimate the source-specific flux of sulfate to Finnish surface waters. The largest sulfate flux, entering mostly the Baltic Sea, originate from agricultural fields on acid sulfate soil (24% of total flux). Forests on mineral soil, which cover 67% of the country’s surface area, form the second largest source (21%). Additionally, agricultural fields on non-acid soil cause noticeable sulfate flux (16%). Pulp and paper mills were the key point sources (20%) for sulfate. We find that anthropogenic activities contribute to elevated sulfate levels in waters potentially affecting the cycling of nutrients, metals and formation of greenhouse gases in naturally sulfate-poor freshwaters. Based on these findings, sulfate should be systematically included in monitoring and
pollution control measures.

1. Introduction

Sulfate (SO$_4^{2-}$) is a critical factor for both ecosystems and humans. Studies on sulfur in aquatic systems were largely related to the effects of acid deposition in the past (Gobran and Clegg, 1992), but the focus has now been shifting to understanding the multifaceted role sulfur has in ecological processes (Holmer and Storkholm, 2001; Orem et al., 2011). Sulfur is able to participate in numerous redox-reactions, which couples the cycling of sulfur to that of many other elements (Burgin et al., 2011). As an example, the end product of dissimilatory sulfate reduction, hydrogen sulfide, can be chemically and microbially re-oxidized by oxygen, nitrate, and iron and manganese oxides. Anaerobic nitrate reduction by sulfides results in the release of nitrogen gas and thereby removes nitrogen from the system (Brettar and Rheinheimer, 1991). In addition, sulfides react with metals and form insoluble sulfides. In iron sulfide formation the ability of iron to bind phosphate is inactivated, which increases the release of phosphorus from sediments. This process is called sulfate-induced eutrophication, with adverse effects on the ecological status of lakes, riverine floodplains and fens (Hasler and Einsele, 1948; Loeb, 2008; Ohle, 1953; Roden and Edmonds, 1997; Smolders and Roelofs, 1993). Another pathway of sulfate reduction includes anaerobic oxidation of methane (Boetius et al., 2000), which highlights the importance of sulfate in the inhibition of release of greenhouse gases. On the other hand, high sulfate levels may be directly harmful for freshwater biota, such as fish, mussels and mosses (Elphick et al., 2011). However, the toxicity of sulfur is greatly strengthened when hydrogen sulfide is formed, it being poisonous to multicellular life forms (Smolders and Roelofs, 1993). Sulfate also has a role in the formation of toxic methyl mercury (Gilmour et al., 1992). Moreover, sulfate levels have been related to fluxes of dissolved organic carbon into aquatic ecosystems (Monteith et
Massive amounts of sulfate exported to lakes may increase density of water and create a stagnant near-bottom water layers with drastic change in the ecosystem (Leppänen et al., 2017). Finally, sulfate and hydrogen sulfide increase corrosion of concrete and metals in built structures (Neville, 2004; Wiener et al., 2013). Thus, in addition to being one of the key nutrients, sulfate affects the cycling of other nutrients, emissions of greenhouse gases, binding of metals, formation of toxic substances, survival of biota and state of constructions.

In boreal freshwaters, the sulfate level is typically some milligrams per litre, depending on environmental and anthropogenic factors (Geochemical Atlas of Europe, 2017). Natural sulfate sources include the weathering of rocks containing sulfur, non-anthropogenic oxidation of sulfides in former sea sediments and non-anthropogenic deposition. When bedrock is granitic, surface waters tend to be sulfate poor, whereas high sulfate concentrations are related to sulfidic minerals, occurring in for example black schists and postglacial deposits formed during ancient marine phases (Tenhola and Tarvainen, 2008). Moreover, the close location to the sea increases sulfate input through marine aerosols (Tenhola and Tarvainen, 2008).

Anthropogenic activities are an integral part of sulfate sources, as sulfuric acid is one of the most voluminously used chemicals. Moreover, sulfur is released in the burning of fossil fuels, causing atmospheric deposition and elevated sulfate concentrations distant from the emission source (Stoddard et al., 1999; Vuorenmaa et al., 2014). Sulfate is also released in acid mine drainage (Kleeberg, 1998) and drainage induced pyrite oxidation (Boman et al., 2008). Less apparent origins of sulfate include industry, municipal wastewaters and land use (Korkman, 1973; Mattsson et al., 2007), as sulfur-bearing chemicals are used e.g. in pulp mills, water purification and fertilizers. Unfortunately, industrial sulfate emissions are seldom monitored, and there is limited data on land-cover specific sulfate losses from agriculture, forestry, urban
areas and peatlands. However, Palviainen et al. (2015) estimated specific sulfate losses by performing a multivariate regression analysis for 27 catchments with varying proportions of agricultural land (Field%), peatland (Peat%) and forests on mineral soils (Forest%). They found that agricultural fields produce large losses of sulfate, but peatland acts as a sink for sulfate.

We performed a comprehensive inventory on the contribution of point and diffuse sources on sulfate export to surface waters in Finland by using data available from the administrative data bases. Such an overview would help to identify the cases where human activity may increase the sulfate export to surface waters and thus potentially exerting environmental impacts. Our findings of national inventory for Finland give insight on the potential importance of sources and their monitoring need for other countries as well.

2. Material and methods

2.1. Study area

Finland is located between latitudes 60° and 70° N in northeastern Europe (Fig. 1). The climate is characterized by high seasonal and spatial variation. During the period 1981–2010, the mean annual temperature ranged from −3 °C in the north to +6 °C in the southern coastal area. Mean annual precipitation is 400–750 mm, being lowest in northern Finland (Pirinen et al., 2012). The bedrock, belonging to the Scandinavian shield, mainly consists of metamorphic gneisses and schists and acid plutonic rocks. Young sediments were formed during the Quaternary period and they cover bedrock as a layer with an average thickness of 8.5 meters. Glacial till is predominant sediment and in southern and western coasts till is covered with waterlaid silt and clays. Paludification, i.e. accumulation of organic matter over time, is promoted by climate, flat topography and acidity of soils, and especially northern Finland is rich in peatlands. Podzol is the major soil type in forests. Europe’s largest
occurrence of sulfide containing sediments are located in the south western and western coasts. When excavated these sediments become susceptible to oxidization and develop to actual acid sulfate soils.

According to CORINE2012 data (spatial resolution of 20 × 20 m, Finnish Environment Institute, 2019a), forests on mineral soils account for 58%, peatland 21%, agricultural land 7%, urban areas 3%, other land use types 1% and freshwater 10% (Fig. 1). Of the agricultural land, about 1300 km$^2$ is on acid sulfate soils, classified as *Typic Sulfaquepts* and *Sulfic Cryaquepts* (Yli-Halla et al., 1999). The parent sediments of acid sulfate soils were formed about 7000 years ago in a more saline and warmer stage of the Baltic Sea. Later, the sulfidic sediments have been covered by non-sulfidic sedimentary material and the areas have surfaced due to postglacial land uplift.

2.2. Atmospheric deposition

The Finnish Meteorological Institute measures bulk deposition at ten sites in Finland, with sufficient spatial coverage (Makkonen, 2020, personal communication; Ruoho-Airola, 2014). We excluded two coastal sites with a marine impact and used the mean value for the years 2014–2018 of the remaining eight sites (as weighted by their approximate spatial coverage) as a bulk sulfate deposition in Finland (Fig. 1). Information on throughfall (wet + dry deposition) was available for two of the sites in Vuorenmaa et al. (2018).

2.3. Land-use based diffuse sources

The multivariate regression analysis performed for 27 Finnish catchments by Palviainen et al. (2015) predicted sulfate loss (mol km$^{-2}$ y$^{-1}$) from field and peat areas as follows:

$$\text{SO}_4^-\text{-loss} = 16024 + 624 \text{ Field}\% - 200 \text{ Peat}\% \quad (r^2 = 0.67, \ p < 0.001, \ \text{RMSE} = 7156). \quad (1)$$
The catchments examined by Palviainen et al. (2015) had three major land use types: forest on mineral soils, peatland and agricultural fields. Therefore, the intercept may be interpreted to describe the average loss from forest on mineral soils (after unit conversion 1540 kg km$^{-2}$ y$^{-1}$). For 100% agricultural land Eq. 1 gives a specific load of 7530 kg km$^{-2}$ y$^{-1}$, which we used here for the export from agricultural fields non-acid soils. However, for 100% peatland Eq. 1 produces a negative load (−380 kg km$^{-2}$ y$^{-1}$), suggesting that peatlands retain sulfate.

The data studied by Palviainen et al. (2015) included four catchments with Forest% > 90. As Eq. 1 does not explicitly include forest areas, we used the average sulfate loss from these four catchments (1080 kg km$^{-2}$ y$^{-1}$) as a national estimate for the export from forests on mineral soil. The sulfate loss from the four catchments ranged widely (361–2260 kg km$^{-2}$ y$^{-1}$), thus using the mean value masks local variation.

Approximately 7% of agricultural fields are located on acid sulfate soils in Finland. To estimate their sulfate load, we used a specific loss of 190 000 kg km$^{-2}$ y$^{-1}$, found by Virtanen et al. (2016) and Österholm and Åström (2004) from their intensively monitored field plots in western Finland.

We verified the above estimates for the sulfate losses from agricultural areas by calculating the losses for four Finnish catchments not included in Palviainen et al. (2015). These catchments have been monitored for daily runoff and monthly sulfate concentrations for 2000–2013 (Table 1, Finnish Environment Institute, 2019d). Sulfate was analysed using ion chromatography, and the losses were calculated as the flow-weighted mean concentration times mean runoff. Flow-weighing was used due to an inverse relationship between sulfate concentrations and flow (Mattsson et al., 2017). Only one of the catchments was 100% agricultural field, while the three other catchments also had peatland, forest and urban areas. Furthermore, one catchment was on an acid sulfate soil. Agricultural load was obtained by
subtracting the load from other sources from the total load (using specific losses for the other land use types). The catchments have been described in detail by Vuorenmaa et al. (2002).

Similarly, we verified the retention of sulfate by peatlands, as suggested by Palviainen et al. (2015), by examining sulfate concentration data from 15 catchments with active forestry, 11 catchments with pristine peatlands and 6 catchments with restored peatlands in southern Finland. Peat% ranged from 7 to 100 and the catchments were sampled for water quality on average 20 times during 2010–2017 (Finnish Environment Institute, 2019d). Water flow was not measured in these sites.

Urban sulfate loss has been monitored in three small catchments in the capital city of Helsinki, which are part of the international Long-Term Socio-Ecological Research (LTSER) network. We used the 2010–2015 data from two catchments which represent typical semi-urban areas in Finland. The data consisted of weekly concentrations, analysed from a composite of runoff-based cumulative samples (Taka et al., 2017) and accurate runoff data, all collected in the stormwater sewer at the catchment outlet. Continuous monitoring produced year-round data of the urban sulfate export. The urban sulfate loss was obtained as the mean loss of these two catchments by taking into account other land use types similarly as described above.

Finally, the land-use specific sulfate losses for all the diffuse sources were extrapolated for the entire country of Finland by extracting the different land use and land cover types from CORINE2012. The sulfate loss for minor land use types (accounting for 0.9% of total area) was assumed to be equal to that of forests on mineral soils.

2.4. Industry

Pulp and paper mills form the major industrial sector in Finland. The Finnish Pollutant
Release and Environmental Enforcement Register (Finnish Environment Institute, 2019c) contained data on industrial sulfate loads for 12 enterprises, only one of which was a pulp mill. The annual sulfate load was calculated as an average for the years 2010–2018 (excepting 2016) and this was referred to as sulfate load from “Other industry” (plants listed in Supplementary table 1). In addition, we used the register data on sulfate loads from waste dumps or waste handling units and energy production.

In Finland there are 15 plants that produce pulp using a sulfate process, with sodium sulfide and sodium sulfate being used in the process, and two plants that produce semi-chemical fluting. For these plants (classified here as “Forest industry”), the sulfate load was estimated based on the information from two pulp mills and one fluting mill (producing semi-chemical fluting) that voluntarily monitored their sulfate load. With this data we calculated a specific sulfate load versus pulp produced, a value that was then extrapolated for the remaining plants on the basis of the total production capacity of pulp in the country (Table 2).

2.5. Mines and ore mills

Finland has a history of more than 100 mines (Kauppila et al., 2011). Of presently operating mines, 11 produce metal ores, 13 carbonates, 11 mines industrial minerals or rocks and 7 mines jewels or interior design materials. In addition, there are 3 ore mills (Supplementary Table 2). The number of active mining enterprises changes from year to year and closed operations also cause loading. The load from this sector was based on average load data between 2010 and 2018 (excepting 2016) for 24 Finnish mines or ore mills, some of which no longer operate (Finnish Environment Institute, 2019c).

2.6. Water supply

About 90% of the Finnish population (5.5 million) lives in areas covered by a centralised
water supply and 84% is connected to municipal sewer systems (Finnish Environment Institute, 2019b). There are more than 200 municipal wastewater plants with person equivalents above 1000. None of the plants has an environmental permit for sulfate discharges and thus monitoring of sulfate is not obligatory. However, we were able to include sulfate data from two plants in the capital region. Plant 1 is the largest in Finland, serving more than one million inhabitants, while nationally the third largest, Plant 2, serves 0.33 million inhabitants (Table 3). Their annual sulfate loads were calculated by multiplying the wastewater discharge by the mean sulfate concentration in wastewater as analysed in weekly (Plant 1) or monthly sampling (Plant 2) in 2013. The sulfate load in purified effluent for the entire country was obtained by multiplying the average per capita load of these two plants by the population served by municipal wastewater plants and corrected for sulfate in the source water (see 3.8). The origin of sulfate in effluent was estimated from the internal data on the use of chemicals in the treatment process.

2.7. Sulfate concentrations in freshwaters and loading sources

To get an overview of the sulfate levels in Finnish rivers and lakes, the concentrations of all surface water sample sites in 2000–2019 were retrieved from the national water quality database (Finnish Environment Institute, 2019d). The spatial sulfate concentration data set based on 123 558 water samples in 5804 sites was converted to a 10 km square grid data set with arithmetic mean, using ArcGIS 10.5.1 with the Spatial Analyst extension Point To Raster tool. For the grids belonging to the highest concentration class (sulfate > 150 mg l⁻¹), the probable cause, such as mines and point sources, was identified by using information in the Pollutant Release and Environmental Enforcement Register and a map examination. For comparison, we obtained the sulfate concentrations in groundwater from the data on monitored bedrock wells (n = 263, Lahermo et al., 2002)
To relate sulfate concentrations in the loading sources to the surface water concentrations we calculated the mean, minimum and maximum sulfate concentrations in above loading sources as follows. Firstly, the concentrations in rain were calculated by dividing above deposition data by annual precipitation in each site. For agricultural runoff we used the concentrations in the three “validation” catchments, for runoff from forests on mineral soils those in the four forested catchments examined by Palviainen et al. (2015), and for urban runoff the concentrations reported in Taka et al. (2017). In addition, the concentrations in tap water and municipal wastewater was based on the above data from two treatment plants. Finally, for forest industrial wastewater and mine effluent, in lack of data, we had to rely on environmental reports of a single plant and mine.

2.8. Validation of the load estimate

The “emission-based” estimate of sulfate load, presented above, was validated using data from 31 Finnish monitored rivers (see Räike et al., 2019). The catchments of the rivers accounted for 64% of the Finnish territory. Sulfate fluxes by rivers were calculated using flow-based interpolation of the daily concentrations and measured daily flow (Ekholm et al., 2015). The national sulfate loss was calculated by weighing the loss of each river by the catchment area and extrapolating the value for the entire country.

3. Results and Discussion

Our analysis highlights the importance of diffuse sources on sulfate export and the high spatial heterogeneity of the results. At a national scale, 65% of the sulfate flux originated from diffuse sources, indicating challenges in management attempts. The key diffuse sources were fields on acid sulfate soils (24%) and forests on mineral soils (21%).

3.1 Atmospheric deposition
In a European context, the bulk deposition of sulfate is low in Finland (Waldner et al., 2014). The mean spatially weighted deposition at the eight sites was 290 kg km\(^{-2}\) y\(^{-1}\). The range among individual sites was 200–610 kg km\(^{-2}\) y\(^{-1}\), with deposition being the lowest in northern Finland. Atmospheric deposition entering directly into lakes accounts only for 1% of the total sulfate losses entering the surface waters (Table 4). According to the measurements in two forested catchments, throughfall in a pine forest was 64% larger than bulk deposition (Vuorenmaa et al., 2018). If this value holds for the entire country, the mean spatially weighted atmospheric deposition would increase from 290 to 480 kg km\(^{-2}\) y\(^{-1}\) in forested areas. Deposition has decreased in Finland; in the southern parts of the country it had come down about 80% from 1990 to 2018 (Makkonen, 2020, personal communication). Sulfate deposition is projected to decrease even further throughout Europe (Lamarque et al., 2013). Because about 80% of the sulfate is long-range transported, the future deposition in Finland depends on the countries responsible for the emissions.

### 3.2 Forests on mineral soils

The sulfate loss from the four forested catchments ranged from 361 to 2260 kg km\(^{-2}\) y\(^{-1}\) (Palviainen et al., 2015). The highest loss (2260 kg km\(^{-2}\) y\(^{-1}\)) was found in the southernmost catchment, which may reflect the fertility of the soil (Kortelainen et al., 2006) and high atmospheric deposition in southern Finland.

The mean specific sulfate loss from forests on mineral soils (1080 kg km\(^{-2}\) y\(^{-1}\)) exceeded the present deposition even with the inclusion of the throughfall component (480 kg km\(^{-2}\) y\(^{-1}\)). Part of the sulfate during the high deposition period in the 1970s and 1980s has been bound by soil and vegetation and is probably now releasing, as found in higher deposition areas in Europe (Kopáček et al., 2014; Vuorenmaa et al., 2017). The surplus may also represent losses
due to weathering and mineralisation (Gobran and Clegg, 1992), possibly accelerated by the forestry operations.

Because forests on mineral soils account for as much as 66% of the land cover in Finland, forests were responsible for 21% of the total national load entering the surface waters (Table 4). A significant share of forest runoff enters freshwaters, but the ecological response may be reduced by the small specific load (i.e. low concentrations, Fig. 4), likely to decrease further in time due to depletion of sulfur storage.

In 1997–1999, during higher atmospheric deposition, sulfate losses from 29 unmanaged forested Finnish catchments ranged from 220 to 4570 kg km\(^{-2}\) y\(^{-1}\) (mean 1040 kg km\(^{-2}\) y\(^{-1}\)), with the losses increasing southwards, again correlating with the spatial variation in deposition (Finér et al., 2004). Peat% correlated inversely with sulfate losses. Additionally, a forested catchment in northern Sweden was found to be a net source of sulfate, presumably due to release of the largely organic sulfur pool, accumulated during the period of higher deposition. At this site, weathering presumably played a negligible role in causing an average sulfate loss of 1200 kg km\(^{-2}\) y\(^{-1}\) (Ledesma et al., 2016).

3.3 Peatland

Both the data used in Palviainen et al. (2015) and our verification data showed the mean sulfate concentration in runoff to exhibit an inverse relationship with Peat% (Fig. 2). Whereas Palviainen et al. (2015) found a large negative SO\(_4\) loss for peatlands (−380 kg km\(^{-2}\) y\(^{-1}\)), the verification data had more areas rich in peat and gave a lower value: according to a linear fit −30 kg km\(^{-2}\) y\(^{-1}\), assuming an annual runoff of 300 mm.

The negative specific loss suggests that some peatlands capture sulfate, not only from atmospheric deposition but also by it being transported from the upper reaches of mineral
soils in the catchment. However, there seems to be a lot of variation.

An example to illustrate this variation is given by two neighbouring catchments in southern Finland. Catchment 1 consists of forests on mineral soil under active forestry. The last clearcuttings took place 20 years ago. Catchment 2 has forested headwater streams with 31% ditched peatland and the lower part consisting largely of a fen, a peatland type dependent on the hydrological connection to the upper catchment. The mean SO\textsubscript{4} concentration in Catchment 1 was 6.8 mg l\(^{-1}\) (corresponding to a loss of 2040 kg km\(^{-2}\) y\(^{-1}\) with a 300 mm runoff), representing a reference value for a forested area in the region. At the outlet of the forested upper reaches of Catchment 2, the SO\textsubscript{4} concentration was only 4.4 mg l\(^{-1}\), suggesting that drained peatland may also capture SO\textsubscript{4}. The concentration was as low as 1.6 mg l\(^{-1}\) in the outlet of the fen, showing that the mire had removed approximately 910 kg km\(^{-2}\) y\(^{-1}\) SO\textsubscript{4}, a value about 2.4 times of that derived from Eq. 1 (380 kg km\(^{-2}\) y\(^{-1}\)).

The ability of peat to retain sulfur may be explained by microbial sulfate reduction forming sulfides in waterlogged peatlands, sulfur being finally incorporated mainly in an organic form into accumulating organic matter (Brown, 1986; Brown and MacQueen, 1985; Pester et al., 2012). Accordingly, peat is rich in sulfur (average concentration 0.24%, dry weight), the concentration increasing with stage of decomposing (Herranen, 2010). Whether peatland acts as a source or sink for sulfate may be controlled by a diversity of environmental factors, e.g. hydrology, vegetation, trophic status, management such as ditching and fertilization and the amount of atmospheric deposition. The hydrology seems to be of paramount importance.

For a negative specific loss, a peatland must receive inputs from the catchment, in addition to direct deposition, as in fens. Bogs, relying on direct deposition as their source of inorganic elements, have a positive loss, although small, because they also retain a greater part of the sulfate in deposition. In Fig. 2 a catchment of 100% natural bog has a mean concentration of
0.3 mg l$^{-1}$ of sulfate. Drainage ditches cut off totally or significantly the access of upland runoff to the peatland, and by creating aerobic conditions to the surface peat layer, reduce the ability of the peatland to retain sulfur. However, in the data set, there are also catchments giving slightly negative specific losses for drained peatlands. This can be explained by narrow riparian peatlands between forests on mineral soil and the peatlands, acting as traps of sulfur, in a same way as undrained fens. Depending on the definition of peatland, up to one third of the Finnish land area is covered by peatland, of which 53% is drained for forestry and a significant part of the undrained area is affected by draining of adjacent areas (Sallinen et al., 2019).

Combining the data by Palviainen et al. (2015) and the verification data gives a very small negative specific leaching rate for peatlands (Fig. 2). Natural fens may be somewhat overrepresented in our data set. Peatlands exhibit a very large variation in specific sulfate losses, but our best estimate, accurate enough for the present purpose, is a zero specific leaching rate for peatlands.

3.4 Agricultural fields

Assuming a specific sulfate loss of 7530 kg km$^{-2}$ y$^{-1}$ (Palviainen et al., 2015), agricultural fields produced 16% of the total sulfate load in surface waters (Table 4). Already Korkman (1973) found a positive relationship between riverine sulfate concentration and Field% of the catchment. We made an effort to verify the specific sulfate loss by examining three intensively monitored Finnish agricultural catchments and found the losses to range from 2710 to 14 800 kg km$^{-2}$ y$^{-1}$ (Table 1) suggesting that here again the use of a single value for sulfate loss hides considerable spatial variation and increases uncertainty.

A field-scale study on a clayey experimental field in southern Finland found a sulfate loss of
4800 kg km\(^{-2}\) y\(^{-1}\) in 1980–1982 (Turtola and Jaakkola, 1986). A Swedish study reported the losses to be 7800 kg km\(^{-2}\) y\(^{-1}\) (Brink, 1982), and a Norwegian lysimeter research 2400–2700 kg km\(^{-2}\) y\(^{-1}\) (Uhlen, 1989). Leaching studies performed outside the Nordic countries, relying largely on lysimeter experiments, have reported losses to range from 600 to 39 000 kg km\(^{-2}\) y\(^{-1}\) and to depend e.g. on soil type, fertilization, manure use, plant cover and the amount of drainage (Scherer, 2001).

The higher sulfate loss from agricultural than forested areas may be explained by the input of sulfate in fertilizers. Previously, fertilizers contained sulfate as an “impurity”, e.g. in ammonium sulfate, potassium sulfate, superphosphate and complex fertilisers, the use peaking at 8990 kg km\(^{-2}\) y\(^{-1}\) sulfate in 1965 in Finland, following with a rapid decline due to the advent of phosphoric acid based concentrated fertilizers (Korkman, 1973). However, to avoid sulfur deficiency, the leading fertilizer producer decided to guarantee a sulfur level in most chemical fertilizers (usually 1.5–2.5%) in the early 1970s (Yli-Halla et al., 2011). More recently, the declined atmospheric deposition has increased the need to add sulfur to fertilizers. Sulfur in manure can vary from 0.45 to 0.70% of dry weight, poultry manure being richer in sulfur than cattle manure. Manure spreading may thus form local hot spots of sulfate losses.

In 2004, the fertilizer input amounted to ca. 3890 kg km\(^{-2}\) y\(^{-1}\) sulfate in Finland (Yli-Halla et al., 2011), almost ten times the present atmospheric deposition (290 kg km\(^{-2}\) y\(^{-1}\)). The output of sulfate in yield was ca. 980 kg km\(^{-2}\) y\(^{-1}\). Using these values, a field soil balance for sulfate would equal to 3340 kg km\(^{-2}\) y\(^{-1}\), about half of our estimate for the sulfate loss (7530 kg km\(^{-2}\) y\(^{-1}\)). Losses exceeding the current inputs could be explained with sulfur build up in soil during earlier higher fertilization and atmospheric deposition levels. Approximately 95% of sulfur in most soils is of an organic form (Scherer, 2001). If this value also holds for Finnish
agricultural soil, the majority of sulfate is likely mobilized by mineralization (Ledesma et al., 2016). Desorption forms a less likely option, since sulfate is bound onto soil particles relatively weakly in the typical pH (mean 6.1) of Finnish fertilized agricultural mineral soil (Geelhoed et al., 1997; Yli-Halla, 1987). Sulfate sorption increases with lowering pH and phosphorus saturation of soil (Yli-Halla, 1987).

The highest specific loss was found for fields on acid sulfate soils (192 000 kg km\(^{-2}\) y\(^{-1}\)) (Virtanen et al., 2016). A lower value was obtained for a small catchment located on sulfate soils (83 100 kg km\(^{-2}\) y\(^{-1}\), Table 1), perhaps because not all the fields in the catchment have been on sulfidic soils producing acidity. Due to the high specific loss, acid sulfate soils form the largest single source of sulfate for Finnish surface waters (24% of the total load), although they form only about 0.5% of the Finnish land area (Table 4). In acid sulfate soils, sulfate mainly originates from oxidation of iron sulfides when the groundwater table goes down to horizons containing sulfidic materials, the median sulfur concentration in fine grained acid sulfate soils being as high as 0.5% (Pihlaja et al., 2019). Therefore, sulfate has a natural origin, but its losses are accelerated by drainage. According to an ongoing survey, the total area of acid sulfate soils likely exceeds the earlier estimate of 3360 km\(^2\) (Pihlaja et al., 2019), of which some 1300 km\(^2\) was estimated to be agricultural land (Yli-Halla et al., 1999). If so, the sulfate loss from this land type may be still higher than presented here.

Acid sulfate soils are mainly found in the coastal regions of the country, and due to the lack of lakes, the bulk of the sulfate load directly enters the Baltic Sea. Thus, from an ecological viewpoint the load is likely unimportant, with freshwater and slightly saline systems such as rivers and estuaries potentially forming an exception (this conclusion does not apply to metal and metalloids mobilized from acid sulfate soils (Nystrand and Österholm, 2013). There is also some peat mining on acid sulfate soils and areas with black shale that give rise to
elevated sulfate losses, but these sources were excluded here for lack of data.

3.5 Urban areas

Urban areas produced 0.27% of the sulfate total load entering the surface waters. Because this value is based only on two catchments in the southernmost Finland, the extrapolated sulfate load for the entire country is especially uncertain. Urban areas introduce new pollutant sources and pathways for sulfate, and in general, sulfate levels are higher in storm drains compared with forest streams (e.g. Kaushal and Belt, 2012). A case study from urban catchments highlighted the importance of the hydrology in the loss of sulfate, which challenges reliable estimates of annual export (Taka et al., 2017). According to Taka et al. (2017), the share of urban land cover had a positive relationship with sulfate export, but interestingly sulfate stood out from the other ions (sodium, potassium, calcium, magnesium, chloride and nitrate). For example, the statistical significances of the co-occurrence of sodium and chloride, and potassium and magnesium were evident, but sulfate did not have similar pattern with any other ion. Further, it did not have any significant relationship with the type of urban land cover. In addition, its export was highest in summer months when runoff was low, and the temporal variation in export was significant, indicating extreme conditions for receiving ecosystems (see Taka et al., 2017 for details). Even though the sulfate concentrations did not follow the urban land cover gradient, they were in agreement with previous urban studies (e.g. Fitzpatrick et al., 2007; Nagy et al., 2012), but higher than in rural regions (Banks et al., 2001; Fitzpatrick et al., 2007).

3.6. Industry

On a national scale, 35% of the sulfate flux originated from point sources. Pulp and paper mills were the key sources and contributed to 20% of the national sulfate load (Table 4). About half of the pulp and paper industrial load entered the freshwaters. As an example, the
southern part of Lake Saimaa (southeastern Finland) receives wastewaters from several pulp mills. In winter, the elevated sulfate concentrations in the near-bottom layer can be detected dozens of kilometers from the source sulfate (Kraft, 2019).

The share of other industry in the total sulfate load was 6.4%. This other industry consisted of manufacturing of fertilisers, viscose, pigments, metals, explosives and packaging material. Only one presently operating plant discharges wastewaters into freshwaters. The load from other industry is potentially an underestimation, because only a few industrial activities had an obligation to monitor sulfate.

3.7 Mining

The sulfate load from the mines and ore mills was 3.9% of the total load entering the surface waters (Table 4). A third of the load originated from a multimetal bioleaching site in eastern Finland (producing Ni, Zn, Co and Cu), and two thirds from three largest sources, which also included an Au mine and a Cu/Zn/FeS₂ mine (Supplementary Table 2). The sulfate loss from mining activities originates from the mineral itself (sulfidic rocks) or from sulfuric acid and other sulfur-bearing chemicals used to extract metals. Similar to many other sectors, the sulfate load from mines may be underestimated, since there was data from only a fraction of the numerous closed mines. Due to the great variation in the ores, extracting chemicals and other technical features, it is impossible to extrapolate the load from the closed mines.

Most of the sulfate from mines and ore mills entered the freshwaters with sometimes strong local effects. For example, the massive load of sodium sulfate from the bioleaching mine created a halocline and hypoxia in small forest lakes downstream (Leppänen et al., 2017). Additionally, the eutrophication of a small lake (Kolmisoppi, eastern Finland) has been accelerated by sulfate leaching from a dumping area of attle of a fertilizer plant (Saarijärvi et
al., 2013). The external nutrient load of the lake did not increase, but elevated sulfate (from about 10 to 50–60 mg l⁻¹) has apparently interfered with the iron-phosphorus associations in the bottom sediments resulting in an increased phosphorus flux from sediments.

3.8 Water supply

The mean sulfate load per capita in the two wastewater treatment plants was 8.8 kg ind⁻¹ y⁻¹ (Table 3). Multiplication with the total number of persons served by municipal wastewater plants (4.62 million) gives a load value of 40 500 t y⁻¹. Although we only had data from two out of the more than 200 wastewater plants, the two plants accounted for about 25% of total wastewater volume in Finland. The sulfate concentration along the route of water from its original source to the outlet from the plant follows an interesting pattern. The capital city area takes water from Lake Päijänne, where the sulfate concentration is 8–10 mg l⁻¹, but in the tap water it is 23–30 mg l⁻¹ due to the use of ferric sulfate to remove organic matter in lake water and sulfuric acid to regulate the pH. When entering the wastewater treatment plant, the concentration has increased to 40–50 mg l⁻¹, probably due to sulfate in domestic chemicals and human excreta. Finally, the concentration is almost doubled in the wastewater treatment plant, the level in final effluent being 88 mg l⁻¹. The increase in sulfate in the wastewater treatment plant could mainly be explained by the sulfate in the precipitation chemical (ferrous sulfate). Thus, about 66% of the sulfate in the purified wastewater originated from precipitation chemicals used in drinking water and wastewater purification, 24% from domestic waste and 10% from lake water. This source apportionment excluded seeping of water from the Baltic Sea or from acid sulfate soils, likely to occur to some extent in the area (HSY, 2019 Personal communication). Our estimate may not be valid for the entire country, since sulfate-free chemicals are also used in the purification process and at the national level more than 60% of drinking water is produced from groundwater with a lot of local variation.
in sulfate concentration, the 2% and 98% percentiles being 1.15 and 91.9 mg l$^{-1}$, respectively, in wells drilled into bedrock (Lahermo et al., 2002).

Excluding the 10% originating from the source water, the sulfate load per capita is 7.9 kg ind$^{-1}$ y$^{-1}$ and the additional sulfate load caused by purified municipal wastewater is 36 400 t y$^{-1}$, 3.6% of the total load entering the surface waters (Table 4). There is no information on the sulfate load from 0.88 million inhabitants not connected to sewer systems. If the amount of domestic waste per capita is the same in rural and urban areas, the load would be only 1820 t y$^{-1}$. Here it is assumed that no reduction occurs in septic tanks or individual purification systems and no sulfate-containing chemicals are used in purification.

Finally, sparse data of the waste dumps and handling units and energy production were used for the national inventory. Most of the reported sulfate load from these sources originated from power plants, the largest individual case being a combined heat and power producing plant using peat as its primary fuel. The summed load from the other sources was as low as 1180 t y$^{-1}$ (0.1 % of the total load entering the surface waters). However, the value is likely an underestimation as there was information on only a few power plants using fossil fuels out of the dozens that still operate in Finland. In such power plants the original source of sulfate is the fuel itself, peat having the highest sulfur concentration. In flue-gas desulphurisation, sulfur is captured e.g. as gypsum. In waste management, sulfate may originate from biowastes and from gypsum and other sulfur-containing building and demolition waste. Here, too, the load is most likely underestimated.

3.9 Sulfate concentrations in freshwaters

The national median and mean sulfate concentrations of freshwaters in Finland were 3.8 mg l$^{-1}$ and 15.2 mg l$^{-1}$, respectively. The maximum values were found in rivers draining acid sulfate soils and in the vicinity of mines (Fig. 4). The sulfate concentration in outlets from
many sources exceeds the levels present in freshwaters (Fig. 4), although from the viewpoint of ecological effects, absolute amount (= load) is likely more important than the concentration in the incoming flux.

World Health Organization does not propose any health-based guideline value for sulfate in drinking water (World Health Organization, 2004). Unfortunately, there is no agreement on a “safe” level of sulfate that would be tolerated by a body of water. The lack of a threshold value is understandable, because the effect of sulfate on biogeochemical processes not only depends on its concentration but also on the availability of labile organic carbon (electron donor) and site-specific factors, such as the supply of oxygen and other electron acceptors than sulfate (Holmer and Storkholm, 2001; Mattsson et al., 2017; Palviainen et al., 2015). As an example, the formation of sulfides, and consequently the benthic phosphorus release, increased in the sediments of a Lithuanian lake with a sulfate concentration of 29–41 mg l$^{-1}$, when the input of organic carbon to sediments was elevated due to a change in the catchment (Krevš et al., 2019).

3.10. Validation of the sulfate load

The sulfate fluxes transported by the 31 rivers ranged from 650 kg km$^{-2}$ y$^{-1}$ in a northern, peaty catchment to 14 400 kg km$^{-2}$ y$^{-1}$ in a south-western catchment, probably impacted by acid sulfate soils (Supplementary table 3). The mean loss, as weighted by the catchment area, was 2930 kg km$^{-2}$ y$^{-1}$. Extrapolation to the entire Finland gave a sulfate load of 892 000 t y$^{-1}$, which compares well with the emission-based estimate of 1 020 000 t y$^{-1}$, taking into account that (1) some of the industrial and wastewater load enters directly into the Baltic Sea and is not included in the river fluxes and that (2) part of the sulfate is retained in lakes as sulfides and organic sulfur in sediments (the lake percentage of the catchments was 0–18, mean 6). Eutrophic lakes may retain sulfate more than oligotrophic ones (Holmer and Storkholm, 2001).
3.11 Ways forward

Although sulfate is one of the key players in biogeochemical cycles and voluminously used and released by human actions, it seems that comprehensive inventories of the sulfate sources have not been earlier made. Our Finnish case showed a large spatial variation in the diffuse sources, which confounded the extrapolation for the entire country. In turn, the data on point sources were surprisingly scarce, even if a few specific sources of sulfate (some mines and pulp mills) have received a lot of attention in Finland. The national loading database contained information on only those point sources that had an environmental permit. The lack of data may be related to the fact that there are few proven cases where the impacts in freshwater ecosystems have been traced back specifically to increased loads of sulfate. The lack of knowledge and unawareness of the effects of sulfate can be the reasons why there are no limits or norms related to sulfate in surface waters in the national or European water legislation. Based on our findings of the complicated matrix of sulfate sources, we recommend monitoring sulfate discharges from all activities using sulfur containing raw materials or chemicals. Awareness of the role sulfate exerts on the environment, coupled with a more comprehensive monitoring of sulfate sources, could result in more stringent environmental permits in cases where sulfate is considered to have an impact on eutrophication, toxic substances or greenhouse gas emissions. Our findings for Finland are not directly transferable to other countries. For example, acid sulfate soils are a Finnish specialty in the boreal region. However, our inventory hopefully gives insights on the methodology and monitoring need of potential sulfate sources. Finally, our work showcases how the administrative open data services are useful for scientific purposes.

3 Conclusions

About one million tons of sulfate annually enters the surface waters in Finland, the majority
(66%) originating from diffuse sources, such as agricultural and forested land. Agricultural fields on acid sulfate soils are responsible for one quarter of the total load. Diffuse sources show a large spatial variation and, excepting acid sulfate soils, have relatively low sulfate concentrations in runoff. Here sulfate originates from fertilizers and from the mobilisation of atmospheric sulfur bound in soil. Peatlands can act as a sink for sulfate, especially if hydrologically connected to the upstream catchment.

While the load from diffuse sources control the overall concentrations of sulfate in freshwaters, point sources, such as pulp and paper mills and mines cause local effects. Sulfur-containing chemicals are widely used in industrial processes, water treatment and consumer products. Compared with runoff from land areas, point sources were characterised by high sulfate concentrations in the outlet. Due to lack of data, the contribution of point sources has likely been underestimated and we recommend monitoring sulfate from all activities using sulfur containing raw materials or chemicals.

Acknowledgements

We are grateful to several persons in the Helsinki Region Environmental Services Authority HSY for advice and data on water supply, to Seija Virtanen (Drainage Foundation) on informing us about acid sulfate soils, to Kimmo Silvo, Johanna Mikkola-Pusa and Timo Jouttijärvi (Finnish Environment Institute) on guidance on point-source load, to Sari Mitikka for help with sulfate concentrations in freshwaters, Antti Räike for calculating the riverine sulfate loads and the reviewers whose comments helped to improve the text. This study synthesises results from three projects: TEAQUILA (Fluxes of Terminal Electron Acceptors: Linking Human Disturbance to the Health of Aquatic Systems) and URCA (Urban Catchments), funded by the Academy of Finland (project numbers 263476, 263308, 263320, 263335) and VACCIA (Vulnerability Assessment of ecosystem services for Climate Change...
Impacts and Adaptation), funded by the EU Life+ programme.

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Table 1. Characteristics of the four catchments used to estimate the losses of sulfate from agricultural areas.

<table>
<thead>
<tr>
<th>Catchment</th>
<th>Area</th>
<th>Field</th>
<th>Forest</th>
<th>Urban</th>
<th>Peatland(^A)</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>km(^2)</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Hovi</td>
<td>0.12</td>
<td>100</td>
<td>0</td>
<td>0.0</td>
<td>0.0</td>
<td>211</td>
</tr>
<tr>
<td>Savijoki</td>
<td>15.0</td>
<td>39</td>
<td>56</td>
<td>3.9</td>
<td>1.2</td>
<td>216</td>
</tr>
<tr>
<td>Löytäneenoja</td>
<td>5.64</td>
<td>77</td>
<td>21</td>
<td>0.0</td>
<td>1.0</td>
<td>168</td>
</tr>
<tr>
<td>Haapajyrä</td>
<td>6.09</td>
<td>58</td>
<td>42</td>
<td>0.0</td>
<td>0.0</td>
<td>211</td>
</tr>
</tbody>
</table>

\(^A\) Includes other minor land use types

<table>
<thead>
<tr>
<th>Mean concentration(^B)</th>
<th>Mean runoff</th>
<th>Specific loss</th>
<th>Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg l(^{-1})</td>
<td>1 s(^{-1}) km(^{-2})</td>
<td>kg km(^{-2}) y(^{-1})</td>
<td></td>
</tr>
<tr>
<td>10.3</td>
<td>8.4</td>
<td>2 710</td>
<td>2000–2010</td>
</tr>
<tr>
<td>8.4</td>
<td>10.3</td>
<td>5 200</td>
<td>2000–2012</td>
</tr>
<tr>
<td>44.8</td>
<td>8.2</td>
<td>17 600</td>
<td>2000–2013</td>
</tr>
<tr>
<td>196</td>
<td>7.9</td>
<td>84 600</td>
<td>2000–2013</td>
</tr>
</tbody>
</table>

\(^B\) Flow-weighted
Table 2. Characteristics of the forest industrial plants with adequate sulfate data.

<table>
<thead>
<tr>
<th>Plant</th>
<th>Production capacity</th>
<th>Sulfate load</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>t y(^{-1})</td>
<td>t y(^{-1})</td>
</tr>
<tr>
<td>Pulp Mill 1</td>
<td>867 000</td>
<td>21 900</td>
</tr>
<tr>
<td>Pulp Mill 2</td>
<td>530 000</td>
<td>15 000</td>
</tr>
<tr>
<td>Fluting Mill 1</td>
<td>330 000</td>
<td>1 643</td>
</tr>
</tbody>
</table>

Table 3. Characteristics of the two wastewater treatment plants with adequate sulfate data.

<table>
<thead>
<tr>
<th>Plant</th>
<th>Person equivalents</th>
<th>Wastewater discharge</th>
<th>Mean sulfate concentration</th>
<th>Sulfate load</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ind.</td>
<td>m(^3) s(^{-1})</td>
<td>mg l(^{-1})</td>
<td>t y(^{-1})</td>
</tr>
<tr>
<td>Plant 1</td>
<td>1 050 000</td>
<td>3.1</td>
<td>80</td>
<td>7680</td>
</tr>
<tr>
<td>Plant 2</td>
<td>335 000</td>
<td>1.1</td>
<td>97</td>
<td>3430</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td>88</td>
<td></td>
</tr>
</tbody>
</table>
Table 4. Estimated annual load of sulfate to surface waters based on monitoring data and on specific sulfate loads expressed per production volume, person or area multiplied by the national production volumes, number of individuals or land cover area.

<table>
<thead>
<tr>
<th>Source</th>
<th>Specific load</th>
<th>Volume</th>
<th>Load to surface waters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Unit</td>
<td>Volume</td>
</tr>
<tr>
<td><strong>Diffuse sources</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deposition to freshwater</td>
<td>290</td>
<td>kg km⁻² y⁻¹</td>
<td>34 325</td>
</tr>
<tr>
<td>Forests on mineral soils</td>
<td>1080</td>
<td>kg km⁻² y⁻¹</td>
<td>199 846</td>
</tr>
<tr>
<td>Peatland</td>
<td>0</td>
<td>kg km⁻² y⁻¹</td>
<td>71 930</td>
</tr>
<tr>
<td>Agricultural fields, non-acid soils</td>
<td>7530</td>
<td>kg km⁻² y⁻¹</td>
<td>21 680</td>
</tr>
<tr>
<td>Agricultural fields, acid sulfate soils</td>
<td>192 000</td>
<td>kg km⁻² y⁻¹</td>
<td>1300</td>
</tr>
<tr>
<td>Urban areas</td>
<td>2970</td>
<td>kg km⁻² y⁻¹</td>
<td>9 338</td>
</tr>
<tr>
<td>Sparse population</td>
<td>2.1</td>
<td>kg ind⁻¹ y⁻¹</td>
<td>880 000</td>
</tr>
<tr>
<td><strong>Point sources</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pulp &amp; paper mills, sulfate process</td>
<td>26.8</td>
<td>kg t⁻¹ y⁻¹</td>
<td>7 685 000</td>
</tr>
<tr>
<td>Pulp &amp; paper mills, semi-chemical fluting</td>
<td>5.0</td>
<td>kg t⁻¹ y⁻¹</td>
<td>630 000</td>
</tr>
<tr>
<td>Other industry C</td>
<td>65 200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mines and ore mills C</td>
<td>40 100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Municipal wastewaters</td>
<td>7.9</td>
<td>kg ind⁻¹ y⁻¹</td>
<td>4 620 000</td>
</tr>
<tr>
<td>Other point sources C</td>
<td>1 180</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1 020 000</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^A Areas based on CORINE 2012, except for fields on acid sulfate soils which is based on Yli-Halla et al. (1999).

^B Includes 3124 km² of minor land use/land cover types.

^C Information from the Finnish Pollutant Release and Environmental Enforcement Register.
Fig. 1. Main land cover classes according to CORINE2012 (Finnish Environment Institute, 2019a) in Finland. White circles show the monitoring sites for atmospheric deposition, white squares show the sites were throughfall was also measured.

Fig. 2. Sulfate concentration in runoff as a function of peatland percent of the catchment in the data examined here and by Palviainen et al. (2015). The right vertical axis shows the corresponding sulfate loss with a typical runoff of 300 mm.

Fig. 3. Mean sulfate concentration in freshwaters in 2010–2019 by 10 ∙ 10 km² pixels. In white areas there are either no water bodies or data.

Fig. 4. Typical sulfate concentration in selected sources. The dashed line shows the median concentration in Finnish lakes.
Declaration of competing interest

The authors have no competing interests to declare.
Credit Author Statement
Ekholm initiated the study and carried the main responsibility of data analysis and writing,
Lehtoranta was responsible for environmental effects of sulfate, Taka for urban losses,
Sallantaus for peatland losses and Riihimäki for GIS analyses. All authors took part in
writing and drawing the conclusions.
Graphical abstract

Highlights
1. SO$_4$ controls aquatic biogeochemistry, but its sources are not fully known
2. We made an inventory of the key SO$_4$ sources of surface waters in Finland
3. Agricultural and forest areas were the dominating diffuse sources of SO$_4$
4. Pulp and paper mills accounted for 20% of the total SO$_4$ load
5. SO$_4$ should be systematically included in monitoring and control measures