Contribution of ferric iron to the light absorption by chromophoric dissolved organic matter

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Backgrounds

- Iron (Fe), Manganese (Mn) and Aluminium (Al) – key elements controlling the cycling of organic carbon in aquatic ecosystems (Kone Foundation)

- Contribution of Fe to the light absorption by CDOM
Backgrounds

- Why?

  - CDOM (or DOC) is one of the most important components affecting water color (Williamson et al. *Limnol Oceanogr* 1999);
  - CDOM or water color is typically measured directly from the absorbance of filtered samples (Hongve and Akesson, *Wat Res* 1996);
  - In natural waters with pH>5, dissolved Fe is primarily associated with CDOM (Shapiro, *J Am Water Works Assoc* 1964);
  - The contribution of Fe to light absorption by CDOM is not assessed
Backgrounds

Aims

- The aim of this study was to quantitatively determine how much Fe(III) contributes to the light absorption by CDOM when associated with HS (HS-Fe);

- We calculated Fe-specific absorption coefficient spectrum ($a_{\lambda,\text{Fe}}^*$) for HS-associated Fe;

- Applied this $a_{\lambda,\text{Fe}}^*$ to different types of surface waters to assess the contribution of (HS-associated) Fe to water colors
Materials & Methods

- **HS standards** 10 mg L⁻¹
- **Fe(III) solution** pH 1

**Mixtures** Raise pH 8

- Dark, 12 h, 200 r min⁻¹

**GF/F filtration**

- Remove particle Fe

**0.2-μm filtration**

**Cation exchange chromatography**

- Remove freely dissolved Fe

**HS-Fe solution**
Materials & Methods

GF/F filtration of PLFA with Fe solutions

Materials & Methods Diagram:

- HS standards 10 mg L⁻¹
- Fe(III) solution pH 1

Mixtures
Raise pH 8

Dark, 12 h, 200 r min⁻¹

GF/F filtration

0.2-μm filtration

Cation exchange chromatography

Total absorption

<GF/F absorption

<0.2μm absorption

After IEC absorption

GF/F filtration of PLFA with Fe solutions

Cation exchange chromatography
Materials & Methods

- **Analysis**
  - UV-vis spectrophotometry
  - Fe (ICP-MS/OES)
  - DOC

- **Fe-specific absorption coefficient** \( (a_{\lambda, \text{Fe}}^*, \text{m}^2 \text{ g}^{-1}) \)

\[
a_{\lambda, \text{Fe}}^* = \frac{a_{\text{HS-Fe}} - a_{\text{HS}}}{c_{\text{Fe}}} \quad (\text{eq.1})
\]

In chemical literatures, \( a_{\lambda, \text{Fe}}^* \) is known as molar absorptivity \( (\varepsilon_\lambda) \) calculated as the unit L mol\(^{-1}\) cm\(^{-1}\).
Results

Fig 1. Light absorption coefficient by (A) SRFA (10 mg L\textsuperscript{-1}), (B) Fe (32.3 µmol L\textsuperscript{-1}) and (C) SRFA with Fe adjusted to pH 8
Fig 2. Spectral slope coefficients of HS alone and with associated Fe (HS-Fe)
Results

Fig 3. Light absorption by SRHA and SRFA as a function of associated Fe at 410 nm.

\[ a_{\text{SRHA-Fe}} = 0.160 \pm 0.010 \text{ Fe} + 9.154 \pm 0.471 \]
\[ R^2 = 0.985 \]

\[ a_{\text{SRFA-Fe}} = 0.161 \pm 0.006 \text{ Fe} + 3.619 \pm 0.298 \]
\[ R^2 = 0.995 \]
Results

**Fig 3.** The spectral Fe-specific absorption coefficient ($a_{\lambda, \text{Fe}^*}$) (left y-axis) and apparent molar absorptivity ($\varepsilon_\lambda$) (right y-axis)
Fig 4. The light absorption coefficient of CDOM ($a_{\lambda,\text{CDOM}}$) (A, D), calculated absorption by HS-associated Fe ($a_{\lambda,\text{Fe}}$) (B, E), and the ratio of $a_{\lambda,\text{Fe}}$ to $a_{\lambda,\text{CDOM}}$ (C, F).
The contribution of Fe to CDOM absorption in big rivers ranged from 0.61% (Mississippi) to 8.64% (Congo) at $\lambda = 410$ nm.
Conclusions

- Association of Fe with HS increases the absorption coefficient by CDOM;
- HS-associated Fe reduced spectral slope coefficient of CDOM;
- The contribution of HS-associated Fe to light absorption by CDOM can be high (up to 58%) in natural waters.

Yi-Hua Xiao et al. Contribution of ferric iron to the light absorption by chromophoric dissolved organic matter. (under revision to Limnology and Oceanography).
Filtration in the field by Yi-Hua Xiao

Thank you!