Contribution of ferric iron to light absorption by chromophoric dissolved matter

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Introduction
In surface water at pH > 5.5, most dissolved ferric iron (Fe(III)) is associated with humic substances (HS) and forms Fe-HS. Both Fe and HS absorb light, and thus contribute to the chromophoric dissolved organic matter (CDOM). When CDOM is measured from waters with Fe-HS, it is known how much of the absorbance arises from Fe or HS.

In this work, we estimated the contribution of Fe(III) to light absorption by CDOM with Fe-HS in laboratory. We determined molar absorptivity of Fe associated with HS (\( \alpha_{Fe-HS} \)) and applied it to surface waters across large geographic scales.

Materials & Methods
- Humic substance standards (HS): Swannie River Humic and Fulvic Acids (SRHA, SRFA) from USA; Pony Lake Fulvic Acid (PLFA) from Antarctica
- Natural water samples: lentic waters (a spring, a lake and a coastal site from Finland) and ten major rivers from five continents
- Fe-HS association: mix acidic Fe(III) sulfate solution with HS standards (10 mg L\(^{-1} \) Fe-HS association: mix acidic Fe(III) sulfate solution with HS standards (10 mg L\(^{-1} \))) and raising the pH to 8 with NaOH. Maximum Fe-binding capacity of HS was obtained by increasing Fe concentration.
- Molar absorptivity (\( \alpha \)) was calculated by dividing the increase in light absorption of Fe-HS by the concentration of associated Fe.
- Two-step of filtration (GF/F and 0.2-µm filter (<0.2 µm), and after cation exchange chromatography (IEC).
- Fe was analyzed with ICP-MS/OES; DOC was measured with a total organic carbon analyzer.

Results
Effects of Fe on light absorption of HS solutions
- The association with HS maintained a high concentration of Fe in solution and consequently increased the light absorption (Fig. 1).
- Light absorption by Fe-HS increased linearly as a function of the increasing concentration of associated Fe in the solutions after IEC (Fig. 2).
- The maximum Fe-binding capacities calculated per mg of C for SRHA, SRFA and PLFA in Milli-Q water (at pH8) were 13.0, 13.5, and 7.6 µmol Fe [mg C]\(^{-1} \), respectively.

Estimation of light absorption of dissolved Fe in natural waters
- The molar absorptivity (\( \alpha \)) and Fe-specific absorption coefficient (\( \alpha_{Fe} \)) were spectrally similar among three HS standards (Fig. 3).
- Calculated contribution of Fe to the absorption by dissolved matter increased with wavelength (Fig. 4).
- In natural surface waters examined, Fe contributed from 0.6% to 58% to light absorption by total dissolved matter at \( \lambda = 410 \) nm (Fig. 4).

Conclusions
- The association of Fe with HS increases the absorption coefficient of CDOM.
- Terrestrial-derived CDOM (SRHA/FA) has a higher Fe-binding capacity than microbial-derived CDOM (PLFA).
- Molar absorptivity of associated Fe are similar among HS.
- Fe can account for a significant part of the light absorption by CDOM.

We propose the term chromophoric dissolved matter (CDM) for cases where inorganic absorption cannot be separated from the absorption by organic chromophores.

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