

# Effects of natural organic matter photoirradiation on its adsorption to and dissolution of goethite at pH 3.5 and 5.5

Michael J. Pullin

*New Mexico Institute of Mining and Technology, New Mexico, USA*

Christina A. Proggess and Patricia A. Maurice

*University of Notre Dame, Indiana, USA*

**ABSTRACT:** Natural organic matter (NOM) adsorbs to Fe oxyhydroxides, and it may enhance Fe dissolution rates by either ligand-promoted or reductive dissolution mechanisms. This research focused on the how photoirradiation of NOM and adsorption of photoirradiated or non-irradiated NOM to goethite (pH 3.5 and 5.5, 22 °C, 0.10 M NaClO<sub>4</sub>) affected total Fe concentration and Fe(II):Fe(III) ratios. Photoirradiation preferentially removed higher molecular weight, more aromatic NOM components, and formed new low molecular-weight components. These changes resulted in a substantially decreased adsorption affinity of NOM for goethite at pH 3.5, but only a small decrease at pH 5.5. NOM irradiation also affected its interactions with iron in solution and at the goethite surface. Most noteworthy, interaction of irradiated NOM with goethite at pH 3.5 resulted in much greater increases in solution Fe(II) concentrations relative to Fe(III) concentrations than in the non-irradiated adsorption experiment, indicating a potential shift in the dominant dissolution mechanism.

## 1 INTRODUCTION

Fe and natural organic matter (NOM) are closely associated in many environments, and they affect one another's behavior with respect to such processes as adsorption, precipitation or coagulation, and photo-transformations. This work focuses on how the exposure of NOM to light affects its subsequent interactions with the Fe(III)oxyhydroxide mineral goethite.

In solution, NOM binds Fe(III) strongly, and it may also associate more weakly with Fe(II) (Pullin and Cabaniss, 2003a, b and refs. therein). Fe(III) solution complexes with organic ligands (including NOM) are photoreactive, leading to the reduction of the Fe and the oxidation of the ligand (Voelker et al., 1997). Previous work has shown that NOM can also act as a chemical or "thermal" reductant for Fe(III) in solution (Waite and Morel, 1984; Voelker and Sulzberger, 1996; Pullin and Cabaniss, 2003b). The rate of thermal reduction has been shown to increase after exposure to light, presumably due to the photochemical formation of long-lived radical species (Emmenegger et al. 2001).

NOM also adsorbs to Fe(III)oxyhydroxide mineral surfaces, achieving a maximum adsorption at low pH ( $\leq 4$ ) and decreasing adsorption with increasing pH. As reviewed by Zhou et al. (2001), several groups have suggested that intermediate and/or high molecular weight, more aromatic components of the

NOM mixture adsorb preferentially to Fe(III) oxyhydroxide surfaces, leaving behind lower molecular weight, more aliphatic components in solution.

During adsorption, the formation of an inner-sphere surface complex between an organic ligand and Fe(III) surface atoms can initiate several possible dissolution mechanisms, depending on the ligand and mineral structures and the solution conditions. In ligand-promoted dissolution, the formation of this surface complex decreases the bond strength between the Fe(III) and its neighboring atoms within the mineral surface matrix. Consequently, the Fe(III) is detached from the surface and brought into solution, the rate limiting step in this dissolution mechanism. Some organic ligands can also thermally reduce Fe(III) at the surface, greatly decreasing the strength of its bonds with its neighbors, further promoting dissolution. This process can be catalyzed by electron transfer from a solution Fe<sup>2+</sup> to the Fe(III)-ligand surface complex. Reductive dissolution of Fe oxyhydroxides in the presence of NOM can be also catalyzed by light, through a ligand-to-metal charge transfer during light absorbance by the surface complex, producing an oxidized ligand molecule and weakly bound surface Fe(II), which slowly dissociates into solution (Sulzberger et al. 1989).

The purpose of this study was to determine the effect of prior photoirradiation on the interactions of NOM with the surface of the Fe oxyhydroxide mineral goethite, focusing on Fe-NOM interactions. Considering that NOM physicochemical properties

are altered by photoirradiation, we hypothesized that adsorption and Fe release mechanisms were also likely to be affected. We tested this hypothesis by comparing the adsorption to goethite of photo-irradiated versus non-irradiated NOM, following solution Fe(II):Fe(III) speciation and total Fe concentrations.

## 2 MATERIALS AND METHODS

### 2.1 Goethite and NOM samples

We used synthetic goethite (BET surface area = 51.5 m<sup>2</sup>/g), in a 4.85 g/L stock suspension in deionized water.

NOM-rich surface water was concentrated on-site from Nelson's Creek, a first-order stream in the Ottawa National Forest (MI, USA), using a portable RealSoft PROS/IS reverse osmosis (RO) system. Operation of the RO system included in-line treatment with Dowex-50 cation exchange resin (Na<sup>+</sup> form) to remove polyvalent cations prior to passing through the RO membrane. The final [DOC] of the retentate was 4.5 g C/L. Physicochemical characteristics of the RO isolate are provided in Maurice et al. (2004, this volume).

### 2.2 Batch Photoirradiation and Adsorption Experiments

Photodegradation and batch adsorption experiments were conducted at pH 3.5 and 5.5. For each pH, 1 L of 27 mg C/L stock solution was made by diluting RO retentate with deionized water (> 17.8 MΩ). The pH was adjusted to 3.5 or 5.5 using 0.1 M NaOH and 0.1 M HCl, after which the stock solution was split into two 500 mL volumes, one for irradiation and the other as a non-irradiated control. The non-irradiated control was stored in the dark at room temperature in a Parafilm M® covered glass beaker. The second half was irradiated in an acid-washed and combusted 1 L jacketed beaker, through which cooled water was circulated to maintain a constant sample temperature of 18°C during the irradiation process. The NOM sample was placed in a Suntest CPS+ solar simulator and irradiated for 48 hours at a dosage of 750 W/m<sup>2</sup>, ~2-3 times the intensity of noontime summer sunlight. The final collective irradiation dosage to a sample was 129,600 kJ/m<sup>2</sup>.

Immediately following irradiation, batch-mode adsorption experiments were conducted at pH 3.5 and 5.5. The irradiated and non-irradiated stock solutions were diluted with deionized water to a range

of concentrations, including NOM-free blanks. 1.0 M NaClO<sub>4</sub> was added to obtain a final electrolyte concentration of 0.1 M NaClO<sub>4</sub> and the pH of each was adjusted to either 3.5 +/- 0.1 or 5.5 +/- 0.1 (as appropriate) using dilute NaOH and HCl. 23 mL of each dilution were then added to 4 acid washed polypropylene centrifuge tubes and 2 mL of the goethite stock (or deionized water for control) was added to 3 of the 4 tubes. After the addition of goethite, the pH of each tube was readjusted. The samples were shaken for 24 hrs in the dark on a rotary shaker at room temperature. The samples were centrifuged at 13,500 rpm and filtered through pre-cleaned 0.2 μm PES filters. Samples for the analysis of total dissolved iron were immediately acidified to pH < 1 by adding 15 μL of trace metal-grade concentrated HCl to 5 ml of filtered sample. UV-Vis absorbance and iron(II) analyses were conducted immediately. Samples were stored in dark refrigeration until analyzed by other methods.

### 2.3 DOC, Fe, and NOM analysis

[DOC] was analyzed on a Shimadzu TOC-5000 analyzer. Total dissolved Fe concentrations were analyzed on a Perkin Elmer ICP-OES at 238.204 nm. Fe(II) analysis was conducted by Ferrozine colorimetric analysis at 562 nm using 1.0 cm quartz cuvettes on a Varian Cary 3 double beam spectrometer. The Fe(II) analysis used MES to buffer the pH at 6.0 so that the Ferrozine did not induce iron(III) reduction (Pullin and Cabaniss 2001).

High pressure size exclusion chromatography (HPSEC) was used to determine the average molecular weight (weight average, M<sub>w</sub>; number average, M<sub>n</sub>) of light-absorbing (254 nm) NOM (Zhou et al., 2000). The analysis was calibrated using random coil polystyrene sulfonate polymers (PSS; Polysciences, Inc., PA), acetone, and sodium salicylate. Low molecular weight (LMW) carboxylic acids were measured by the ion-pairing reversed phased HPLC of their 2-nitrophenylhydrazide derivatives, as described in detail by Goldstone et al. (2002).

## 3 RESULTS AND DISCUSSION

### 3.1 Effects of irradiation on NOM and its sorption to goethite

Photoirradiation resulted in a decrease in high molecular weight components, and an increase in low molecular weight components, together leading to substantial decreases in average molecular weight. (Table 1). Formic acid was produced in the highest

concentration at both pH values, followed by acetic and malonic acids (Progress et al., in review). At pH 5.5, we also observed a slight net increase in oxalic acid due to irradiation. These results are consistent with those of a number of researchers (e.g., Bertilsson and Bergh, 1999) who demonstrated that exposure of NOM to solar radiation results in cleavage of the higher molecular weight molecules to produce lower molecular weight photoproducts, with a consequent decrease in the average molecular mass.

Table 1. Change in NOM properties upon irradiation

Sample	[DOC] (mgC/L)	M <sub>w</sub> (Da)	M <sub>n</sub> (Da)
pH 3.5			
non-irradiated	27.4	2259	1446
irradiated	22.9	1209	771
pH 5.5			
non-irradiated	33.8	2531	1593
irradiated	31.2	1197	791

Figure 1 shows adsorption isotherms for the non-irradiated and irradiated NOM at pH 3.5 and 5.5. At pH 3.5, non-irradiated NOM adsorption did not attain a clear plateau over the range of concentrations studied herein. However, the greatest observed adsorption density was up to  $\sim 2$  times larger for non-irradiated than irradiated samples,  $0.37 \pm 0.03$  vs.

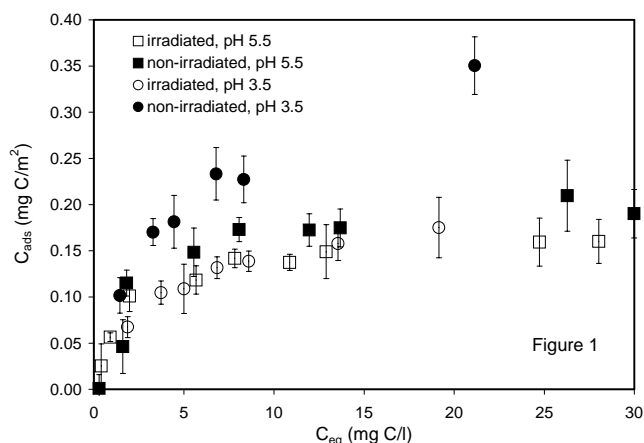


Fig. 1. Comparison of adsorption isotherms for irradiated and non-irradiated NOM on goethite at pH 3.5 and 5.5

$0.17 \pm 0.03$  mg C/m<sup>2</sup>. While the differences in the maximum adsorption density between the non-irradiated ( $0.18 \pm 0.02$  mg C/m<sup>2</sup>) and irradiated NOM ( $0.15 \pm 0.01$  mg C/m<sup>2</sup>) were smaller at pH 5.5, their difference was still statistically significant (95% confidence level, t-test). In agreement with results of previous studies (e.g., Tipping, 1981; Zhou et al., 2001), we observed that adsorption of non-irradiated NOM to goethite decreased with decreasing pH from 5.5 to 3.5. However, in the case of the irradiated NOM, the difference between the maximum adsorption density at pH 5.5 and the greatest observed adsorption at pH 3.5 was much smaller.

As described in detail by Progress et al. (in review), adsorption of non-irradiated NOM at pH 3.5 to 5.5 was dominated by the most abundant intermediate molecular weight (1251-3750 Da) fraction, although the 451-250 and 3751-11350 Da fractions also contributed to adsorption at pH 3.5. The substantial decrease in NOM adsorption affinity at pH 3.5 after irradiation was primarily due to the loss of components in the 1251-3750 and 3751-11350 Da fractions. At pH 5.5, the loss of components in the 3751-11350 Da fraction upon irradiation had little effect on adsorption because they played little or no role in the non-irradiated sample at this pH; therefore, irradiation resulted in only a small decrease in overall NOM adsorption affinity at pH 5.5.

### 3.2 Effects of irradiation on Fe-NOM interactions

Figures 2 and 3 show the effects of irradiation and adsorption on the total dissolved Fe concentration and the dissolved Fe(II) concentration at pH 3.5 and 5.5 ( $< 0.2$   $\mu$ m). At pH 3.5, the majority of the iron is initially present as Fe(II), both before and after irradiation, although Fe(II) increases upon irradiation. The presence of Fe(II) in the non-irradiated sample is due to thermal (or “dark”) reduction of Fe(III) by reducing moieties on the NOM, possibly quinines or catechols (Pullin and Cabaniss 2003b).

At pH 5.5, only about 20% of the total iron was present as Fe(II), prior to irradiation. This is due to slower rates of thermal reduction and faster rates of oxidation at this pH value, relative to pH 3.5 (Voelker and Sulzberger, 1996; Pullin and Cabaniss, 2003a,b). After irradiation, Fe(II) increased to  $\sim 50\%$  of the total Fe. The equilibrium Fe(II) is smaller after irradiation at pH 5.5 than at pH 3.5. This is due to faster rates of Fe(II) oxidation and slower rates of photoreduction at the higher pH.

Following the reaction of non-irradiated NOM with goethite at pH 3.5, the concentration of Fe(II) increased a small amount, and that of Fe(III) (= total Fe - Fe(II)) increased considerably more, suggesting ligand-promoted dissolution by the NOM. Exposure of the goethite to the irradiated sample increased Fe concentrations almost exclusively as Fe(II), suggesting reductive dissolution by the NOM or by some other photo-produced reductant, indicating a possible shift in mechanism. However, it is also possible that ligand-promoted dissolution occurred through a non-reductive mechanism, followed by thermal reduction of Fe(III) to Fe(II) in solution. Additionally, overall dissolution was greater with the non-irradiated sample, suggesting that the highest molecular weight fraction, which was removed by irradiation, played an important role in dissolution in

the non-irradiated sample.

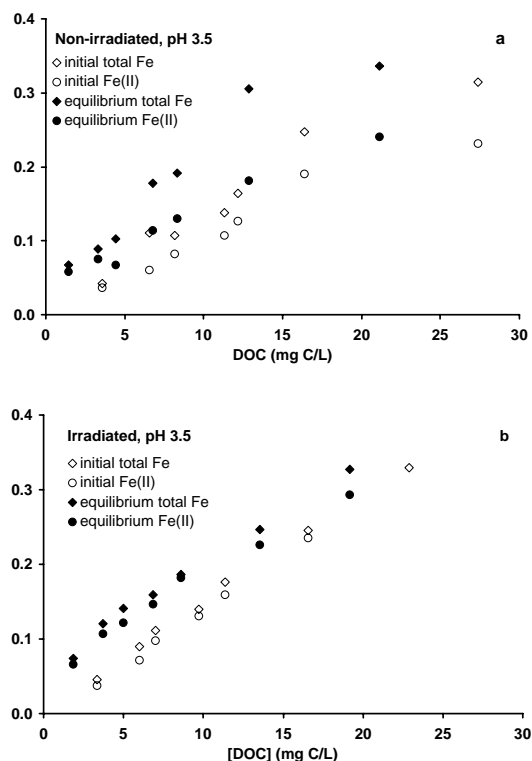


Figure 2. Comparison of Fe(II) and total Fe concentrations prior to and following reaction of non-irradiated (a) and irradiated (b) NOM with goethite at pH 3.5.

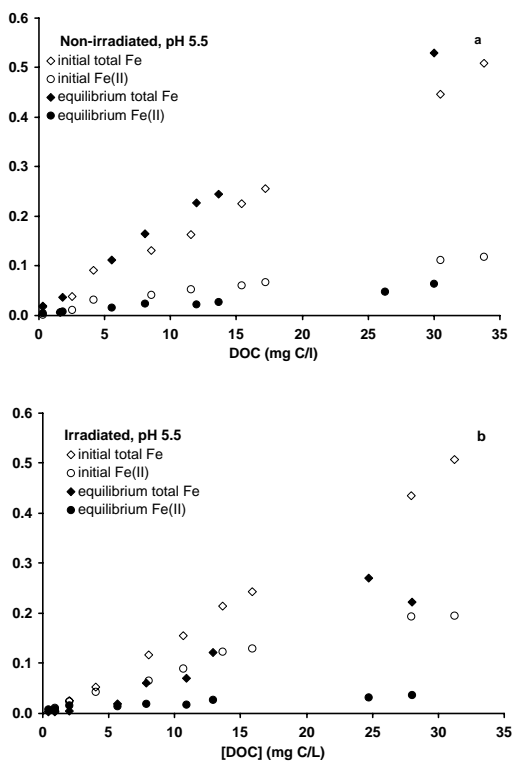


Figure 3. Comparison of Fe(II) and total Fe concentrations prior to and following reaction of non-irradiated (a) and irradiated (b) NOM with goethite at pH 5.5.

At pH 5.5, with non-irradiated NOM, total increased slightly during adsorption, indicating net dissolution. However, Fe(II) decreased during NOM adsorption, suggesting Fe(II) adsorption to the

goethite surface, or Fe(II) oxidation. In contrast, at pH 5.5 with irradiated NOM, Fe(II) and total Fe concentrations both decreased substantially upon reaction of NOM with goethite. Since Fe(II) was initially a larger fraction of the total iron in this case, this suggests that the Fe(II) generated by the irradiation process adsorbed to the goethite surface, or that it was transformed first to Fe(III) and then adsorbed.

#### 4 ACKNOWLEDGMENTS

We thank the National Science Foundation (hydrologic sciences) for funding this research. We thank the CEST and EMSI at Notre Dame for use of analytical equipment.

#### REFERENCES CITED

- Bertilsson, S. and Bergh, S. (1999) Photochemical reactivity of XAD-4 and XAD-8 adsorbable dissolved organic compounds from humic waters. *Chemosphere* **39**, 2289-2300.
- Emmenegger, L., Schönenberger, R., Sigg, L., and Sulzberger, B. (2001) Light-induced redox cycling of iron in circumneutral lakes. *Limnol. Oceanogr.*, **46**, 49-61.
- Progress, C.A., Pullin, M.J., and Maurice, P.A. Effects of photoirradiation on the adsorption of dissolved organic matter to goethite. In review.
- Pullin, M.J. and Cabaniss, S.E. (2001) Colorimetric flow-injection analysis of dissolved iron(II) and total iron in natural waters containing dissolved organic matter, *Water Res.* **35**, 363-372.
- Pullin, M.J. and Cabaniss, S.E. (2003a) The effects of pH, ionic strength, and iron redox state on iron-fulvic acid interactions. I. Iron(II) oxidation and iron colloid formation., *Geochim. Cosmochim. Acta*, in press.
- Pullin, M.J. and Cabaniss, S.E. (2003b) The effects of pH, ionic strength, and iron redox state on iron-fulvic acid interactions. II. The kinetics of complexation and dark reduction., *Geochim. Cosmochim. Acta*, in press.
- Sulzberger, B., Suter, D., Siffert, C., Banwart, S., and Stumm, W. (1989) Dissolution of Fe(III)(hydr)oxides in natural-waters - laboratory assessment on the kinetics controlled by surface coordination. *Mar. Chem.* **28**, 127-144.
- Tipping, E. (1981) The adsorption of aquatic humic substances by iron oxides. *Geochim. Cosmochim. Acta* **45**, 191-199.
- Voelker, B.M. and Sulzberger, B. (1996) Effects of fulvic acid on Fe(II) oxidation by hydrogen peroxide. *Environ. Sci. Technol.* **30**, 1106-1114.
- Voelker, B.M.; Morel, F.M.M. and Sulzberger, B. (1997) Iron redox cycling in surface waters: Effects of humic substances and light. *Environ. Sci. Technol.* **31**, 1004-1011.
- Zhou, Q., Cabaniss, S.E., and Maurice, P.A. (2000) Considerations in the use of high-pressure size exclusion chromatography (HPSEC) for determining molecular weights of aquatic humic substances. *Water Res.* **34**, 3505-3514.
- Zhou, Q., Maurice, P.A., and Cabaniss, S.E. (2001) Size fractionation upon adsorption of fulvic acid on goethite: Equilibrium and kinetic studies. *Geochim. Cosmochim. Acta* **65**, 803-812.