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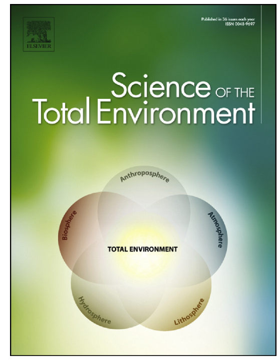

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PII: S0048-9697(20)30253-9

DOI: https://doi.org/10.1016/j.scitotenv.2020.136743

Reference: STOTEN 136743

To appear in: *Science of the Total Environment*

Received date: 24 September 2019

Revised date: 8 January 2020

Accepted date: 14 January 2020

Please cite this article as: M. Saari, P.M. Rossi, H. Postila, et al., Predicting iron transport in boreal agriculture-dominated catchments under a changing climate, *Science of the Total Environment* (2020), https://doi.org/10.1016/j.scitotenv.2020.136743

Predicting iron transport in boreal agriculture-dominated catchments under a changing climate

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Abstract

Increases in iron (Fe) concentration have been reported in boreal regions in recent decades, raising concerns about the fate of ecosystems along water courses. In this study, the SWAT (Soil and Water Assessment Tool) model was applied to the river Mustijoki catchment in southern Finland to determine the current state of Fe transport and to evaluate possible effects of ongoing environmental change in this agriculture-dominated catchment. The model was calibrated using five-year discharge, suspended solids, and Fe data, and validated with a three-year dataset of the same parameters. Further, the model was run with spatially downscaled and bias-corrected climate change scenario data to the year 2100 obtained using five different global climate models. The results were divided into 20-year time steps (2020-2039, 2040-2059, 2060-2079, 2080-2099) and compared against a reference modeling period (1997-2016). With present catchment characteristics of the river Mustijoki, Fe transport was shown to be related to soil erosion and suspended solids transport, driven by hydrological conditions. Arable fields, especially with steeper slopes, were identified as the most likely source of Fe loading. Climate change-induced alterations in riverine Fe transport were simulated as concentrations and as annual mass fluxes. High Fe transport season is already shifting from spring snowmelt events to autumn and winter, and this change is likely to increase in coming decades. Based on modeling results, annual peak concentration in the River Mustijoki was projected to decrease by up to 32% (from 6.2 mg L^{-}1 to 4.2 mg L^{-1} in scenarios RCP4.5 and RCP8.5) in the coming 20-year period, while lowest winter concentration was projected to increase by 126% (from 1.5 mg L^{-1} in the reference period (1997-2016) to 3.5 mg L^{-1} in 2080-2099 in scenario RCP8.5. To compensate for these changes in Fe transport dynamics, water protection and land use management planning must be improved.

Keywords: iron, suspended solids, modeling, SWAT, climate change, land use

1 Introduction

Recent studies show increasing iron (Fe) concentrations in rivers in boreal regions (Neal *et al.*, 2008; Kritzberg and Ekström, 2012; Knorr, 2013; Sarkkola *et al.*, 2013; Björnerås *et al.*, 2017). The main factors driving Fe transport, their interconnections, and how they are responding to a changing environment are still partly unknown. Iron plays a fundamental role in many ecosystem processes and element cycles (e.g., for nitrogen (N), carbon (C), sulfur (S), and phosphorus (P)) (Lovley, 1991; Stumm, 1996). Thus, it is important to identify the key mechanisms driving Fe fluxes within the environment. The concentration of Fe and its mobility through catchments have many direct and indirect effects on river systems and their habitats, and on recreational and municipal water usages (Vuori, 1995). Iron strongly influences many biogeochemical processes and e.g., regulates P transport and leaching in water and sediment systems (Stumm, 1996; Lehtoranta and Heiskanen, 2003). For example, in Dutch lowland agriculture dominated catchments, Fe-bound P was identified as the most significant particulate P fraction as it covered 74% of the total PP (van der Grift *et al.*, 2018).

Increased Fe concentrations and fluxes may affect in particular the conditions in stream beds, through sedimentation of particulate Fe and formation of blankets of Fe-reducing bacteria (Wellnitz *et al.,* 1994). Toxic properties of certain Fe compounds are problematic for some fish and insect species (Gerhardt, 1992; Peuranen, 1994). Fe also increases turbidity and decreases visibility and light conditions in water courses, and thus inhibits primary production and negatively influences stream biota. In river systems utilized for drinking water, increasing Fe concentrations are troublesome for the water purification process. The effect of Fe precipitates and bacterial blooms on environment aesthetics (e.g., water color (Xiao *et al.*, 2015)) and ecosystem services is also an issue in these waters. As Fe is transported out of the riverine system via flowing water, it becomes a factor in marine ecosystems.

Iron transport in freshwaters is a natural phenomenon and possible drivers behind its recent enhancement have been identified in previous research. There is a relationship between the transport dynamics of dissolved organic matter (DOM) and of Fe in water courses (Heikkinen, 1994; Kortelainen *et al.*, 2006; Neal *et al.*, 2008; Kritzberg and Ekström, 2012; Sarkkola *et al.*, 2013; Weyhenmeyer *et al.*, 2014; Ekström *et al.*, 2016; Björnerås *et al.*, 2017), as DOM causes Fe to remain in soluble form (Stumm, 1996). However, increased DOM as the main driver behind the recent rise in Fe concentrations has been questioned, as it is suggested that existing levels of DOM are able to retain more Fe in soluble form than is available (Kritzberg and Ekström, 2012; Kritzberg *et al.*, 2014; Ekström *et al.*, 2016).

Decreased S deposition is reported to be one possible reason for the increase in Fe in aquatic systems (Knorr, 2013). This relationship derives from the chemical and biochemical properties of Fe and sulfate (SO_4), which are known to form compounds that remain stable in the soil, preventing them from ending up in water bodies (Berner, 1984; Davison, 1993).

Ekström *et al*. (2016) identified soil redox conditions as an important factor in Fe transport through catchments. This is partly connected to the longer-term change in climate in boreal regions, with increasing precipitation and warmer and wetter winters (Räisänen *et al.*, 2004), and thus more anoxic conditions that promote redox intensity, which is reported to increase Fe concentrations in rivers (Ekström *et al.*, 2016). With changing precipitation patterns, hydrological changes can also be assumed. This is expected to affect the flushing rates of catchments, resulting in decreased sedimentation of particulate Fe, especially in lakes (Björnerås *et al.*, 2017).

In Finnish catchments, a link between high Fe export and land cover has also been found, with e.g., high percentages of peat and agricultural land tending to correlate with high concentrations of Fe in river water (Palviainen *et al.*, 2015). However, the temporal dynamics of Fe transport also differ between catchments dominated by peat and catchments dominated by agricultural land. In peatland-dominated areas, Fe transport and mobility are mostly associated with release of accumulated secondary Fe from the peat, as indicated by the close relationship between DOM and Fe. This release is affected by variations in soil conditions, including redox intensity and microbial activity. In agriculture-dominated landscapes, the Fe concentrations closely match total suspended solids (TSS) concentrations, presumably because most of the Fe in the riverine water in these areas is transported via eroded fine soil particles (Palviainen *et al.*, 2015).

This study used a catchment-scale modeling approach to study Fe transport dynamics, with the aim of filling knowledge gaps regarding the transportation process in an agriculture-dominated catchment discharging to the Gulf of Finland and the Baltic Sea. No similar study has been carried out previously and the results can be of interest to many research fields and environmental agencies. A modeling approach was chosen in order to reduce the temporal uncertainty associated with 2-4-week grab sampling intervals, and to enable projections of future developments using climate change scenarios as model input. Specific objectives were to i) obtain more accurate estimates of Fe transport dynamics, ii) simulate changes in Fe concentrations and fluxes with a future changing climate, and iii) identify management measures for reducing Fe loading in the study area.

2 Methods

2.1 Site description

The site selected for the study was the Mustijoki catchment, a typical river catchment in southern Finland discharging into the Gulf of Finland and Baltic Sea. River water is used by local industry and suffers strongly from sudden changes in water quality, mainly involving suspended solids (SS) and Fe concentrations. Total catchment area is 780 km² and it is dominated by agriculture (37%) and forests (58%) (Figures 1a and 2).

The bedrock of the catchment is mainly microcline granite (43%), granodiorite (19%), biotite paragneiss (14%) and mafic volcanic rock (10%) (Hakku- database, Geological Survey of Finland). The soils are typical Finnish coastal clays (35%) and glacial tills (43%). The clay deposits of the area include multiple types of post-glacial clays, the main clay minerals being trioctahedral mica and illite. There are also vermiculite and chlorite groups present. The average thickness of the clay layers is 8.6 m (Punakivi *et al.*, 1977). The till layers in the catchment are rather shallow, and the formations are rarely more than 4 – 5 m thick (Punakivi *et al.*, 1977). Based on the soil classification, 20 % of the catchment area is covered by a till layer no thicker than 1 m (Hakku- database, Geological Survey of Finland). The grain size analyses for the two dominant soil types in the catchment that are till (Punakivi *et al.*, 1977) and clay (Holma, 1970), are presented in Table 1. Based on XRF-analyses, the median Fe content in surface soils of forested areas is 20 756 mg/kg (n = 72) as in agricultural fields (n = 47) it is 50 030 mg/kg (Tarvainen *et al.*, 2003).

Table 1. Particle size distributions for a) Till (n = 70) and fo b) clay (n = 180) in the area of River Mustijoki Catchment.

a) Till particle size [mm]	<0.002	0.002 - 0.006	0.006 - 0.06	0.06 - 2	2 - 20
%	2.07	10.32	33.72	30.47	23.42

b) Clay particle size [mm]	<0.002	0.002 - 0.02	>0.02
%	52	37	8

Low lake percentage (1.5%), lack of other apparent long-term water storage (e.g., aquifers), and soil characteristics result in a flashy discharge pattern. Long-term (1988-2016) annual temperature in the area is 5.2°C and long-term annual precipitation is 643 mm (Pirinen *et al.*, 2012). Long-term mean monthly temperature (1988-2016) varies from 17.5 °C (July) to -5.2°C (January).

2.2. Water quality measurements

Long-term discharge and water quality monitoring (Finnish Environmental Institute, Hertta-database) is conducted near the catchment outlet (7 km from the sea), including analyses of TSS and Fe concentrations, both relevant for this study. On average, Fe concentrations are measured 14 times per year and TSS concentrations 23 times per year. There is a strong correlation between riverine Fe concentration and TSS ($r^2 = 0.939$) in the river Mustijoki (Figure 1b). In addition, the average Fe/TSS ratio in the river water is 0.075, which reflects the Fe content of the parent soil (clay). Based on results in Sippola (1974), the Fe content in Finnish soils tends to be lower in coarser soils (1.6 ± 0.8 % for sand) than in finer soils (7.1 ± 0.6 % for clay). These values indicate that riverine Fe is in particulate form and is mobilized by soil erosion occurring in the clay soils in the river Mustijoki catchment. This indication is supported by a link between catchment hydrological conditions and Fe concentration, whereby the timing of high Fe concentrations is closely related to high flows, conditions promoting high soil erosion. Thus, we used TSS as a surrogate to extend the Fe time series. For the model calibration period (2006-2010), a total of 119 Fe/TTS measurements were available, with approximately 2-week sampling intervals.

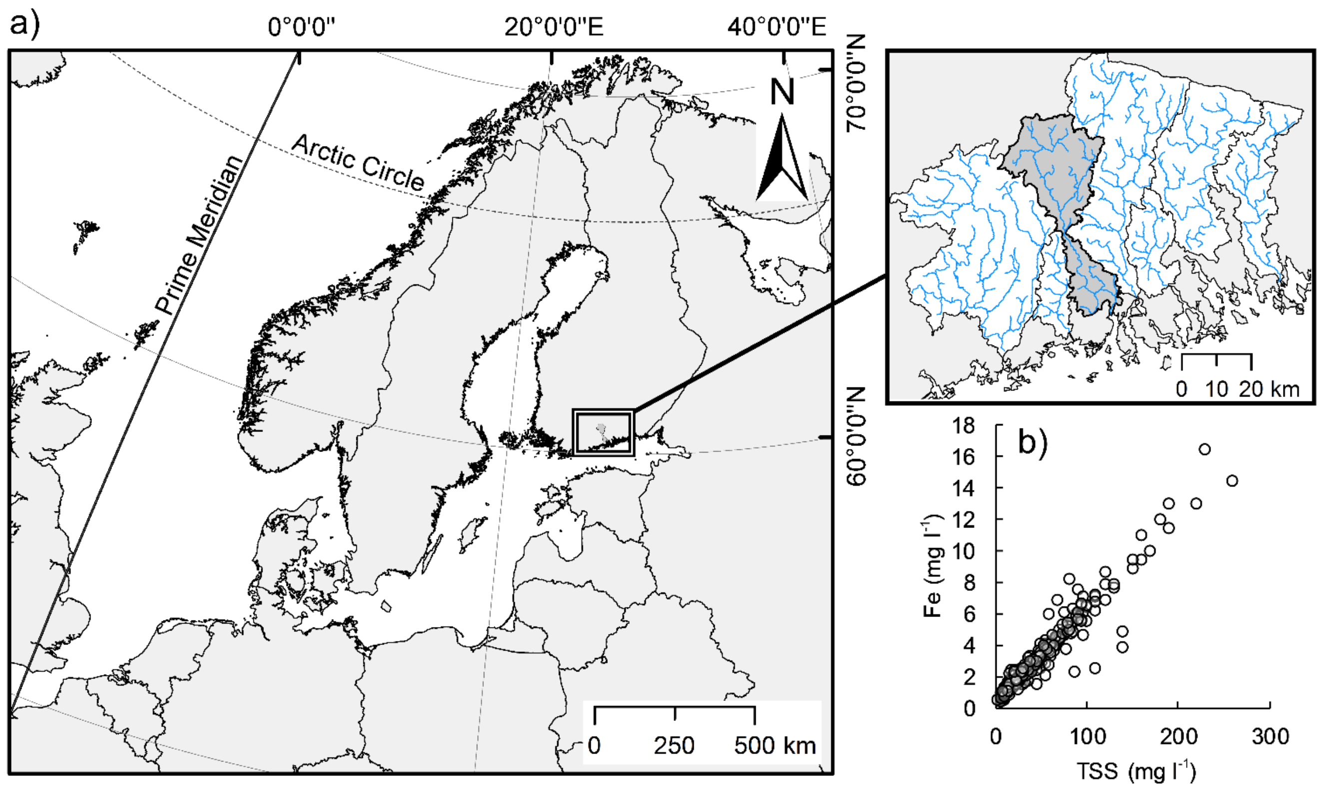

Figure 1. a) Location of the river Mustijoki catchment (darker gray) in southern Finland and b) correlation (r^2 = 0.939, n = 279) between total suspended solids (TSS) and iron (Fe) concentrations measured near the catchment outlet, 1997-2016.

2.3 Model description and inputs

Catchment-scale modeling and evaluation of Fe transport and fluxes was performed using the semi-distributed Soil and Water Assessment Tool (SWAT) (Arnold *et al.*, 1998). The structural components of the model include a digital elevation model (DEM; 10 m x 10 m, Land Survey of Finland, Paituli-database), a soil map (25 m x 25 m, Geological Survey of Finland, Hakku-database), and a land use map (25 m x 25 m, Corine 2012, Paituli-database). Here, the soil map was modified to include the following soil types: silt, till with shallow bedrock <1, outcrop, sand, muck, peat, clay, and till with deeper bedrock. The land use map consists of eight different types (broad-leaved forest, coniferous forest, urban area, agriculture, mixed forest, peat, transitional woodland/shrub, and water). The three input datasets and the classification of the study catchment are shown in Figure 2. The model combines these spatial datasets to form sub-catchments and then again to smaller entities called HRUs (hydrological response units). Each HRU (in total 4443 in our model) is provided with unique characteristics extracted from the three spatial datasets.

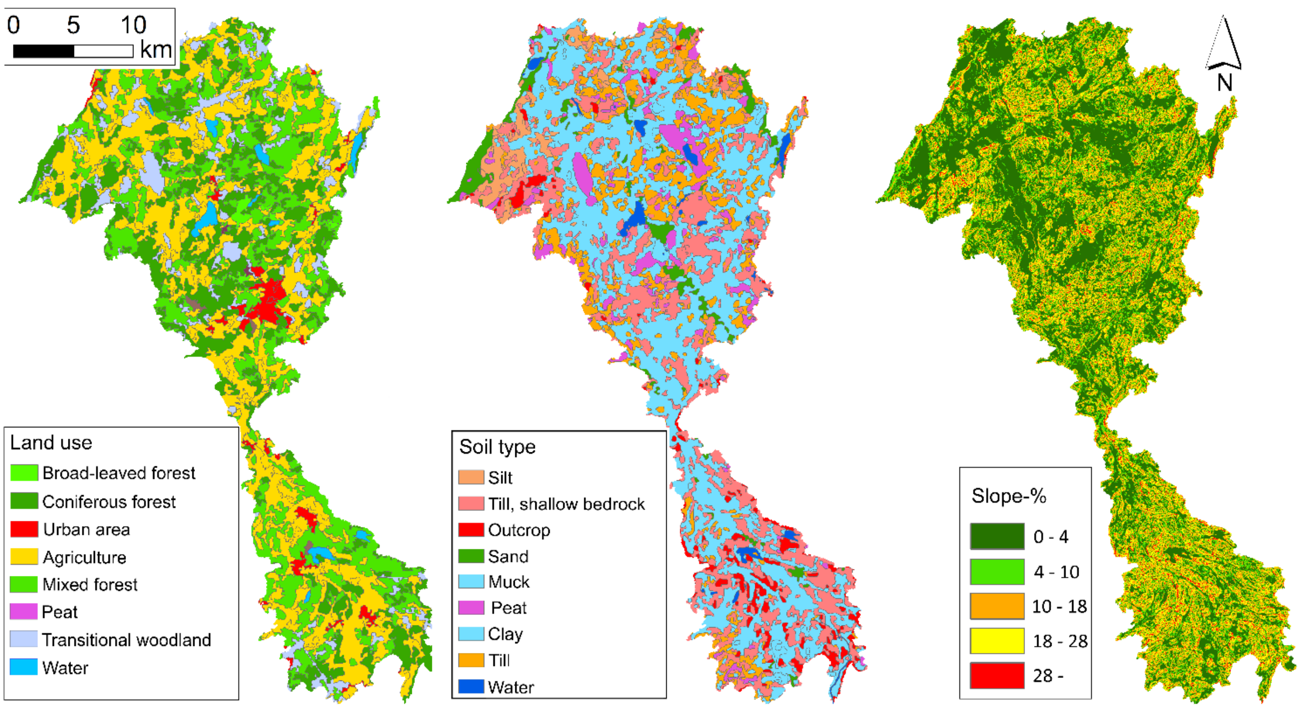

Figure 2. Spatial datasets used in SWAT modeling. Land use map (Corine Land Cover 2012), soil typology map (Geological Survey of Finland), and slope map derived from a digital elevation model (Land Survey of Finland).

Gridded (10 km x 10 km) multiparameter (precipitation, air temperature, radiation, humification, wind speed) weather datasets for 1997-2099 from the Finnish Meteorological Institute (FMI) were used as input in the model. Within this period, measured data were used for calibration, validation, and the reference period (1997-2016), and climate model data for future scenarios (2020-2099).

SWAT can produce numerous output data series related to hydrology, environmental loadings, and in-stream water quality. The model is divided into land and in-stream phases, where the land phase simulation describes the quantity and quality of water entering the stream network at sub-catchment level. The in-stream phase continues by combining these and eventually simulates the catchment outlet. The sediment transport in SWAT is modeled by combining the Modified Universal Soil Loss Equation (MUSLE) (Williams, 1975) and the Bagnold equation (Bagnold, 1977). MUSLE provides the model with a simulation of the sediment load caused by soil erosion, while the Bagnold equation is used to model SS transport in the reach.

2.4 Model calibration & validation

The semi-automatic tool SWAT-CUP (Abbaspour, 2007) was used to perform global sensitivity analysis, and calibration and validation of the model. The algorithm used was SUFI-2 (Abbaspour *et al.*, 2004; Abbaspour *et al.*, 2007). The goal with this calibration procedure for hydrology is to find best parameter ranges, rather than the absolute “best” parameter set. This provides the benefit of allowing all parameter uncertainties to be included in the calibration results, as the output is an area covering all possible predictions with given parameter ranges. SUFI-2 is an iterative process, where the user, with the assistance of the semi-automatic tool, provides better performing parameter ranges until the desired modeling result is achieved (Abbaspour *et al.*, 2004). The process is called semi-automatic since the expertise of the user is crucial, as the iterative process may provide unrealistic parameter ranges and values that must be restrained to correlate with the conceptual model and reality. The goodness of fit of the present simulation is illustrated by objective function Nash-Sutcliffe model efficiency coefficient (NSE) (Nash and Sutcliffe, 1970) for hydrology and by r^2 for water quality (TSS).

The SWAT model for the Mustijoki catchment was calibrated for the years 2006-2010 and validated for the years 2011-2013. These periods were chosen to include both drier and wetter periods. The model for Fe concentration was calibrated using TSS data measured at 2-week intervals. The modeling result was then transformed to Fe concentration by linear correlation (see Figure 1b). As overland flow directly affects the amount of ongoing erosion, and thus Fe transport, the hydrological part of the model was first calibrated with filtered hydrological data. This ensured that there were realistic proportions of different stream inflow components (overland flow, inter flow, groundwater recharge). The WETSPRO tool (Willems, 2009) was used to filter daily amounts of overland flow, inter flow, and base flow from the measured daily discharge. After satisfactory calibration results for the parameters affecting the overland component were obtained, the other hydrological parameters were calibrated, followed by the parameters affecting water quality. Assumptions in the quality modeling included the predetermined cultivation and harvest times for the agricultural areas. This was done to replicate the temporal conditions that include vegetation cover during summer and bare soil from autumn to spring. A flow chart of modeling steps used in this study is presented in Figure 3.

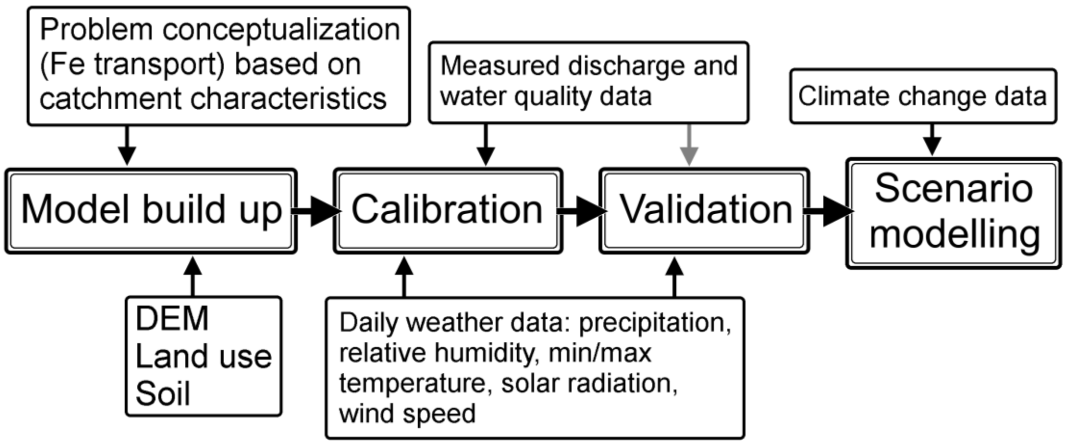

Figure 3. Flow chart of steps in modeling iron (Fe) transport in the river Mustijoki catchment.

2.5 Climate change scenarios

The climate change datasets used consisted of statistically downscaled and bias-corrected data specifically for Finland. The downscaling was drawn from five different global climate models (CanESM2, CNRM-CM5, GFDL-CM3, HadGEM2-ES, and MICRO5). This method of downscaling is presented in more detail by Lehtonen *et al.* (2016a) and Lehtonen *et al.* (2016b). Each model was then used to simulate two different future greenhouse gas (GHG) emission scenarios (RCP4.5 and RCP8.5). In RCP4.5, the increase in GHG emissions was set to stabilize at 2040, while in RCP8.5 the increase went on indefinitely. The set had data until 2100 and included daily values for precipitation, minimum and maximum temperature, relative humidity, solar radiation, and wind speed (grid scale, 10 m x 10 km). The effect of climate change on Fe transportation was evaluated by dividing the modeling results into four 20-year periods (2020-2039, 2040-2059, 2060-2079, and 2089-2099) and comparing these against the reference period (1997-2016).

3 Results

3.1 Model performance and parameter sensitivity

Hydrological modeling for the Mustijoki river successfully replicated the flashiness in flow conditions caused by catchment characteristics such as shallow bedrock and high areal coverage of clay soils with limited infiltration capacity. This is indicated by the accurate modeling results for low and high flows and their recessions (Figure 4). The time series of measured and modeled discharge at the station near the catchment outlet used for calibration and validation periods is shown in Figure 4. The simulated flow is illustrated with area including modeling uncertainties aimed to encompass measured flow and the best simulation of the set. The best parameter set gave NSE of 0.768 for the calibration period and 0.798 for the validation period.

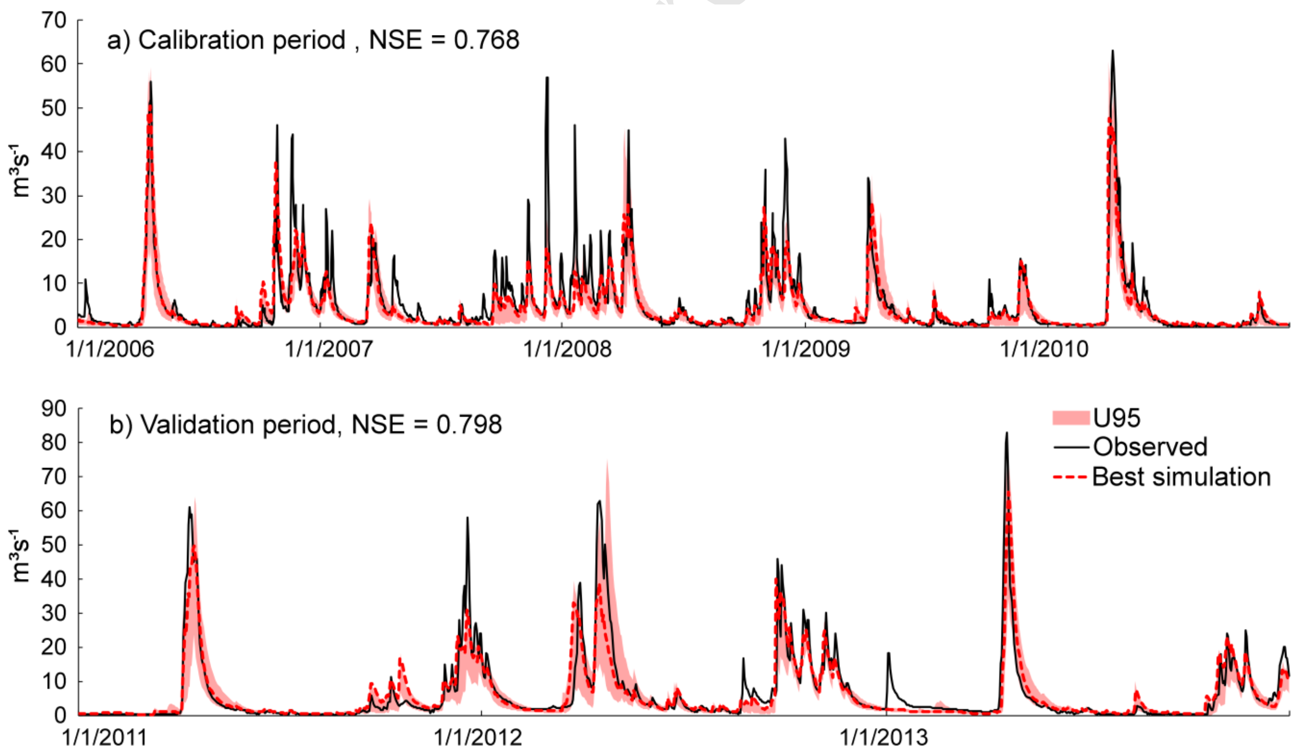

Figure 4. a) Calibration period (2006-2010) and b) validation period (2011-2013) results for the hydrology part of the SWAT model. U95 represents the 95% uncertainty band, observed is measured discharge, and best simulation is the simulation

result with the highest Nash-Sutcliffe model efficiency (NSE) among the 500 simulations. [NSE = 0.768 in (a), NSE = 0.798 in (b)]

The SWAT model performed well in modeling SS and Fe concentrations. The goodness of fit of the model (r^2) was 0.692 for the calibration period and 0.603 for the validation period when calibrated with more available TSS concentration data. The time series for these periods with observed data is shown in Figure 5. As Fe concentration for the period 2006-2013 was modeled with linear transformation, the goodness of fit (r^2) was 0.422.

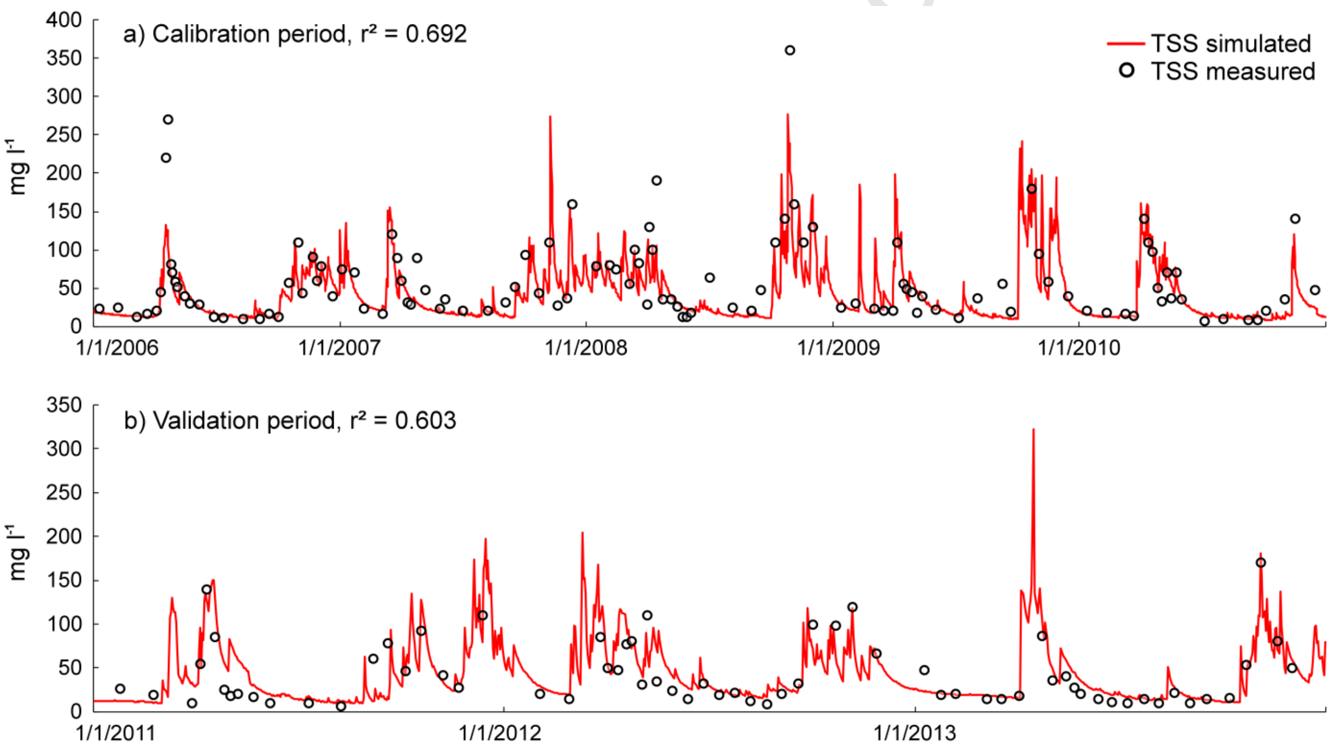

Figure 5. a) Calibration period (2006-2010) (r^2 = 0.692) and b) validation period (2011-2013) (r^2 = 0.603) results for total suspended solids (TSS) concentration. Red line represents modeled TSS, black circles represent measured values.

The parameter sensitivity was covered with the global sensitivity analysis in SWAT-CUP. The most sensitive parameters in the model affecting hydrology were all related to surface runoff generation and included e.g., snow parameters and curve number (CN). The parameter set used for calibration and sensitivity analysis is presented in Supplementary Material.

3.2 Iron transport, dynamics, and yield in the river Mustijoki

Based on model results, the variation in Fe concentration in the river Mustijoki was closely related to hydrological changes. The concentration tended to be highest during high and sudden discharge events. The highest peaks of concentration were observed during snowmelt peaks and late autumn rainfall events, when evapotranspiration was low and the soil was presumably pre-wetted, resulting in high surface runoff and erosion generation. During the reference period (1997-2016), the mean Fe concentration in river water was modeled to be 3.02 mg L^{-1} (minimum 0.74 mg L^{-1}, maximum 22.21 mg L^{-1}).

The catchment yield of Fe during the reference period was 29 kg ha^{-1} $year^{-1}$. The Fe loadings from different land use practices and from agricultural land of differing slope are shown in Table 1. According to the results, most soil erosion (94%), and thus Fe loading (71 kg ha^{-1} $year^{-1}$), occurred in agricultural areas. At annual level, fields with low slope produced the most loading because of their large acreage. However, parts of fields with steeper slopes (>10% gradient) produced 24% of the annual load while occupying only 8% of the agricultural area in the catchment. Based on the modeling results, this contribution to total Fe loading would diminish if soil erosion from steeply sloping field areas were prevented by better land use management or water protection measures.

Table 2. a) Iron (Fe) loading deriving from different land use practices and b) from fields with different degrees of slope

a) Land use type	Load, kg ha^{-1} yr^{-1}
Agriculture	71

b) Slope, agricultural land [%]	Load, kg ha^{-1} yr^{-1}	% of agricultural land
0-4	33	69.8

Urban	4	4-10	140	22.1
Forests	3	10-18	191	6.3
		19-28	268	1.5
		28-	297	0.3

3.3 Impact of changing climate

The effect of climate change on Fe transportation processes was illustrated by modeling mean day of the year values of concentration and monthly sum of daily median Fe fluxes for 20-year periods between 2020 and 2099. A comparison was made to the corresponding values for the reference period (1997-2016). The results of concentration modeling (Figure 6) included the average values (red and blue lines) from all five climate change models and the uncertainty arising from using these five different models (red and blue areas). The most prominent change in the annual pattern of concentration in future compared with the reference period was during spring time. The reference period had a distinct peak in concentration in mid-April, but in the first 20-year period (2020-2039) of climate change modeling, this peak concentration was reduced by 32%, from 6.2 to 4.2 mg L^{-1}, in both the RCP4.5 and RCP8.5 scenarios. In later 20-year periods, the change in peak concentrations was minor compared with that between the reference period (1997-2016) and 2020-2039. In addition to this change in spring, which is already taking place and will continue to do so in the near future, there was a more continuous increase in winter concentrations over the whole 80-year modeled period. Colder months (November-March) showed an increase in Fe concentration in all combinations of climate change models and scenarios modeled. This increase was higher in the RCP8.5 scenario than in the RCP4.5 scenario, and higher in later time spans (2060-2079 and 2080-2099). The lowest Fe concentration in February during the reference period increased at most by 126%, from 1.5 to 3.5 mg L^{-1} in the period 2080-2099 in scenario RCP8.5 (Figure 6).

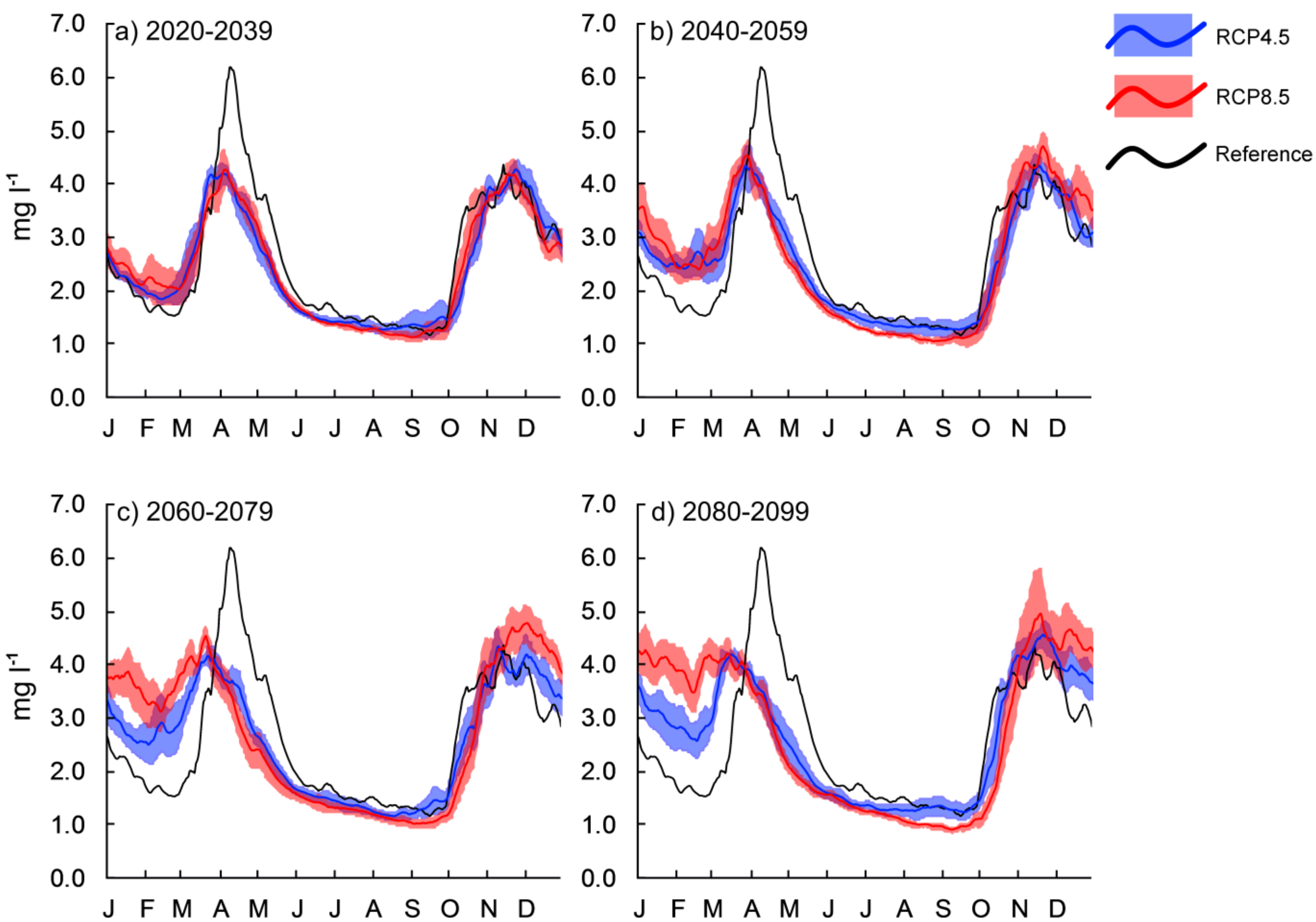

Figure 6. Day of the year median value for iron (Fe) concentration (mg/L) in: a-d) different 20-year periods starting from 2020. Blue (RCP4.5) and red (RCP8.5) indicate the two scenarios studied, black lines indicate the average reference values obtained with five different climate change models. The area between the lines shows the uncertainty deriving from using multiple models.

The amount of Fe transported out of the catchment with river water on a monthly basis is shown in Figure 7, where the two different scenarios (RCP4.5 and RCP8.5) are compared against the reference period (1997-2016) for 20-year periods (2020-2039, 2040-2059, 2060-2079, and 2080-2099).

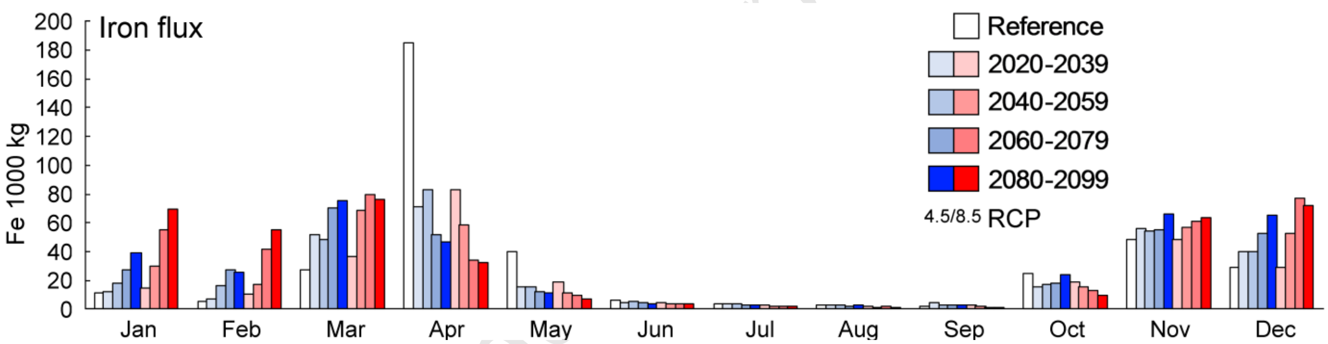

Figure 7. Monthly sum of iron (Fe) flux out of the catchment (1000 kg) in different climate change scenarios (blue = RCP4.5, red = RCP8.5) and 20-year periods (2020-2039, 2040-2059, 2060-2079, 2080-2099) compared with the reference period (1997-2016, white bars).

In the reference period, the Fe flux showed a distinct peak in April, with 48% of annual Fe transport to the sea occurring during this month. With future changes in climate conditions, this spring peak was reduced substantially. Already during the first 20-year period (2020-2039), the flux in April was modeled to decrease from 182 Mg Fe to 71 Mg Fe (61% reduction) in RCP4.5 and to 83 Mg Fe (54% reduction) in RCP8.5. A similar reduction in flux was observed in May and to some extent during summer low flows, although the absolute flux values were smaller.

During other months, especially winter months, Fe fluxes showed an increasing trend in a changing climate. This increase occurred throughout the whole modeling period (2020-2099). In scenario RCP8.5 during 2080-2099, the flux in February in comparison with the reference period (1997-2016) was modeled to increase by over 10-fold, from 5 Mg Fe to 56 Mg Fe.

The results indicated a sharp reduction in total annual Fe flux when comparing the reference period (1997-2016) and the first 20-year climate change period (2020-2039). The flux was reduced from 388 Mg Fe to 286 Mg Fe (26% decrease) in RCP4.5 and to 272 Mg Fe (30% decrease) in RCP8.5. The total annual Fe flux increased with the increase in fluxes during winter months as the climate change models were run on. During the last 20-year period (2080-2099), the flux was modeled to be 366 Mg Fe (5.7% less than during reference period) in RCP4.5 and 394 Mg Fe (1.5% more) in RCP8.5.

4 Discussion

4.1 Can a catchment-scale modeling tool project iron transport?

The recently reported increases in Fe concentrations in freshwaters and the key role of Fe in many environmental cycles (N, C, S, P) have renewed the interest of the scientific community in the Fe transportation process. Previous studies have identified several factors causing this increase in boreal landscapes. It has been attributed to interactions between e.g., Fe and DOM (Sarkkola *et al.*, 2013; Björnerås *et al.*, 2017), Fe and TSS (Palviainen *et al.*, 2015), Fe and declining atmospheric S deposition (Knorr *et al.*, 2009), Fe and intensified soil redox conditions (Ekström *et al.*, 2016), and Fe and longer-term climatological changes (Ekström *et* *al.*, 2016; Björnerås *et al.*, 2017). This indicates that there is no consensus on the single main driver behind the increase in Fe on a larger spatial scale.

In the case of the river Mustijoki, catchment properties enabled us to represent catchment-scale Fe transport in a manageable and simple form, and to identify the main force behind Fe transport as hydrological conditions responsible for soil erosion and for moving the eroded, Fe-rich soil to and through the riverine system. The SWAT model was able to produce accurate estimates (NSE = 0.768 for discharge, r^2 = 0.692 for TSS and 0.422 for Fe concentration). Problematic occasions for SWAT when modeling hydrology, soil erosion, and Fe transport in the Mustijoki catchment were mainly winter periods when freeze-thaw cycles were taking place. This is most likely because of the day-degree factor used in snow modeling, which does not take account of all snow pack and frozen soil physical processes. The model upscaled measured TSS data (from sampling every two weeks) to daily resolution, which enabled us to study flashy responses in the Mustijoki catchment and how these related to loading. Rapidly changing hydrology and water quality conditions were not represented sufficiently well in analyses using data obtained from sampling only every two weeks. We show that SWAT can efficiently model Fe transport in boreal conditions, especially in cases where Fe transport is closely related to TSS. Our results and model goodness of fit were similar to those obtained in previous modeling efforts with SWAT (Shrestha *et al.*, 2017) and can be considered good in terms of hydrology and satisfactory in terms of TSS (Moriasi *et al.*, 2015). They also showed good agreement with measured concentrations, and thus can be used to estimate annual flux and concentration changes more efficiently.

To obtain a clearer picture of Fe transport on a large scale (Baltic Sea), it should be possible to extend our modeling approach to a wider range of catchment types (in terms of Fe transport) and obtain more detailed information on these. However, in catchments where Fe transport is more dependent on soil redox intensity or DOM transport (Ekström *et al.*, 2016), it will not be driven solely by hydrological conditions, making modeling more complex. Thus, more research is needed to provide information on the issue.

4.2. Catchment properties of the river Mustijoki characterize Fe transport

Based on the simulation results, there are two major seasons per year for high Fe concentration and loading in the Mustijoki river catchment. Spring snowmelt and autumn rainfall events are characterized by intense hydrological processes and soil conditions that promote erosion of Fe-rich clay soils in the area. Under boreal conditions, the annual springtime snowmelt peak causes significant volumes of soil-eroding surface runoff. High Fe loading to the river tends to occur also in late autumn, according to our modeling results. Similar results on annual TSS transport regime have been obtained for other agricultural catchments in southern Finland (Puustinen *et al.*, 2007) and in Denmark (Thodsen *et al.*, 2008). In autumn, soil conditions can also increase Fe transport through other biochemical factors, such as increased redox intensity and associated Fe mobilization. This has been suggested as a major driver of increased Fe concentrations in boreal regions (Ekström *et al.*, 2016), but seems to be of low significance in the Mustijoki catchment, where the dominant mechanism is transport of Fe attached to eroded soil particles. However, in more complex catchments that are not as polarized in terms of Fe transportation dynamics, other recognized drivers of increased Fe transport require more attention.

While Fe transport is a natural process and is strongly linked to the geochemistry of bedrock and soils in the catchment, anthropogenic activities in the area can significantly increase the risk of increased loading. In the agriculture-dominated catchment in southern Finland considered in this study, these risks center heavily around soil erosion and SS transport (Tattari *et al.*, 2017). Based on water quality analyses combined with land cover data, Fe transport is highest in agricultural catchments in Finland (Palviainen *et al.*, 2015). This is presumably a consequence of intensified erosion of Fe-rich soils due to agriculture, resulting from a lack of erosion-inhibiting plant cover in winter and increased hydrological connectivity due to artificial drainage. The modeling results obtained in this study confirm these assumptions, as the main source of Fe in the river Mustijoki was revealed to be agricultural fields.

4.3 Impact of climate change on environmental Fe

Global warming will significantly alter the climate in boreal regions. In particular, the temperature changes in the Fennoscandinavian region are predicted to be twice as high as those in the rest of Europe (Hoegh-Guldberg *et al.*, 2018). Changes in temperature and precipitation patterns may already have affected Fe transportation directly and indirectly in boreal regions (Björnerås *et al.*, 2017). One effect is through the direct change in flushing rates of water courses, which become more capable of exporting Fe as the sediment settling rate decreases (Björnerås *et al.*, 2017). Another is the enhanced redox conditions due to wetter winters, promoting reduction of Fe to a more mobile state within the soil (Ekström *et al.*, 2016).

Based on our modeling of the river Mustijoki catchment, there will be significant changes in annual Fe transportation patterns in the future, with major alterations predicted in spring flood volumes, and thus TSS/Fe transport. Lower Fe concentrations in river water, coupled with a simultaneous reduction in discharge, would result in a strong reduction in peak Fe flux to the marine system. Such a reduction is predicted to occur during the coming decade. The hydrological changes modeled here, which included increases in winter discharge and decreases during spring in Finnish rivers, are in line with findings by Veijalainen *et al. (2012)* and other modeling studies in Scandinavia (Andersen *et al.*, 2006; Räty *et al.*, 2017). In the Mustijoki river, both climate change scenarios studied promoted these changes, but they were more visible in the RCP8.5 scenario.

Our modeling results indicate strongly that the timing of the highest seasonal Fe concentrations in river water will shift from spring to autumn in the near future, and more towards winter months later in this century. In particular, a high increase in December-March was indicated by the modeling results. This is presumably due to a diminishing period of snow cover, which tends to protect the landscape from erosion during winter months, and to more precipitation falling as water instead of snow. This evens out the annual Fe concentration pattern and loading, and may affect river ecology and recreational uses during the periods affected. Higher autumn and winter concentrations can influence fish spawning periods in fall and egg survival over winter months, through settling of Fe flocs negatively affecting river bed conditions (Vuori, 1995).

Modelling results indicate reduction of total annual riverine Fe export to the marine ecosystem in the coming decades (30% decrease in 2020 – 2040), in comparison with the reference period. Considering the scientific consensus that suggests increases in riverine Fe transport due to the changing climate, this might come as unexpected. This is however closely related to the catchment characteristics in River Mustijoki, as the diminishing spring melt water volume plays such a crucial role determining the current annual mass flux of Fe through erosion of agricultural areas. Thus, the assumption of climate change enhanced Fe transport and suggested factors behind it in general still stand in other types of catchments in boreal region.

As the annual high seasons for mass flux of Fe into the marine ecosystem will change over time in a similar way to the concentration, the ecosystem and environmental cycles in coastal estuaries of the Gulf of Finland and the Baltic Sea may come under pressure at these high Fe export times (late autumn and winter). The effect of Fe on the benthic release of P is considered by Lehtoranta and Heiskanen *(2003)*. However, the exact effects require further research on the topic.

4.4 Management options to reduce iron mobilization from agricultural land

Intensive land use, together with changing hydrological regimes due to climate change, require improved water management now, and especially in the future. As indicated in earlier studies (Palviainen *et al.*, 2015) and in the present water quality analysis of the river Mustijoki, the majority of Fe mobilization occurs in arable fields. Thus, management measures should prioritize these areas. As the Fe in the Mustijoki catchment is mainly bound to soil particles (Sippola, 1974; Palviainen *et al.*, 2015) and Fe mobilization is mainly associated with soil erosion, measures to reduce erosion will also reduce Fe loads in receiving water bodies. Previous studies on TSS and P loading in similar agricultural catchments have suggested practical management options to reduce these loads, including reduced soil tillage and maintaining an erosion-reducing permanent vegetation cover on fields (Puustinen *et al.,* 2005). These management options are also relevant for preventing Fe loading in the Mustijoki catchment, as Fe transportation is based on the same erosion-driven process. In SWAT modeling, a significant effect of slope on the magnitude of erosion was found, so avoiding tillage on fields with slope steeper than 10% (8% of agricultural area in the study catchments) would result in a 24% decrease in loading. Effects of sloped agricultural areas on erosion have been also highlighted previously (Puustinen *et al.,* 2005; Puustinen *et al.*, 2007). These field areas with steeper slope tend to be located near water bodies in the study catchment, making them hydrologically well connected and presumably further promoting TSS/Fe loading to the recipient water body, the river Mustijoki. Thus, management actions and/or water protection measures should primarily be targeted at these areas with high erosion potential.

5 Conclusions

Erosion of iron-rich clayey soils and changes in hydrological conditions were identified as the main factors driving Fe transport in the agriculture-dominated river Mustijoki catchment in southern Finland. According to the analysis, the high seasons for iron mobilization throughout the river system occur systematically during spring and autumn high flow periods. Catchment-scale modeling with SWAT revealed marked changes in annual Fe transport dynamics, concentrations, and mass fluxes. Following model calibration and validation with SWAT-CUP, climate change scenario modeling (to the year 2100) was performed with five downscaled, bias-corrected climate models. The known role of erosion processes and suspended solids transport in the study catchment, combined with modeling results, indicate that prevention of soil erosion and management of runoff waters originating from erosion-prone arable fields is crucial in attempts to reduce Fe loading to aquatic systems. Actions to reduce loading should include: conventional agricultural water management procedures such as less erosion-inducing soil tillage and permanent vegetation cover to reduce erosion potential; leaving buffer zones to reduce hydrological connectivity and prevent eroded soil from entering recipient water bodies; and planning land use to avoid intensive actions (e.g., tillage) in areas with high loading potential (e.g., sloping land). Model results indicate that field areas with steepness gradient over 10% produce 24% of the annual Fe and TSS load, while covering only 8% of the total agricultural area. As Fe loading in the Mustijoki catchment is strictly related to erosion driven by hydrological conditioning, the changing climate will exert its effect through changes in surface runoff generation. Modelling indicated that lower spring floods and increasing wetness during winters will shift the high erosion and Fe loading periods more evenly throughout the cold season, with the current peak during the spring flood being evened out. Annual peak concentration in the river Mustijoki was modeled to decrease by up to 32% (from 6.2 mg L^{-1} to 4.2 mg L^{-1} in both the RCP4.5 and RCP8.5 scenarios) in the coming 20-year period (2020-2039). Lowest winter concentration was modeled to increase by 126%, from 1.5 mg L^{-1} (reference period 1997-2016) to 3.5 mg L^{-1} (2080-2099) in scenario RCP8.5. The response of ecological systems to this change is currently unknown, as is the response of the marine system to changes in the temporal chemical composition of riverine exports. Data with low temporal resolution deriving from conventional water analyses performed only bi-weekly, or even less frequently, will have information gaps regarding the dynamics and causalities of Fe transport. To fill these gaps, continuous measurements and/or modeling are recommended in future research. The increase in riverine Fe concentrations may cause increasing economic expenditures for the water purification processes for domestic water intake plants and industrial facility purposes. The negative impacts of lowered water quality in socio-economic values of the river environment and nature should also be considered while making economic evaluations.

Acknowledgements

The study was funded by Älyvesi-project (Business Finland) and Maa- ja vesitekniikan tuki ry and Olvi- Foundation.

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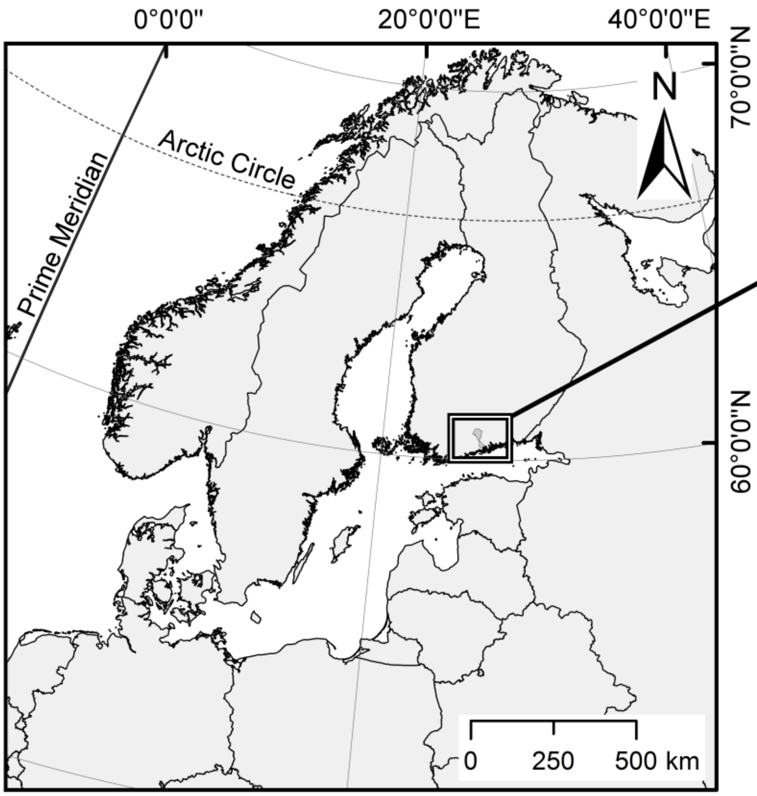
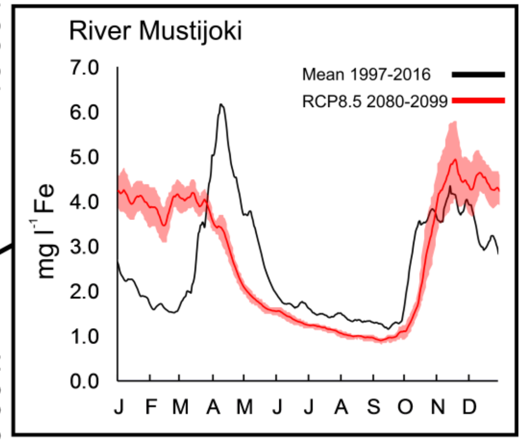
Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical abstract





- Agriculture dominated (37%) catchment
- SWAT was applied to evaluate Fe transport driven by soil erosion
- Climate change alters annual patterns of riverine Fe transport by shifting peak from spring time to winter and autumn

Highlights

- Riverine iron (Fe) transport dynamics depend on catchment properties
- In agriculture dominated catchments of Boreal region Fe transport is driven by soil erosion
- Climate change is shifting high seasons of Fe transport in agricultural catchments from spring to winter and autumn