

Response to Referee 1 comment on “Technical note: Effects of iron(II) on fluorescence properties of dissolved organic matter at circumneutral pH”

Please note the reviewer’s comments are in *purple italic Verdana font* and our responses are in Times New Roman, with proposed revisions to the text in blue.

Anonymous Referee #1 **General comments:**

The authors present a characterisation study on the effect of dissolved Fe(II) on the fluorescence properties of organic matter dissolved in groundwater. The study is novel and the experimental observations are well performed. This makes the manuscript suitable for publication. However, the paper does not fit well to the HESS audience as this audience is less focused on analytical geochemistry. The paper refers to the second scope of HESS: it is noted that one groundwater sample is used for characterisation which makes spatial or temporal characterisation not that strong. To me, the paper would better fit in Appl Geochem or Chem Geol or so. I leave it to the editor to decide on this.

We addressed this comment in our initial response to Referee 1 (Author Comment 1, available at <https://doi.org/10.5194/hess-2020-150-AC1>). Quoting from Author Comment 1:

“The scope of HESS includes ‘the role of physical, chemical, and biological processes in the cycling of continental water in all its phases, including dissolved and particulate matter, at all scales.’ Along these lines, ‘biogeochemical processes’ is a subject area for the journal. The manuscript type we submitted (technical note) is for papers relating to ‘experimental and theoretical methods and techniques which are relevant for scientific investigations within the journal scope.’... Additionally, because HESS is an open access journal, the article will be able to reach the widest possible audience compared to traditional subscription-based geochemistry journals.”

The referee’s comment “*one groundwater sample is used for characterisation which makes spatial or temporal characterisation not that strong*” points to a misapprehension. The purpose of the manuscript is not to characterize DOM at the site from which the sample (stock solution) was collected. Rather, it is to understand how ferrous iron affects the fluorescence properties of DOM in groundwater. We selected our single stock solution because it was typical of the deltaic aquifer groundwaters that can contain high ferrous iron concentrations. We will revise the manuscript to make this objective clearer.

Original:

In this study, up to 300 mg/L Fe(II) was added to DOM-containing groundwater to assess the influence of Fe(II) on the fluorescence properties of DOM.

Proposed revision:

The objective of this study was to assess the influence of high concentrations of Fe(II) on the fluorescence properties of DOM by titrating up to 300 mg/L (5.4 mM) Fe(II) into groundwater collected from a deltaic aquifer in Richmond, British Columbia, Canada.

First, the relevance of high Fe in groundwater is not illustrated. The authors use Fe concentrations up to 300 mg/L. This is a very high value that is rarely found in groundwater, especially when it has a neutral pH. The authors should thus present their paper within the framework of high-fe groundwater: what has been observed and for which hydrological conditions.

Our study is motivated by the high, naturally-occurring iron concentrations we have observed in groundwaters in deltaic sediments of south Asia, and at the Kidd 2 field site in Vancouver Canada. High iron concentrations are common in deltaic sediments, although the over 300 mg/L found in parts of the Kidd 2 site is unusual for circumneutral groundwater. Similarly, organic contamination (fuel spills, landfills) can also drive iron reduction and produce high iron concentrations under circumneutral pH conditions. We have revised our motivational statement to make this clearer to the reader.

Original:

The fluorescence quenching effect in Fe(II)-rich groundwater is still poorly understood and warrants further investigation, given the prevalence of high DOM and Fe(II) in groundwater in deltaic sediments (Bolton & Beckie, 2011) and contaminated sites (Christensen et al., 2001). Fe(II) is often present in groundwater in organic-rich settings where the oxidation of organic matter is coupled to solid-phase Fe(III) reduction, dissolving Fe(II) into groundwater. For example, 1.5-10 mg/L Fe(II) in groundwater is commonly observed in the organic-rich groundwaters of the Bengal Basin (Harvey et al., 2002).

Proposed revision:

The fluorescence quenching effect in Fe(II)-rich groundwater is still poorly understood and warrants further investigation, given the prevalence of high DOM and Fe(II) in groundwater in deltaic sediments (Bolton & Beckie, 2011) and sites contaminated with organics, for example, from landfills or fuel spills (van Breukelen & Griffioen, 2004; Christensen et al., 2001; Heron et al., 1994). In most instances, these high Fe(II) groundwaters are found when the oxidation of organic matter is coupled to solid-phase Fe(III) reduction, dissolving Fe(II) into groundwater at circumneutral pH. For example, 1.5-10 mg/L Fe(II) in groundwater is commonly observed in the organic-rich groundwaters of the Bengal Basin (Harvey et al., 2002), and up to 90 mg/L Fe(II) has been observed in landfill leachate in the Netherlands (van Breukelen & Griffioen, 2004).

Second, the authors discuss that the effect of Fe(II) on the fluorescence properties is due to aqueous complexing but do not elaborate on this. They should pay more attention to this and discuss why this effect is so strong for Fe(II). Might one expect a similar effect for dissolved Ca which is more omnipresent. If not, what makes Fe(II) so unique besides Fe(III) and Al(III)?

Our intention is not to determine the mechanisms of *why* Fe(II) may affect the fluorescence properties of groundwater. While this is a legitimate topic of inquiry, it is beyond the scope of our study, which is empirically focused on characterizing the relationship for Fe(II) specifically. We hope this study motivates other research groups to characterize the effects of other cations such as Ca²⁺ on fluorescence properties and to compare their results with the results in this paper. No revisions made.

Third, as said before, the paper is oriented towards analytical chemistry. To make it understandable for the HESS audience, they should explain specific details of the technique, etc. Now, the paper will not reach the HESS audience as the relevance is not well illustrated (comment 1) and the text is too technical.

We will add some additional text to the Introduction explaining the methodology.

Original manuscript (line 28):

Fluorescence spectroscopy has been widely used to characterize the properties of organic matter as it is highly sensitive to the structures and functional chemistry of aquatic organic matter (Fellman et al., 2010).

Proposed revision:

Fluorescence spectroscopy has been widely used to characterize the properties of dissolved organic matter as it is highly sensitive to the structures and functional chemistry of aquatic organic matter (Fellman et al., 2010; Helms et al., 2008; Stedmon et al., 2003; Weishaar et al., 2003). In this method, light at a known wavelength (the excitation wavelength) is passed through a sample, and the absorbance at that frequency and fluorescence (emission) at other frequencies is measured. Such spectra can be used to derive commonly utilized fluorescence indices that correlate to specific forms of organic matter (Aiken, 2014; Coble et al., 2014; Hudson et al., 2007; Murphy et al., 2013). These indices include the fluorescence index (FI), which is calculated as the ratio between the emission at 470 nm to that at 530 nm at an excitation wavelength of 370 nm and relates to the concentration of aromatic, microbially derived lignin-like organic matter (McKnight et al., 2001). Additionally, an excitation-emission matrix (EEM) is prepared by systematically repeating the measurements at a range of different excitation and emission wavelengths. These measurements are highly sensitive to the structures and functional chemistry of aquatic organic matter, which determine the unique pattern of peaks present within the EEM spectra (Aiken, 2014; Coble, 1996; Coble et al., 2014; Fellman et al., 2010). Due to the complexity of the EEM spectra obtained from each unique sample, a number of statistical methods have been used to decompose EEM spectra and relate emission patterns to functional chemistry of organic matter within a sample. Parallel factor analysis (PARAFAC) is a commonly utilized statistical means of compartmentalizing EEM spectra into discrete peaks that may then be compared to broad organic matter classes (Bro, 1997; Murphy et al., 2013; Stedmon & Bro, 2008).

Comments from PDF

Introduction:

Line 29 Omit space.

Line 29 This is not a nevertheless.

These errors have been removed, see revised text in response to the previous comment.

Line 35 does not belong here; move to end of INTRO.

Agreed, moved.

Line 57 better formulate an objective or research question

Agreed. In the last paragraph of the Introduction, we now emphasize that the research question that we are assessing is the effect of high Fe(II) concentrations on groundwater that is representative of deltaic groundwaters which have extraordinarily high Fe(II) concentrations.

Original

In this study, up to 300 mg/L Fe(II) was added to DOM-containing groundwater to assess the influence of Fe(II) on the fluorescence properties of DOM.

Proposed revision:

The objective of this study was to assess the influence of high concentrations of Fe(II) on the fluorescence properties of DOM by titrating up to 300 mg/L (5.4 mM) Fe(II) into groundwater collected from a deltaic aquifer in Richmond, British Columbia, Canada.

2 Study area

Line 68 I cannot see how a wedge enters an aquifer. The wedge is the result.

Line 70 meaning regional gradient unclear. Groundwater gradient of hydraulic heads or surface water gradient of water level?

Line 71 it is not according to the scope of the article, but this description is not that clear in terms of density-driven flow versus hydraulic pressure driven flow. As HESS is a hydrological journal, a better description of the hydrological forces should be given. Is there influence of tide?

Seems to me that reference to Jia 2015 should be made as well.

Line 76 put reference to figure at the start of this paragraph

In response to these four comments, we have corrected the wording to make it clear that inflowing water forms a wedge within the aquifer. We changed “regional gradient” to “regional hydraulic gradient.” The cited reference Neilson-Welch and Smith (2001) describes the density-dependent flow well whereas Jia (2015) focuses on the biogeochemistry. We do not wish to elaborate on the hydraulics of the site as density-dependent flow is complex and our concern is only that the groundwater collected at the site is representative of deltaic groundwaters with high DOM.

Original

At the site, a wedge of denser, saline ocean water enters the aquifer in the hyporheic zone at the river bottom, flows inland along the base of the aquifer to a maximum distance of approximately 500 m inland where it overturns flows back towards the river under a regional gradient from freshwater recharged inland (Neilson-Welch & Smith, 2001).

Proposed revision:

At the site, denser, saline ocean water enters the aquifer in the hyporheic zone at the river bottom, flows inland along the base of the aquifer to a maximum distance of approximately 500 m inland where it overturns flows back towards the river under a regional hydraulic gradient from freshwater recharged inland (Neilson-Welch & Smith, 2001), forming a wedge of saline water in the aquifer (Figure 2).

Line 76 I am puzzled by this high Fe concentration. Provide more details on pH and complexing anions as SO₄ and HCO₃, etc. I also would like to see saturation indices for minerals as FeCO₃ mentioned. And does SO₄ reduction play a role or so.

The biogeochemistry of the site is well described in Jia (2015), who uses a reactive transport model to examine the biogeochemical processes and reconcile them with the data. A detailed description of the site biogeochemistry is beyond the scope of this manuscript. We will cite Jia (2015) on this line to make the connection clearer.

Methodology

Line 80 where does the stock solution come from? is it the groundwater sample?

Yes, the stock solution is the untreated groundwater. We will add the following text as the first sentence of section 3.1.

Proposed revision: For the measurements in this study, we used a single stock solution of natural DOM-containing groundwater, to which we added (titrated) increasing concentrations of Fe(II).

Line 86 teflon is rather air-permeable and I do not know about duct tape but it is a plastic and thin. Can the authors guarantee no aeration at all during 30 days storage time? Seems to me long.

We have clarified that it was a “Teflon-lined plastic cap.” The relatively inert teflon was directly in contact with the sample but there was an additional plastic barrier (the cap) between the sample and the atmosphere. We cannot guarantee that no aeration occurred, but it is likely minimal. The waters have high partial pressures of CO₂ and methane. What headspace may be present in the bottle is likely to be dominated by these exsolved gases. Some post-sampling alteration is tolerable, since our goal is not to characterize the groundwater at the Kidd 2 site, but to examine the effect of high Fe on the fluorescence properties of natural DOM that is representative of deltaic groundwaters.

We have revised this paragraph to clarify that the groundwater was selected as a stock solution and is not a “sample.” The word “sample” may incorrectly imply that we are interested in characterizing the Kidd 2 site groundwater. Also, the Fe(II) addition experiment and fluorescence analysis were conducted within ~14 days after sample collection. The 30 days period is a conservative estimation for all laboratory analysis and data processing. The manuscript has been revised to clarify the sample handling and analysis procedures.

Original

Groundwater was filtered through 0.45 μm cellulose filters, then stored in a 1 L amber glass bottle- with a Teflon-lined cap, without acidification. The bottle was filled with no headspace and duct tape was used to further seal the sample and minimize the oxidation of Fe(II). The collected sample was refrigerated at 4°C until analysis (within 30 days).

Proposed revision

The groundwater was filtered through 0.45 µm cellulose filters, then stored in a 1 L amber glass bottle with a Teflon-lined plastic cap, without acidification. The bottle was filled with no headspace and duct tape was used to further seal the sample and minimize the oxidation of Fe(II). The collected 1 L stock solution was refrigerated at 4°C until fluorescence analysis (within ~14 days). Although some degradation of the DOM may have occurred during the holding period, we expect that this would not significantly affect our conclusions as our intention was to determine how Fe(II) addition affects the fluorescence properties of DOM, rather than to characterize the properties of DOM at the Kidd 2 site.

Line 95 I assume gaseous? say so.

Changed to add the word gaseous.

Original ... which maintains O₂ levels of ...

Proposed revision: ...which maintains gaseous O₂ levels of...

Line 112, Line 251 first word so in full: Iron(II)

Agreed. Changed to **Ferrous iron**

Line 115 are = were

Agreed. Changed to were.

Line 131 turn "was" to regular script

Changed.

Line 141: please provide more info on goodness-of-fit criteria. How was "no obvious residuals" assessed?

This comment points to a misapprehension which was held by both Referees. Our objective was not to develop a model to characterize the fluorescence of the site groundwater, but, rather characterize the effects of Fe(II) on the fluorescence properties of the experimental stock solution (representative of deltaic groundwater). Our original submission was not sufficiently clear on this point. We have clarified this point in the introduction and throughout the manuscript.

Proposed revision to Introduction:

We identified the degree of quenching by Fe(II) based on the excitation-emission matrix (EEMs) regions and peaks. In this study we fit EEM spectra to a previously derived 13-component PARAFAC model (Cory & McKnight, 2005). We chose to use this robust PARAFAC model, which was developed using DOM from a wide range of aquatic environments and has been subsequently applied to interpret EEMs from a large variety of aquatic systems (Jaffé et al., 2008; Larsen et al., 2010). The use of this 13-component model also facilitates the derivation of the redox index (RI), calculated by summing the reduced quinone-like inputs over total quinone-like inputs from components within the model. Finally, derivation of a unique, site-specific PARAFAC model typically requires a large sample set composed of samples from a common organic matter context (Cory & McKnight, 2005; Ishii & Boyer, 2012). As the aim of this study

was to capture how spectral attributes are quenched upon addition of Fe(II), rather than characterization of the underlying organic matter properties, the application of a pre-resolved model ensures that model fitting is not biased by Fe(II) addition.

Proposed revision to section 3.3:

The established 13-component PARAFAC model of Cory & McKnight (2005) was used to fit the EEM spectra within this study. The 13 components consist of seven quinone-like fluorophores, including three oxidized quinones (Q1, Q2, and Q3), four reduced quinones (SQ1, SQ2, SQ3, and HQ), two amino acid-like components (tryptophan and tyrosine), and four remaining unknown fluorophores (Cory and McKnight, 2005). We utilized this pre-resolved model as the intent was not to characterize the underlying DOM characteristics at the site, but to examine how the fluorescence characteristics shift with Fe(II), which is known to quench fluorescence. To ensure that this 13-component model adequately represented the fluorescent organic matter characteristics within the sample set, plots of residual fluorescence remaining after the model was applied were plotted and analysed.

Results

Line 149 omit; the lab observation on 1 sample is not a general observation for an entire site

Agreed. Removed “at the Kidd 2 site” and replaced with “in the groundwater stock solution from the Kidd 2 site.”

Line 154 but the concentration ranges are incomparable; say so

Agreed.

Original: The magnitude of quenching effect was more pronounced in this study than that performed by Poulin et al. (2014), who observed nonlinear fluorescence quenching (7% to 23%) in four different surface water samples, by addition of Fe(II) up to 1.5 mg/L.

Proposed revision:

The magnitude of quenching effect was more pronounced in this study than that performed by Poulin et al. (2014), who observed nonlinear fluorescence quenching (7% to 23%) in four different surface water samples, by addition of Fe(II) up to 1.5 mg/L, significantly lower than the Fe(II) concentrations used in this study.

Line 160 the brings up the question whether the sample cuvetes was covered with a lid during analysis, i.e., could O₂ enter freely or only during sample transfer.

Note that entrance of O₂ may be significant for low Fe(II) but negligible for high Fe(III). Something should be said about this. This might explain the non-linear behaviour or a part of it.

We agree that the oxidation of Fe(II) during analysis is an important question, but feel the original manuscript addressed the question well. As we have stated in the original text, the analysis time was rapid, we did not observe colloids, and previous work by Poulin suggested that oxidation of Fe(II) to Fe(III) only had a limited effect of fluorescence. We have not made any changes to the text.

Line 175 seems ugly English to me, although I am non-native English speaker

Agreed – awkwardly worded. Changed to:

Similar to relative OFI, the relative intensity of Peak A decreased by ~60% as Fe(II) increased from 1 to 306 mg/L, and over 65% of the quenching occurred below Fe(II) concentrations of 101 mg/L (Figure 4c).

Line 180 this doesn't tell the reader anything. Explain better.

Agree, we will reword.

Original text:

This result is consistent with quenching experiments conducted with Everglades F1 water samples, where they observed a distinct shift in the quenching locations with increasing ratio of Fe(II) to DOM (Poulin et al., 2014).

Proposed revision:

Our results are consistent with the study of Poulin et al. (2014) who observed a shift in the quenching location as the Fe(II) to DOM ratio was increased.

Line 180 who is "they"

Agree, this is unclear. We will change “they” to “Poulin et al. (2014).”

Line 194 compare with remark at Fig. 4. Change y-axis accordingly

This line states that “High values of FI (approximately 1.80) indicate that DOM is derived from extracellular microbial activity, whereas low values of FI (approximately 1.20) suggest that DOM comes from terrestrial plant and soil organic matter (Cory & McKnight, 2005).”

The y-axis range for FI on Fig 4b was 1.6 to 1.9 and we will revise the y-axis range to be 1.0 to 2.0. We will increase the y-axis ranges for the other parameters on Fig 4 and 5 as recommended by both reviewers.

Line 203: once more; these studies cannot be intercompared as the Fe range is so different

We will retain the text as written; Poulin et al. (2014) is the only paper we are aware of that examines this issue, so comparison to their results is reasonable. We acknowledge at several points in the manuscript that their experiments covered a much lower Fe range, and that that is a primary motivation for our study.

Line 211 *the figure does not show two stages (steps) but two different slopes*

We have changed “occurred in two stages” to “occurred in two phases with increasing Fe(II), as represented by a change in slope.”

Line 215 *emission intensity ??*

Agreed. Changed “intensity at emission” to “emission intensity.”

Line 223 *it is completely unclear how the result of the fitting exercise looks. This is unacceptable.*

As discussed above (see our response to your comment on line 141 and your major comment 3), the data was fit to pre-solved components; we did not generate the components ourselves. We will add plots of the residuals into the supporting information. See our response to your comment on line 141.

We propose to add the following text in this section:

The excitation and emission spectra of the 13 components are included in our dataset published on Zenodo and the residuals from the PARAFAC modeling (measured data minus model fits) are plotted in the supporting information.

Line 238 *see earlier remark; this finding is not valid for the site as a whole*

Agreed. The wording was not precise. Changed “at the Kidd 2 site” to “in the experimental stock solution from the Kidd 2 site.”

Line 244 *see remark at the figure;*

From Figure 5: *change range of the y-axis. The changes are minor as phrased in the text whereas the figure suggests major changes due to the short range in values.*

We will change the y-axis range for figure 5b to be 0 to 1.

Line 251 *first word: Iron(II)*

Agreed – changed to “Ferrous iron”

Line 255 *without reading Senesi (1990), I doubt this. DOC is only 10.7 mg/L whereas Fe goes up to 300 mg/L. This implies less than 1 mmol organic C/l versus almost 6 mmol Fe(II). There thus seems an excess of Fe to me. Comment on this into terms of molar ratios and complexation constants as found for DOM-Fe complexes.*

We agree and have elaborated our discussion.

Original:

The non-linear quenching of the fluorescence intensity with Fe(II) concentrations indicates a static quenching mechanism, where quenching primarily depends on the fraction of DOM ligands that are complexed to Fe(II), rather than on the Fe(II) concentration itself (Senesi, 1990).

Proposed Revision:

The non-linear quenching of the fluorescence intensity with Fe(II) suggests, following Senesi (1990), a static quenching mechanism. However, our experiment does not allow us to identify quenching mechanisms. While the maximum ratio of Fe(II) to DOM (mg/L per mg/L) was approximately 0.4 in Poulin et al (2014), it is much larger in our study, with a molar Fe to C_{DOM} ratio of approximately 6. While earlier work by Senesi (1990) suggests that quenching primarily depends upon the fraction of DOM ligands that are complexed to Fe(II), our study, with a great excess of Fe(II) over C in DOM, could involve other mechanisms.

Line 259 see before; do not generalise your findings that much

Line 260 explain (comment on mixing of saline and groundwater).

Line 263 but Fe is also much higher

We agree. The effect of mixing was only speculation, so we have removed this from the text.

Original:

The differences in Fe(II) quenching at the Kidd 2 site compared to Poulin's study could be related to the high Fe(II) background in the organic-rich environment and the mixing of saline water and groundwater. It should be noted that the DOC concentration in this study was 10.7 mg/L, significantly greater than that used in previous study (Poulin et al. 2014).

Proposed Revision:

The differences in the impact of Fe(II) on fluorescence quenching between the sample collected from the Kidd 2 site and the results reported by Poulin et al. (2014) could be related to the much higher Fe(II) background in the organic-rich aquifer and groundwater at the Kidd 2 site. It should be noted that the DOC and concentration in the sample collected from the Kidd 2 site was 10.7 mg/L, significantly greater than that in the previous study (Poulin et al., 2014).

Line 266 once more

We have changed "at the Kidd 2 site" to "in the stock solution collected from the Kidd 2 site".

Line 279 indeed; compare with earlier remark

Agreed, see response to comment from line 263.

Line 297 this does not fit to a HESS readership. Explain more

We believe that DOM composition is relevant to our results and it is useful to suggest this to the reader. Water soluble organic matter is also an important component of continental waters and within the scope of HESS (which includes 'the role of physical, chemical, and biological processes in the cycling of continental water in all its phases, including dissolved and particulate

matter, at all scales'). We have provided more background material in the introduction. No changes made in this section.

Conclusions

Line 303 *indicate where the site is as many readers only read CONCLUSIONS*

Agreed. Changed “from the Kidd 2 site” to “from the Kidd 2 aquifer in the Fraser River Delta, Richmond, BC”

Line 304 *should be "concentration is"*

Agreed. Changed to “the DOM concentration is ~10 mg/L.”

Line 305 *This point was not addressed before and no new findings should be presented under CONCLUSIONS. Besides, some ideas on Fe-DOC complexation for the different compounds may be feasible. Note that this text piece is somewhat in conflict with the last two sentences of the CONCLUSIONS. Rewrite.*

We agree with the referee that we did not support this statement in the text. We will therefore add the following at the end of the discussion:

Proposed Revision:

While our study shows that high Fe(II) concentrations can influence fluorescence properties of a representative deltaic groundwater, it is difficult to generalize our results to other terrestrial waters with different DOM compositions without further analyses. We observed non-uniform quenching as a function of Fe concentration in this study, with smaller increases in quenching at concentrations above 100 mg/L. We note that both the DOM and Fe(II) concentrations that we examined were higher than those examined by Poulin et al (2014).

We will also revise the conclusions:

Original:

The proportionally stronger quenching effect at low Fe(II) concentration (below 100 mg/L) suggests that the degree of quenching is difficult to predict. Indeed, because quenching intensity does not change uniformly with excitation and emission wavelengths, it would be difficult to quantify the quenching effect on fluorescence indices in other water samples without performing a similar Fe(II) addition experiment.

Proposed Revision:

While our results are likely applicable to similar deltaic groundwaters, further analyses are required to quantify the quenching effect on fluorescence indices in other terrestrial waters (for example, surface waters with sufficiently high Fe concentrations such that quenching is likely).

We thank both referees for their thorough and constructive reviews of the manuscript.

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