# Iron as a source of color in river waters

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HIGHLIGHTS

- The quantitative contribution of Fe to water color was examined.
- Fe and TOC explained 86% of the color variability in 6128 water samples.
- On average one-third of the color in the examined Finnish rivers comes from Fe.
- Fe is a dominant source of color in Finnish rivers with TOC-to-Fe mass ratio <4.5.

GRAPHICAL ABSTRACT

Fe is the dominant source of color in examined Finnish rivers with a Fe concentration >4.6 mg L^{-1} or TOC-to-Fe ratio <4.5.
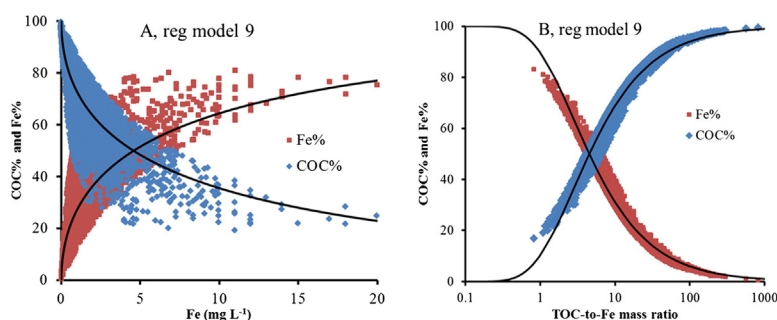
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ABSTRACT

Organic chromophores of total organic carbon (TOC) and those of iron (Fe) contribute to the color of water, but the relative contributions of colored organic carbon (COC%) and Fe (Fe%) are poorly known. In this study, we unraveled Fe% and COC% in 6128 unfiltered water samples collected from 94 Finnish river sites of contrasting catchment properties. According to regression analysis focusing on TOC alone, on average 84% of the mean TOC consisted of COC, while 16% was non-colored or below the color-detection limit. COC and Fe were much more important sources of color than phytoplankton (chlorophyll *a* as a proxy) or non-algal particles (suspended solids as a proxy). When COC and Fe were considered as the only two sources of color, COC% ranged from 16.8% to 99.5% (mean 71%) and Fe% from 0.5% to 83.2% (mean 29%). Similar Fe% and COC% values were obtained when color was estimated from the absorption coefficients of COC and Fe at 490 nm. Fe% increased as a function of the concentration of Fe and was well predicted by the TOC-to-Fe mass ratio. In 608 samples with TOC-to-Fe ratios of <4.5, Fe dominated the color. TOC-to-Fe ratios varied widely within most sites, but in relation to hydrology. In catchments with a peatland coverage of >30%, peak flow exported elevated amounts of TOC relative to Fe and re-sulted in a high COC%. Base flow, instead, mobilized elevated amounts Fe relative to TOC and resulted in a high Fe%. In a catchment covered with 31% of agricultural fields, peak flow transported eroded soil particles high in Fe and thus resulted in a high Fe%, while during base flow the water was high in COC%. This study demonstrated that Fe% and COC% vary widely in river water depending on the catchment properties and hydrology.

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1. Introduction

The color of water (hereafter color) affects the penetration of light, photosynthesis, the energy budget, stratification, and the esthetic appearance of aquatic ecosystems (Jones, 1992; Williamson et al., 1999). It is also a critical factor when natural water is purified to produce good-quality water for domestic and industrial purposes (Chow et al., 2007). During the past two decades over the northern hemisphere, color has increased along with the concentration of iron (Fe) and total organic carbon (TOC) (Roulet and Moore, 2006; Arvola et al., 2010; Haaland et al., 2010; Kritzberg and Ekström, 2012; Köhler et al., 2013; Sarkkola et al., 2013; Weyhenmeyer et al., 2014). The organic chromophores of TOC (referred to here as colored organic carbon, COC; see Table 1 for acronyms used; Coble, 2007; Fichot and Benner, 2011; Carter et al., 2012) and chromophores of Fe (Shapiro, 1964; Kritzberg and Ekström, 2012; Xiao et al., 2013) are important sources of color (Weyhenmeyer et al., 2014). The increase in color is connected to these chromophores, but their relative contributions are poorly known.

The color of filtered water primarily arises from the dissolved part of TOC (DOC) and ferric iron (Fe(III)) bound on it (Vodacek et al., 1995; Coble, 2007; Fichot and Benner, 2011; Carter et al., 2012; Weyhenmeyer et al., 2014). One gram of TOC can bind less than 1.6 mmol Fe(III) (reviewed by Neubauer et al., 2013). At TOC-to-Fe mass ratios <11, when the concentrations of Fe and DOC are such that the complexation of Fe is insufficient to prevent oxide formation, the non-bound Fe(III) forms (oxy)hydroxides, which can grow from filterable colloids to particles (Estapa et al., 2012; Neubauer et al., 2013). Such particles and other iron minerals together with detrital particulate organic matter (part of TOC) are defined as non-algal particles (NAP). In optical studies, NAP is separated from total particulate matter by extraction or bleaching the pigments of phytoplankton, which is another particulate source of color.

The chromophores of Fe and COC are chemically distinct, arising from the d-orbitals of Fe (Sherman and Waite, 1985) or conjugated double bonds and intramolecular charge-transfer reactions between organic chromophores (Del Vecchio and Blough, 2004), respectively. Using the mass-specific absorption coefficient (a^*) for Fe(III) associated with dissolved humic substances and the concentration of dissolved Fe, the contribution of Fe to color (Fe%) was estimated to range from 0.2% (the River Mississippi) to 53% (Löytynlähde spring) in filtered water samples (Xiao et al., 2013). High Fe% can be explained by low TOC-to-Fe mass ratios in groundwater feeding Löytynlähde spring, while low Fe% in the River Mississippi may be related to the selective removal of Fe relative to TOC along with an increasing water residence time (Köhler et al., 2013; Weyhenmeyer et al., 2014). Natural waters also contain suspended particles including Fe and TOC, but Fe% and the contribution of TOC to color (TOC%) in unfiltered waters have not yet been determined.

The aim of this study was to quantify the contribution of Fe% and TOC% (or COC%) to the color of 6128 unfiltered river water samples collected from 94 river sites. We used regression analyses to explain color by the concentrations of TOC, total Fe, suspended solids (SS), and chlorophyll a (Chl a). Color was also estimated as a total absorption coefficient at 490 nm made up from the sum of absorption coefficients of COC, Fe, NAP, and phytoplankton. The latter were calculated by multiplying the concentrations of COC, total Fe, SS, and Chl a by a^*.

2. Materials and methods

2.1. Data source and analytical methods

Our dataset consisted of 6128 river water samples collected between 1977 and 2011 from 94 Finnish river sites covered by the Finnish national water quality monitoring program (Fig. 1, Table 2). All sites belong to the boreal region and are characterized by low altitudinal gradients and a humid climate with a median runoff of 326 mm (Table 2). Forests and peatlands respectively covered 43% (median) and 31% (median) of 83 watershed areas with available land use data (Table 2). Minor land use types included open areas (6% median), agricultural fields (3% median), urban areas (0.05% median), and lakes (3% median). The heterogeneity of river sites was notable (Table 2). Our sites included the River Vuoksi (annual mean flow 617 m³ s⁻¹) and the River Kymijoki (302 m³ s⁻¹), which drain the largest (Lake Saimaa) and the second largest (Lake Päijänne) lakes in Finland. At the other extreme, the annual mean flow was estimated to be 0.003 m³ s⁻¹ in

Table 1
Acronyms used in this study.

| Acronym	Full name
a	Absorption coefficient
$a_{Fe}(490)$	Absorption coefficient of Fe at 490 nm
$a_{Fe}(490)\%$	Contribution of Fe absorption to total absorption by water at 490 nm
a^*	Mass-specific absorption coefficient
$a_{Fe}^*(490)$	Mass-specific absorption coefficient of Fe at 490 nm
b	Regression coefficient
Chl a	Chlorophyll a
COC	Colored organic carbon
DOC	Dissolved organic carbon
Fe%	Contribution of Fe to water color
NAP	Non-algal particles
NCOC	Non-colored organic carbon
SS	Suspended solid
TOC	Total organic carbon
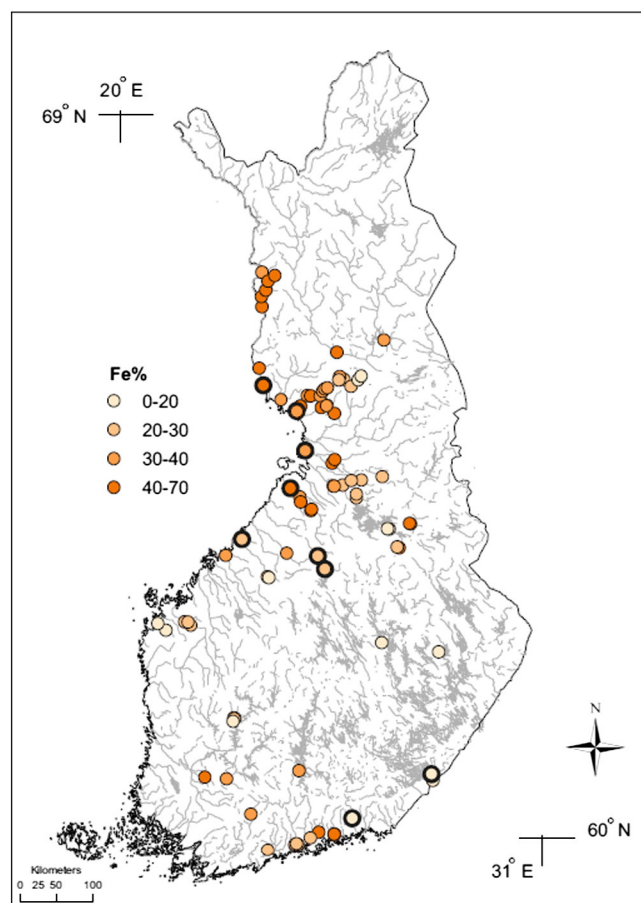
Fig. 1. Sampling sites and the contribution of Fe to color (Fe%, expressed as circles with color gradient) based on regression model 9 reported in Table 4. The sampling sites ($n = 9$) where 388 samples collected during the summer season are marked by bold circles.