Science of the Total Environment 805 (2022) 150256

Contents lists available at ScienceDirect

Science of the Total Environment

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

Review

Iron in boreal river catchments: Biogeochemical, ecological and management implications

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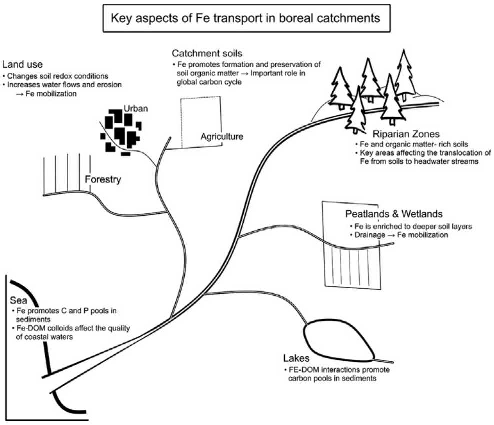
HIGHLIGHTS

- Fe has a key role in biogeochemical and ecological contexts in boreal catchments.
- Fe has many harmful impacts on aquatic organisms and ecosystems.
- Drivers of Fe transport should be better known in water management.
- Catchment-scale approaches are required to create effective management of Fe.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 March 2021
Received in revised form 19 August 2021
Accepted 6 September 2021
Available online 10 September 2021

Editor: Ouyang Wei

Keywords:
Iron
Boreal rivers
Land use management
Ecosystem function
Peatlands

ABSTRACT

Iron (Fe) is an important element in aquatic ecosystems worldwide because it is intimately tied with multiple abiotic and biotic phenomena. Here, we give a survey of manifold influences of Fe, and the key factors affecting it in the boreal catchments and their waters. It includes the perspectives of biogeochemistry, hydrology, ecology, and river basin management. We emphasize views on the dynamics and impacts of different forms of Fe in riverine environments, including organic colloids and particles, as well as inorganic fractions. We also provide perspectives for land use management in boreal catchments and suggest guidelines for decision making and water management. Based on our survey, the main emphases of water protection and management programs should be (i) prevention of Fe mobilization from soil layers by avoiding unnecessary land-use activities and minimizing soil disturbance in high-risk areas; (ii) disconnecting Fe-rich ground water discharge from directly reaching watercourses; and (iii) decreasing transport of Fe to watercourses by applying efficient water pollution control approaches. These approaches may require specific methods that should be given attention depending on catchment conditions in different areas. Finally, we highlight issues requiring additional research on boreal catchments. A key issue is to increase our understanding of the role of Fe in the utilization of DOM in riverine food webs, which are typically highly heterotrophic. More knowledge is needed on the metabolic and behavioral

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Acronyms: DOM, dissolved organic matter; NOM, natural organic matter; TOC, total organic carbon; DOC, dissolved organic carbon; HS, humic substances; HA, humic acids; HAMW DOM, high apparent molecular weight (in excess of 100,000) DOM; HAMW Fe-organic colloids, high apparent molecular weight Fe-organic colloids; FPOM, fine-grained particulate organic matter (diameter < 0.075 mm); SS, suspended solids; TSS, total suspended solids; NP, nanoparticulate; OC, organic carbon.

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https://doi.org/10.1016/j.scitotenv.2021.150256

resistance mechanisms that aquatic organisms, such as algae, invertebrates, and fish, have developed to counter the harmful impacts of Fe in rivers with naturally high Fe and DOM concentrations. It is also emphasized that to fulfil the needs presented above, as well as to develop effective methods for decreasing the harmful impacts of Fe in water management, the biogeochemical processes contributing to Fe transport from catchments via rivers to estuaries should be better understood.

Contents

1. Introduction

The biogeochemical and ecological status of freshwater ecosystems has been under extensive investigation because different anthropogenic pressures have strongly modified lentic and lotic ecosystems during the past decades (Sabater et al., 2018; Reid et al., 2019; Cantonati et al., 2020; Heino et al., 2021). However, the management of natural waters throughout Europe (e.g. based on the EU water framework directive) has not sufficiently considered many local catchment features and elements affecting water quality. One of these elements is iron (Fe) that is naturally present in most rivers and streams, being especially prevalent in the boreal region (Björkvald et al., 2008; Sundman et al., 2014). Fe has been considered an important element because it affects both directly (Vuori, 1995; Karvonen, 1995; Laine et al., 2001; Laine and Heikkinen, 2000) and indirectly (Neubauer et al., 2013) multiple ecosystem functions and organisms in freshwater ecosystems (Namba et al., 2020). Functions that are likely to be affected by Fe in river ecosystems, that are typically heterotrophic (Cummins, 1979), include even organic matter use and decomposition. The key contributors to these processes are organisms (bacteria, fungi, and invertebrates) (Allan and Castillo, 2007). It is, however, still inadequately understood, how such functions are modified by varying iron concentrations, and which kind of repercussions they have for biogeochemical and ecological dynamics.

Recent studies have indicated that Fe concentrations have increased in boreal freshwaters over the last few decades (Kritzberg and Ekström, 2012; Sarkkola et al., 2013; Björnerås et al., 2017; Xiao and Riise, 2021). These increases in Fe concentrations have been linked to changes in precipitation and temperature (Sarkkola et al., 2013), increased occurrence of hydrological extremes (Xiao and Riise, 2021), and increased prevalence of reducing conditions in the catchments (Ekström et al., 2016). Decreases in sulphate depositions (Löfgren and Zetterberg, 2011) and anthropogenic changes in land drainage activities (Vuori, 1995; Laine et al., 2001) have also resulted in elevated Fe concentrations in freshwater ecosystems. As Fe plays a significant role in key biogeochemical processes and ecosystem functions, anthropogenic activities are likely to have increasingly harmful impacts on freshwater ecosystems in near future. In order to successfully decrease and mitigate such harmful impacts on freshwater ecosystems, knowledge on the role of Fe needs to be summarized and inadequately known research areas have to be emphasized to guide further research.

Here, we give a survey of the wide and manifold influences of iron, and the key factors affecting it (Fig. 2) in boreal catchments. Examples on this are given mainly from Finland (Fig. 1), but for reinforcements and comparison also from the other parts of the Fenno-Scandinavia. According to Räike et al. (2012) the area of the 29 river basins in Finland flowing to the Baltic Sea ranges from 357 to 61,466 km^2, the proportion of upland forests underlain by mineral soils from 33 to 54% and that of peatlands from 3 to 40%. The percentage of peatlands is highest at latitudes between 63° and 66°N, where also the River Kiiminkijoki basin, one of the examples presented in this article, is situated. In Finland, the forest cover increases towards the south. The proportion of agricultural land is ranges from 1 to 43%, the majority of the croplands being located close to the southern and western coasts. The phytogeographical differences between the boreal areas in Finland, Sweden and Russia are small. Russian boreal forests (known in Russia as the taiga) represent the largest forested region on Earth (approximately 12 million km^2), larger than the Amazon (WWF).

Our survey focuses jointly on biogeochemistry, hydrology, ecology, and water management. We specifically consider the dynamics and impacts of different forms of Fe in riverine environments, such as organic colloids and particles, as well as inorganic fractions. Moreover, we offer novel perspectives for land use management in boreal catchments as well as suggest guidelines for decision making and river management plans. Finally, we highlight issues for new research and pinpoint issues that require further scrutiny in the research on the significance of Fe in rivers draining boreal catchments.

2. Iron transport in boreal catchments

Iron is a key element influencing biogeochemical processes in the terrestrial-aquatic continuum of soils, sediments, and waters in boreal catchments (Sundman et al., 2014), which are commonly dominated by coniferous forests and peatlands. Such catchments are common in areas ranging from northern Europe and Siberia to Alaska and Canada (Schindler and Lee, 2010). These catchments are characterized by the substantial role played by dissolved organic matter (DOM) in Fe transport, accumulation, and leaching processes, especially if the catchments are dominated by peatlands (Heikkinen, 1990a,b).

The existing knowledge refers to the dynamic nature and behavior of Fe compounds in boreal freshwaters. The analytical methods and detection limits in the studies of these compounds have been updated over time from the main use of gel filtration in 1990s to the use of Dynamic Light Scattering (DLS) and X-ray Absorbance Spectroscopy (XAS) measurements in 2010s. It has been already for a long time known that Fe dissolved in water containing oxygen is bound mainly to humic substances (HS) (Shapiro, 1964), i.e. the main part of the

Fig. 1. Distribution of boreal (and taiga) biome highlighted in green. Darker green represents the location of research studies closely related to this survey (Sweden and Finland) (Olson et al., 2001).

DOM in boreal freshwaters. This form of Fe is often referred to as "dissolved organic Fe". Gel filtration has shown that such Fe is mainly bound to the high apparent molecular weight (HAMW) DOM fraction in boreal lakes (Pennanen, 1972; Kortelainen et al., 1986; de Haan et al., 1987; Jones et al., 1988, 1993) and rivers (Heikkinen, 1990b) in Finland and elsewhere (Ghassemi and Christman, 1968; Koenings and Hooper, 1976). For example, in the River Kiiminkijoki in Northern Finland (Heikkinen, 1990b), the HAMW DOM separated is mainly colloidal by nature, because gel filtration was conducted using waters prefiltered with Whatman GF/C filter (approximate pore size 1.2 μm). According to IUPAC (1997), the material with one or more dimensions in the size range from 1 nm to 1 μm in aquatic systems is typically defined as colloids. The HAMW DOM colloids are weakly fluorescent (Heikkinen, 1990b), and therefore supposed to be composed mainly of weakly fluorescent (Schnitzer and Khan, 1978; Visser, 1981) humic acids (HA). DLS measurements have also identified larger Fe particles and complexes in boreal waters, with some being at least partly composed of organic matter (OM). For example, in the study of Herzog et al. (2020) three size distributions for them were found from three boreal rivers located in southern Sweden: (1) 10–40 nm, consisting mainly of essentially bare Fe(*oxy*)hydroxide nanoparticles, (2) 100–200 nm, consisting mainly of Fe-OM complexes, and (3) 300–900 nm, consisting mainly of Fe(*oxy*)hydroxides. The existence of Fe-organic matter complexes in these rivers was shown also by XAS measurements, as in the Krycklan River catchment in Sweden by Sundman et al. (2014).

The existing knowledge suggests that by contributing to the flocculation and sedimentation processes of DOM in the catchments in many ways, Fe could facilitate the biotic use of the DOM in heterotrophic river ecosystems. There are also observations pointing out the importance of dissolved organic Fe-colloids in the biotic use of phosphate (PO_4) transported in boreal catchments. These issues, as well as the effects of Fe on the photic zone in riverine environments, are considered in more detail in Section 3.

In general, redox potential and pH conditions determine speciation and solubility of inorganic Fe (Pankow, 2020) during its course downstream in the river network. In aerobic freshwaters, inorganic Fe is typically present as thermodynamically stable oxidation state Fe(III), which is precipitated to form brownish (oxy)hydroxides. The oxidation (Pankow, 2020) and precipitation (Neubauer et al., 2013) processes of inorganic Fe are dependent on pH.

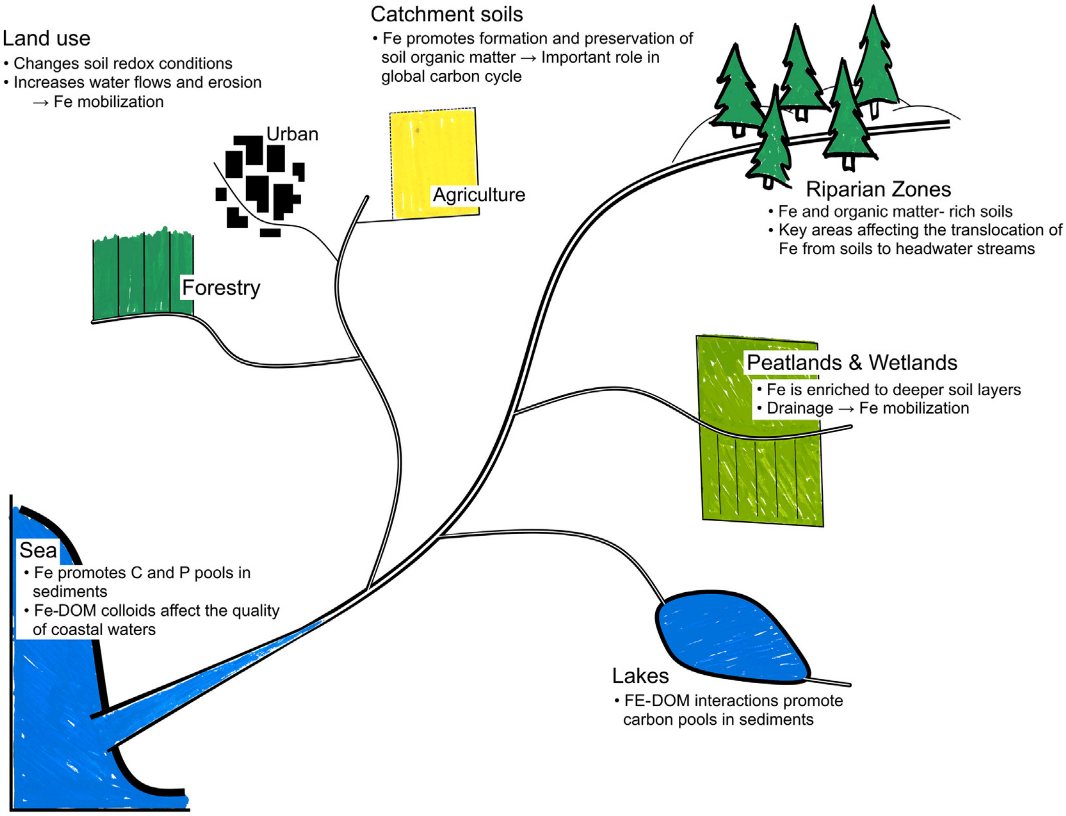

Fig. 2. Key factors affecting Fe transport across the terrestrial-aquatic continuum in a boreal catchment.

Fe originates and is weathered from bedrock and soil minerals in a catchment (Sundman et al., 2014). Peatlands can serve as sinks or sources of Fe in typical boreal catchments, depending on prevailing hydrological and biogeochemical conditions. In many cases, waters draining peatland-dominated catchments have higher Fe concentrations than those draining forest-dominated catchments (Kortelainen and Saukkonen, 1998; Björkvald et al., 2008; Sarkkola et al., 2013; Palviainen et al., 2015).

In boreal minerotrophic peatlands, Fe is enriched in the deeper, partly anaerobic peat layers (Puustjärvi, 1953). It is transported from these peatlands mainly in the form of dissolved organic Fe-P-colloids in boreal areas (Heikkinen, 1990b), which is also a general finding from freshwaters worldwide (Shapiro, 1964; Ghassemi and Christman, 1968; Golterman, 1973; Jackson and Schindler, 1975; Jones et al., 1988). It is also known that HS may enhance weathering of iron-silicate minerals (Krachler et al., 2010). Fe, in turn, can promote soil organic matter decomposition in peatlands if oxygen (O_2) becomes limited (Chen et al., 2020). Furthermore, microbes are driving many element cycles and linking together different chemical elements including Fe (Falkowski et al., 2008; Lauderdale et al., 2020). Electron acceptors, i.e. oxygen, nitrate, Fe, Mn and sulphate, contribute to the decomposition of organic matter in different ecosystems. When energetically more favorable electron acceptors, i.e. oxygen and nitrate, have been depleted, the decomposition is mainly driven by Fe, followed by Mn and sulphate.

Moreover, Fe and Al oxides and oxyhydroxides could promote the stabilization of organic matter in peatlands, as has been observed among a range of field soils by Wagai and Mayer (2007). The impacts of Fe on the formation and preservation of soil organic matter presumably play a significant role in the global carbon cycle, where soil organic matter represents an important carbon reservoir. However, they are poorly understood.

Podzols are typical soils in boreal coniferous forests. Their development is strongly associated with Fe concentrations in soil profiles (Lundström et al., 2000). In the podzolization process, Fe is complexed with organic matter derived from the decomposition of the organic coniferous needle layer. The dissolved organic Fe complexes are subsequently translocated deeper in the soil profile and adsorbed or precipitated in the illuvial horizon, resulting in a whitish, strongly bleached eluvial horizon above. The colour of the illuvial soil horizon is either red or reddish-brown, being strongest in the upper parts of the soil horizon. Many fundamental aspects of podzolization and Fe transport from podzol soils are still poorly understood, however. Based on existing knowledge from peatlands and humic rivers (Heikkinen, 1990b), riparian soil waters (Sundman et al., 2014), lakes (Kortelainen et al., 1986) and headwater streams (Kortelainen et al., 2006), it is probable that Fe from podzol soils is also transported to water bodies mainly as dissolved organic Fe- colloids. This presumption must be verified, however, because improved knowledge would facilitate the development of novel management methods for water pollution control to decrease impacts of land use, for example, under forestry practices in the catchments.

Water passes through the riparian zone, when it enters from the soil to the stream in the terrestrial-aquatic continuum. This step in the continuum is important, as there is a gradient, i.e. redoxcline, where the predominant conditions for the fate of Fe (and for those of other trace elements) change from anoxic to oxic (Lidman et al., 2017; Ingri et al., 2018). Fe occurs in ferric and ferrous ions in oxic and anoxic conditions, respectively, which are influenced by microbial activity. The redoxcline serves as a strip that is shown to have a strong impact on stream water quality in terms of Fe concentrations (Lidman et al., 2017; Ingri et al., 2018). The Fe concentrations in the soil waters (saturated and unsaturated zone) of redoxclines are clearly higher than those in the Podzol soils further away from the riparian zones (Lidman et al., 2017). Riparian zones are also enriched with total organic carbon (TOC) (Lidman et al., 2017), and the speciation of Fe in the riparian soil water is strongly dominated by organic Fe colloids (Sundman et al., 2014). Recently, Ingri et al. (2018) demonstrated the effect of riparian zones on Fe transport in headwater streams. Their results showed that the isotopic composition of Fe in headwaters and riparian soil waters was similar, especially in comparison with the podzol soil water or the water of the mainstem river. Their finding further suggested that riparian zones have a decisive role in determining water chemistry in small headwater streams.

There is a dominant source layer of Fe in riparian soils (Ingri et al., 2018), as in minerotrophic peatlands (Puustjärvi, 1953). Approximately 60% of the total Fe transport from riparian soils originates from this narrow soil layer located between 35 cm and 55 cm near the groundwater table (Ingri et al., 2018). It is also probable that the riparian zones on peaty areas retain Fe-organic colloids derived from the soil waters, as peatlands. This ability of peatlands has been utilized in water pollution control to mitigate harmful impacts caused by peat extraction (Heikkinen and Ihme, 1995; Heikkinen et al., 2018) and by forestry practices (Joensuu et al., 2012) in water bodies.

Rivers are considered major carriers of Fe to coastal areas and to the sea (Saitoh et al., 2008; Krachler et al., 2010). Because of the differences in Fe enrichment and transport processes between peatland-dominated and forest-dominated mineral soil catchments, there are also differences in the annual patterns of the dissolved organic Fe transport between these major types of boreal catchments. In the peatland-dominated catchments, the concentrations of dissolved organic Fe and total Fe increase gradually attaining highest levels during the winter baseflow conditions before the spring snowmelt (Heikkinen, 1990a; Björkvald et al., 2008). A gradual increase in Fe concentrations has also been observed during the baseflow conditions in summer (Heikkinen, 1990a; Joensuu, 2002). During the baseflow conditions, the major runoff component is originating from the deeper, partly anaerobic peat horizons, where Fe is enriched (Puustjärvi, 1953). In certain locations, there may also be direct Fe-rich groundwater seepage to river channels. In contrast, in forest-dominated catchments, total Fe and dissolved organic Fe concentrations are highest during the discharge peak caused by spring snowmelt because the transport of Fe is closely tied to the transport of DOM and particulates (Björkvald et al., 2008; Sundman et al., 2014).

In the humic rivers draining peatland-dominated catchments, Fe is transported mainly in the form of dissolved organic Fe-P-colloids (Heikkinen, 1990a,b). As in the riparian zones, there are probably complex interactions between the formation and transformation processes of inorganic and organic Fe compounds also in the river channel. For example, in the River Kiiminkijoki in northern Finland, there was a gradual and strong increase in the fluorescence intensity (i.e. in the fluorescence/DOC ratio) of the DOM with increasing Fe content of the DOM (i.e. in the Fe/DOC ratio) during low-flow conditions in summer and early autumn (Heikkinen, 1990a). This increase was supposed to indicate precipitation and sedimentation of weakly-fluorescent high molecular weight (HAMW) Fe-organic colloids in summer. This presumption was supported by Marttila et al. (2016), who analyzed temporal changes in SS transport in rivers draining to the Bothnian Bay, based on long-term (1967–2011) data on runoff and SS concentrations. They found that the concentrations of fine (<0.4–1.2 μm) SS particles were high before spring floods, during summer low-flow conditions, and during summer and autumn high-flow periods. During these time periods, also Fe and Al concentrations in the river water were at their highest levels (Marttila et al., 2016).

In the humic Krycklan River, Sweden, draining forest-dominated catchments with patches of *Sphagnum* moss-dominated peatlands, changes in Fe speciation were detected along the flow path of the river by Neubauer et al. (2013). In the peatland -dominated headwaters with the highest DOC concentrations, Fe was mainly transported in the form of dissolved organic Fe-colloids, whereas in larger streams of order >1 and with higher pH-values, the proportion of nanoparticulate iron (*oxy*)hydroxides precipitates within dissolved organic Fe-colloids increased. The DOC concentrations in this river ranged from 53 mg l^{-1}

in the small peatland -dominated catchments to 19.6 mg l^{-1} at the catchment outlet. Humic acids made up ≤13% of the DOM in the river water.

The results from the boreal Krycklan River catchment (Sundman et al., 2014), as well as those from the Suwannee River catchment in the transitional climatic area between the warm, temperate climate of the southeastern U.S. and the subtropical climate of the Florida peninsula (Baalousha et al., 2006; Baalousha, 2009; Chekli et al., 2013) suggest that DOM affects the environmental impacts of iron oxide aggregates in freshwater ecosystems by controlling the formation and permanence of iron oxide NP aggregates. The size of Fe-organic aggregates increases with increasing pH-value and water DOM concentration (Baalousha et al., 2006; Sundman et al., 2014). In the Suwannee River, remarkably high concentrations of HA, one of the main chemical components of HS and DOM in waters, induced the disaggregation of iron oxide NP aggregates with time (Baalousha, 2009). On the other hand, Fe_2O_3 NPs coated by natural organic matter may form stronger aggregates than HA-coated Fe_2O_3 NPs (Chekli et al., 2013). The results indicate that the role of DOM in the formation of iron aggregates is complicated and should be studied further especially in boreal waters with high DOM concentrations.

In boreal rivers with low DOM content, the role of inorganic Fe compounds in Fe transport is probably higher than that of the DOM. It is, however, probable that dissolved organic Fe-colloids play an important role in Fe transport in the headwaters of these rivers. This is because these colloids strongly dominate the riparian zone waters (Sundman et al., 2014). The role of Fe is also important in the sedimentation of organic matter in boreal lakes, where water Fe concentration and carbon pools in sediments are typically strongly correlated (Kortelainen et al., 2004; Einola et al., 2011), a finding similar to that in marine environments (Lalonde et al., 2012; Barber et al., 2017). In addition to clay minerals, Fe(III) oxide particles have been shown to be responsible for the protection and burial of a large fraction of marine sedimentary organic carbon (OC); e.g. 25–62% of total reactive iron was directly associated to OC (Barber et al., 2017). On the other hand, Peter and Sobek (2018) found high variability in Fe–OC content among five Swedish lakes, suggesting that Fe-bound OC may play a minor role for sediment OC release in boreal lakes. Nevertheless, they also concluded that studies of redox-related OC cycling in boreal lake sediments should consider that the amount of Fe–OC can be high in some lakes.

In estuarine environments, Fe compounds tend to be increasingly precipitated with increasing salinity. However, the capacity of river waters to maintain Fe in suspension in the sea varies greatly with their Fe/DOC-ratios (Kritzberg et al., 2014). The lower the ratio, the more Fe remains in suspension. It is also known that the Fe-organic colloids are more resistant to aggregation due to increasing salinity than the (oxy) hydroxide Fe colloids (Herzog et al., 2017, 2020). Far reaching environmental impacts for the dissolved organic Fe from the boreal humic rivers could thus be supposed in the marine environment, especially in coastal areas.

Iron is also attached to the surfaces of the fine soil particulates (tills and clays), as seen for example in the catchments with large areas of agricultural fields on lowland clay soils in the southern parts of Finland (Sippola, 1974). High correlations between total Fe and TSS transports detected in these catchments (Palviainen et al., 2015; Saari et al., 2020) indicate that Fe is transported also in this form to the water bodies and downstream here, as probably also in the whole Baltic Sea region. The transport of particulate Fe is primarily controlled by mechanical SS transport and erosion driven by hydrologic forces in the catchments, thus being high especially during flood events with high surface runoff generation.

Previous findings suggest that more research is needed on the biogeochemical processes affecting Fe transport, precipitation, accumulation, and leaching, as well as on the interactions between inorganic and dissolved organic forms of Fe in boreal catchments. A more comprehensive knowledge base resulting from studies of different types of catchments would facilitate the development of improved management practices for boreal catchments that belong to the group of the most carbon-rich ecosystems worldwide. For example, the importance of iron(*oxy*)hydroxide precipitates with harmful impacts should be increasingly studied in rivers with high DOM and Fe concentrations. Improved knowledge on the biogeochemistry of Fe would also contribute to understanding the importance of Fe and DOM in boreal freshwater and coastal ecosystems.

3. Ecosystem influences

Harmful impacts of Fe loading on the survival, food resources, growth and reproduction of aquatic organisms are typically due to toxic actions of Fe compounds. These compounds may therefore result in decreases in the species diversity and abundance of periphyton, benthic invertebrates and fishes, which has been known for boreal river ecosystems for a long time (Vuori, 1995). More specifically, increases in fine-grained (<0.075 mm) particulate organic matter with high Fe content (Laine and Heikkinen, 2000) and decreases in the incubation success of brown trout (*Salmo trutta*) eggs with increasing SS and Fe loading (Laine et al., 2001) have been detected in northern Finnish rivers.

However, effects of Fe on river ecosystem structure and function are not yet fully known. It is probable that Fe plays a crucial role in the utilization of DOM in river ecosystems that are typically highly heterotrophic, thereby relying on organic matter mainly transported from terrestrial ecosystems to the aquatic environment (Cummins, 1979; Allan and Castillo, 2007). The role of this transport should be better understood because DOM is the dominant organic carbon fraction in most boreal rivers, especially in humic rivers (Heikkinen, 1989). Here, a key issue is to understand the role of Fe in the precipitation of DOM, which enables the biotic use of the DOM in river ecosystems in general (Cummins, 1979; Petersen, 1986).

Current knowledge on the role of Fe in the precipitation of DOM (Heikkinen, 1990a; Marttila et al., 2016) suggests that like in boreal lakes (Kortelainen et al., 2004; Einola et al., 2011) and in marine environments (Lalonde et al., 2012), Fe also contributes to the flocculation and sedimentation processes of DOM in river ecosystems. Indications of flocculation and sedimentation of one portion of the DOM (the HAMW organic colloids), with increasing Fe content have also been found in studies on the impacts of peat-extraction areas on rivers in boreal catchments (Heikkinen, 1990b,c; Laine and Heikkinen, 2000). Here, an increase in Fe mobilization downstream was detected along with a simultaneous augmentation in the Fe content (the Fe/DOC ratio) of the HAMW DOM in the drainage waters at low-flow conditions (Heikkinen, 1990b,c). When studying the impacts of increased loading on water bodies, a simultaneous increase in the amount of FPOM (fine-grained particulate organic matter, diameter < 0.075 mm) with high Fe content was observed at the riffle sites downstream from the peat extraction areas (Laine and Heikkinen, 2000). Also, an interesting ecological observation in the areas of increased loading was a concomitant increase in the abundance of filter-feeding macroinvertebrates (Karvonen, 1995) that mainly feed on FPOM available in the water column (Vannote et al., 1980). Although a quite old observation, this observation should be emphasized because of the significant role of macroinvertebrates in heterotrophic river ecosystems (Allan and Castillo, 2007). This finding also suggests a potentially important role for Fe in the biotic use of DOM in boreal humic rivers with high DOM and Fe concentrations. The HAMW DOM accounts for an average of 16 to 26% of the total DOM concentration in a typical humic river network in Northern Finland (Heikkinen, 1990b). In addition to this, DOM is also shown to participate in the formation of larger (100–200 nm) Fe-organic particles and complexes in boreal rivers (Herzog et al., 2020). The potential role of Fe in enabling the biotic use of DOM in river ecosystems is thus important, but complex and should be studied further.

The decomposition and use of DOM in boreal rivers are also contributed by heterotrophic and mixotrophic microorganisms able to mineralize Fe-organic compounds (Dubinina, 1976; Kuntze, 1982). This was indicated, for example, in the River Kiiminkijoki, where bacterioplankton densities increased with increasing concentrations of dissolved organic Fe (Heikkinen and Visuri, 1990). The importance of these microorganisms in the food webs of humic rivers is inadequately known. What is currently known, however, is that Fe associated with DOM may also stimulate the biodegradation of humic-like DOM in Fe-rich freshwaters, and organically bound Fe can even stimulate bacterial growth on DOM if P is not limiting (Xiao et al., 2016)

Organisms may have different strategies to cope with Fe in boreal humic rivers. For example, increased abundances of filter-feeding macroinvertebrates at river sites downstream from peat extraction areas (Karvonen, 1995) suggest that some macroinvertebrate species have developed natural metabolic and/or behavioral resistance mechanisms against the harmful impacts of high Fe concentrations in river environments. This might also apply to the fish species occurring in humic rivers. For instance, despite naturally high Fe and DOM concentrations, a native salmon (*Salmo salar*) stock was successfully reproducing in the humic River Kiiminkijoki (Erkinaro et al., 2003). This stock was lost in the 1970s (Koli, 1998), i.e. during the period of most widespread drainages of peatland for forestry in this region. During the same period, increasing accumulation of Fe in the pools of the river channel was also observed in the River Sanginjoki that is situated near the River Kiiminkijoki (Tolkkinen et al., 2014). Similar accumulation of Fe has probably been the case in the River Kiiminkijoki, where peatlands account for 58% of the river basin. At present, half of the original cover of peatlands in the River Kiiminkijoki basin is drained, and drained peatlands account for 30% of the basin. However, natural salmon reproduction has again been observed in this river, resulting from fish stockings within the Baltic Salmon Action Plan of the International Baltic Sea Fishery Commission (IBSFC) (Erkinaro et al., 2003; HELCOM, 2011), although the production of the juvenile salmon is far from the targets set in these programs. The evidence acquired thus far suggests that more research is needed on the mechanisms affecting the ecotoxicological effects of Fe in boreal river ecosystems. Also, similarly important is to understand if these effects differ among key organism groups (i.e. algae, macroinvertebrates and fish) typically used in assessing ecological influences of metals on rivers across the world (Namba et al., 2020).

Iron and HS also play a role in enabling the use of P reserves in catchment soils to be available as nutrient sources for aquatic organisms. For example, PO_4 is typically associated with the HAMW Fe DOM fraction (Heikkinen, 1990b), both in the drainage waters from peatlands and in humic river waters. Similar findings have been made in other systems (Golterman, 1973; Jackson and Schindler, 1975; Jones et al., 1988). However, more importantly, Francko and Heath (1982) have shown that PO_4 may be released from Fe-organic colloids by a mechanism involving UV-induced photoreduction of ferric iron to the ferrous state.

Effects of Fe on the photic zone may also be significant for the biota of boreal humic rivers (Vuori, 1995), although this impact of Fe has seldomly been examined. It should, however, be understood, because in these rivers increase in water colour values (absorbance$_{420}$) with increasing Fe concentrations has been shown (Heikkinen, 1990b). This is also the case in other types of water bodies (Shapiro, 1966; Kortelainen et al., 1986; Kritzberg and Ekström, 2012; Xiao and Riise, 2021). The results of Weyhenmeyer et al. (2014), based on a comprehensive database of boreal lakes, streams and river mouths from Sweden and Canada, indicated that although water colour is primarily driven by DOC, it is increased through the formation of Fe-DOM colloids in catchments. Increases in water colour producing properties of Fe-DOM colloids with increasing Fe concentration have also been reported in humic rivers in Northern Finland (Heikkinen, 1990b). In addition, Fleming-Lehtinen et al. (2015) showed that Fe was a better predictor than TOC for the variation in Secchi depth in Finnish coastal waters. The existing research also indicates that increasing Fe concentrations contribute to the brownification of boreal water bodies, which has been shown in the last decade (Kritzberg and Ekström, 2012; Sarkkola et al., 2013; Weyhenmeyer et al., 2014; Björnerås et al., 2017; Hayden et al., 2019; Kritzberg et al., 2020; Xiao and Riise, 2021). In this context, brownification may negatively affect the abundances of invertebrates, thereby having potentially harmful effects on the entire food webs in northern lakes (Arzel et al., 2018; Hayden et al., 2019). Similar changes are also possible in boreal rivers, where increases in dissolved organic Fe load may negatively affect the availability of light for benthic algae (Otto and Svensson, 1983; Vuori, 1995), an important group of primary producers in river ecosystems (Allan and Castillo, 2007). More knowledge should be acquired on the ecosystem-level impacts and changes of photic zones in boreal rivers.

4. How to consider iron processes in catchment management?

The natural patterns of Fe transport are temporally variable and linked to the hydrological and biogeochemical processes in boreal catchments. In this framework, it is not surprising that land use practices also influence Fe mobilization and transport, as indicated by the findings from boreal regions.

One typical land use practice increasing Fe transport in boreal areas is drainage of peatlands for the purposes of agriculture and forestry, as well as for peat extraction locally in Finland. It was started already in the 1860s in Finland where systematic peatland drainage for forestry was initiated in estates owned by the state in 1908 (Cajander, 1906, 1913), and in private forests in 1929, a year after the Parliament of Finland had adopted the first forest improvement law (Lukkala, 1937; Heikurainen, 1959). Today, a large proportion of peatlands are drained in Northern Finland (Suoninen, 1982), where minerotrophic peatlands typically account for 50–60% of the catchment areas (Kalliola, 1973). Previous studies have shown that drainage increases Fe transport from minerotrophic deep-layered peatlands to rivers (Heikkinen, 1990c). Paleolimnological studies (Tolkkinen et al., 2014) have shown that the old peatland drainage activities have also increased Fe leaching. Peatland drainage has also resulted in increased Fe contents of the HAMW DOM in the drainage waters during low-flow conditions in summer (Heikkinen, 1990b).

In catchments with large areas of agricultural fields on lowland clay soils the main drivers behind the mobilization of particulate Fe from soils to watercourses are the surface runoff generation bound erosion processes (Palviainen et al., 2015; Saari et al., 2020). These fields are more prone to erosion especially, when there is no vegetation cover inhibiting the erosion throughout the year and the hydrological connectivity is high due to the drainage systems. This transport of Fe particles may be highly problematic in some catchments, as it weakens stream bed conditions by silting and increases water SS concentrations. The Fe particles settled on the stream- and riverbeds may also act as Fe sources in anoxic conditions. In water management these harmful environmental impacts are decreased by controlling the time and intensity of soil drainage and field irrigation, by taking care of the field-soils agricultural condition, by reducing surface runoff and surface erosion with subsurface drainage and dams in outlet drains, and by reducing the SS loads transported with subsurface runoff and treatment wetlands and setting up buffer zones along water bodies (Häggblom et al., 2020).

As shown for peatlands (Puustjärvi, 1953) and riparian soils (Ingri et al., 2018), there are dominant soil source layers contributing most of the mobilized Fe. With alteration of water table location through drainage activities, the mobilization of Fe may be enhanced especially if the potential formation of new dominant source layer is lowered to deeper, more Fe-rich peat layers. Additionally, drainage may cause oxidation of mineral soil layers below organic layers, which leads to increased transport of Fe and other metals. For example, acid sulphate soils with stable conditions can significantly increase metal transport when oxidized (Hartikainen and Yli-Halla, 1986). These soils can be found in river basins partially located in ancient sea bottoms

(Andriesse and van Mensvoort, 2005). For example, areas previously covered by the postglacial Litorina Sea comprise present-day Finnish coastal areas, the extent of which being largest in the north where land uplift is also fastest (Mattsson et al., 2007). Drainage activities change also water flow paths and water table levels in soil layers, influencing thus directly on their oxidation and anaerobic conditions. Also, for catchments with organic soils, drainage activities may lead to peatland-dominated headwaters and man-made ditches tending to be more acidic than the mainstem river (Saarinen et al., 2010). This facilitates the out-of-system transport of Fe, as acidic conditions allow Fe to be in a more soluble and movable form.

So far, promising experiences on the use of peatland-based treatment wetlands in water pollution control have been achieved in peat extraction areas in Finland. The long-term mean of total Fe reduction in the 12 treatment wetlands (OFAs), constructed on natural, undrained peatland areas, with lateral overland flow on their peat surface layers, was 51%, and that in the 13 treatment wetlands (DOFAs), constructed on drained peatland areas, 24% (Heikkinen et al., 2018). The OFAs retain effectively also dissolved organic Fe, the mean reduction ranging from 46 to 57% at low-flow conditions during the frost-free periods (Heikkinen and Ihme, 1995). An important advantage of these treatment wetlands is that they decrease the Fe-content of the HAMW DOM (Heikkinen et al., 1995), thereby also decreasing the tendency of DOM to precipitate in the waters downstream.

Treatment wetlands are also constructed on undrained or drained peatlands in the water pollution control related to forestry (Joensuu et al., 2012), which is the most widespread land use activity in boreal catchments. Such treatment wetlands are also constructed on mineral soils. The Fe reductions of these water purification structures on mineral soils are not yet adequately known and should be studied further. Finally, filter strips, typically located on peat and mineral soils between water bodies and disturbed areas, are also used in water pollution control of forestry practices (Joensuu et al., 2012).

Use of restored peatland areas as wetland buffers is nowadays one tool to mitigate the harmful impacts of peatland drainage on water bodies. However, it has been noted that the use of this method comes with a high risk of increased Fe transport (Koskinen et al., 2017; Nieminen et al., 2020). Especially nutrient-rich peatlands face risk for higher leaching after restoration actions (Koskinen et al., 2017).

There are also more cost-efficient water pollution control methods for mitigating harmful environmental impacts of Fe in boreal catchments. First, we should avoid unnecessary land use activities and soil disturbances in areas of increased risk of Fe transport. Second, we should prevent Fe mobilization from such areas by utilizing environmental risk assessment and careful catchment planning. The most likely risk areas include minerotrophic peatlands, other wetlands and naturally moist areas, groundwater seepage areas and springs, stagnant water areas, and riparian zones. These environments are typical Fe storages and important supplies of Fe entering water bodies. There are also certain areas that are extremely prone to mobilization of Fe and other metals in case of groundwater table manipulation, such as on soils affected by mineralized black shales (sedimentary rock formations rich in S and Fe with >0.5% organic carbon) (Parviainen and Loukola-Ruskeeniemi, 2019). Additionally, Fe leaching should be considered also in peatland restoration cases (Koskinen et al., 2017).

Spatial analysis tools could be used for the identification of risk areas related to excess Fe impacts in water management. In this context, for example, recently developed moisture indices could be useful tools in catchment-scale mapping (Lidberg et al., 2020). In most cases, avoiding land use activities on these areas is critical to diminish harmful impacts of increased Fe transport on river ecosystems. For example, drainage of such natural “hotspot areas” should be avoided to diminish the likelihood of Fe-rich GW entering streams. In reduced conditions, GW seepage containing Fe is typically clear, but GW oxidation creates Fe particles, sometimes even causing massive siltation of stream beds.

If soil disturbance and land use change have already taken place or cannot be avoided, the ways to mitigate harmful impacts of increased Fe loading consist mainly of traditional water protection means. First, it is crucial to avoid the promotion of increased artificial hydrologic connectivity, especially in catchments with drained peatland dominated headwaters. If areas prone to Fe mobilization are directly hydrologically connected to recipient water bodies, problems associated to high Fe concentrations are likely obvious. On the other hand, if these dominant Fe sources have been isolated with buffer strips or other natural load-inhibiting systems, e.g., field-based purification and treatment solutions, the harmful ecological effects can be alleviated.

The development of means to mitigate the harmful impacts of Fe in the catchments would be facilitated by better environmental monitoring of dissolved and particulate inorganic and organic Fe compounds in waters draining from areas of different catchment land use activities. Reaching this goal also requires better understanding of the processes that increase Fe mobilization. Especially more data on the processes leading to the formation of particulate inorganic and organic Fe in the soil and water environments should be acquired. The role of the DOM in these processes should be better understood.

A suitable guideline for water pollution control and resource planning requires that peatlands, other wetlands and naturally moist areas, groundwater seepage areas and springs, stagnant water areas, and riparian zones that are typical Fe storages are identified in the catchments. Therefore, any anthropogenic activities conducted in such areas are likely to contribute to higher levels of Fe mobilization in downstream water bodies.

To summarize, the main emphases of water pollution control programs should be: i) prevention of Fe mobilization from soil layers by adequate pre-risk assessments, avoiding unnecessary land-use activities and minimizing soil disturbances; ii) disconnection of Fe-rich GW discharge to watercourses; and iii) decreasing Fe transport to watercourses via using efficient water pollution control methods.

5. Where to go from here?

Fe plays an important role in boreal catchments, ranging from the headwaters to the sea. Given its importance, Fe dynamics should be carefully considered in water management and land-use planning at the catchment level. However, knowledge on the nuanced roles of Fe and possibilities to mitigate its harmful impacts in boreal catchments is still small.

Fe has traditionally been seen to possess many harmful impacts on rivers by decreasing the species diversity and abundance of periphyton, benthic invertebrates and fishes. However, the role of Fe in the utilization of DOM in river ecosystems that are typically highly heterotrophic should also be known because DOM is the dominant organic carbon fraction in most boreal rivers. More knowledge is also needed on the metabolic and behavioral resistance mechanisms that organisms, such as fish and invertebrates, may have developed against the harmful impacts of Fe in rivers with naturally high Fe and DOM concentrations. In addition, the incubation success of eggs and young-of-the-year survival of fishes should be examined in relation to direct and indirect effects of siltation by iron-rich sediments.

To decrease the harmful environmental impacts of increasing Fe concentrations in watercourses, key underlying reasons for such increases should be better understood. The processes responsible for Fe transport from catchments via rivers to the sea should also be given more scrutiny. Interdisciplinary research is required on this topic, including joining approaches and ideas derived from biogeochemistry, hydrology, and ecology. Furthermore, knowledge sharing among stakeholders and land managers about the role and risks of Fe leaching in water management should be increased.

Effective water pollution control against the harmful impacts of Fe in freshwater environments requires comprehensive information on the origin, formation and quality of particulate Fe and suspended solids

(SS), as well on the origin and formation of Fe(II). In this respect, a crucial aspect from the sustainable catchment management angle is identifying high-risk areas for Fe leaching and transport. Here, GIS tools can be used for their identification, benefitting from recently developed soil moisture maps based on the depth-to-water table (DWT) index or other similar indices.

Further studies should distinguish between the different sources of very fine-graded suspended solids and acknowledge the role of metal-hydroxide-humus colloids in their formation. Although Fe is among the elements included in the monitoring programs in Finland and Sweden, for example, it should be considered in environmental monitoring more broadly ecologically and more widely geographically across the whole boreal region. In addition, national monitoring programs should also include parameters describing the quality of SS (e.g. loss-of-ignition and Fe) to provide information relevant to river basin management.

Effective water pollution control approaches are needed for decreasing the impacts of Fe in water bodies. Thus far, promising technologies of certain water pollution control measures pave the way for improved water pollution control in boreal catchments. Additional knowledge on the seasonal roles of the main biogeochemical processes affecting Fe transport and retention should be acquired for further development of water pollution control methods. Such methods should be important for maintaining ecosystem integrity and biodiversity of boreal rivers.

CRediT authorship contribution statement

Kaisa Heikkinen, River ecosystems and management, peatland-based treatment wetlands, humic substances.

Markus Saari, catchment processes of Fe.

Jani Heino, River ecosystems and fauna, language proofing.

Anna-Kaisa Ronkanen, River ecosystems, peatlands and related.

Pirkko Kortelainen, Ecosystems, lakes, catchments.

Samuli Joensuu, Forestry.

Annika Vilmi, Ecosystems.

Satu Maaria Karjalainen, River ecosystems, management.

Seppo Hellsten, Water restoration and reservation, biology, management.

Mirkka Visuri, Acid sulphate soils, management.

Hannu Marttila, Water resources management, river ecosystems and dynamics, peatland water quality.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The study was supported by NordForsk through the project BIOWATER, a Nordic Centre of Excellence under the Nordic Programme of Bioeconomy (NF Project Number 82263), by the project FRESHABIT LIFE IP (LIFE14/IPE/FI/023), by Maa- ja Vesitekniikan Tuki Ry, by K.H. Renlund foundation, by The European Regional Development Fund (ERDF), by the Water JPI program funded WaterPeat-project, and by Finnish Ministry of Agriculture and Forestry through the project Tools and means for managing peatland forests - how to diminish impacts on water and climate (TurVI). We thank Atso Romakkaniemi, senior scientist in the Natural Resources Institute Finland (Luke), for sharing knowledge about the development of salmon stocks in Finland.

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