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The role of iron and dissolved organic carbon in the absorption of ultraviolet radiation in humic lake water

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Abstract. Absorption of solar ultraviolet radiation (UVR) in aquatic ecosystems is primarily controlled by dissolved organic carbon (DOC). The role of iron (Fe) has also been suggested to contribute to UVR attenuation either directly or by interactions with DOC. Here we present findings from three laboratory manipulations of Fe and DOC on changes to the dissolved UVR absorption ($a_{d,320}$) in a mid-latitude, dimictic, humic lake. In a laboratory simulation of lake turnover where anoxic, hypolimnetic water was oxygenated $a_{d,320}$ significantly increased from 23.3 to 81.7 m^{-1} ($p < 0.0001$). In a second laboratory experiment, addition of ferrous Fe to deoxygenated lake water increased $a_{d,320}$ upon reoxygenation up to a concentration of 1.0 mg l^{-1} Fe, where a solubility saturation threshold may have been reached. *In situ* lake experiments were designed to simulate release of UV absorbing substances from anoxic sediments by placing 20-l carboys (open at the bottom, sealed at the top) onto the lake bottom. UV absorption at 320 nm increased over time for samples from within the experimental carboys. Finally, samples from several lake profiles and sediment experiments were analyzed for $a_{d,320}$, total Fe, and DOC. UV absorption of dissolved substances at 320 nm and total Fe concentration both increased with depth, however DOC remained relatively constant over depth. Furthermore, total Fe and spectral slope showed tight coupling up to 1 mg l^{-1} total Fe in our survey analysis. Our results provide evidence for the importance of anoxic sediments as a source of ferrous iron and UV absorbing substances and suggest a role for ferric iron in increasing UVR and PAR absorption in lake water. We suggest that as this ferrous Fe oxidizes, its absorptive properties increase, and it may bind with dissolved organic matter, enabling it to remain in solution and thus increasing the dissolved absorption of lake water for extended periods of time.

Introduction

The attenuation of solar ultraviolet radiation (UVR) in aquatic ecosystems, represented as $a(\lambda)$, can be expressed by:

$$a(\lambda) = a_{\text{phyto}}(\lambda) + a_{\text{CDOM}}(\lambda) + a_{\text{det}}(\lambda) + a(\lambda) \qquad (1)$$

where a_{phyto}, a_{CDOM}, a_{det} and a_{w} represent absorption due to phytoplankton, chromophoric dissolved organic matter (CDOM), detritus, and water respectively. CDOM refers to chromophoric moieties; i.e., UVR absorption is localized to specific molecular substructures of dissolved organic carbon (DOC) compounds (Larson and Weber 1994). A current paradigm suggests that CDOM is responsible for most dissolved absorption in lakes (Williamson et al. 1999), though particulate absorption appears to be relevant seasonally (Scully and Lean 1994; Morris et al. 1995), most likely due to lake mixing and re-distribution of particles. Two recent reviews of photochemistry and photobiology in aquatic ecosystems have emphasized the effects of UVR on natural waters (Hansell and Carlson 2002; Hebling and Zagarese 2003).

As CDOM and UVR interact, several important photochemical reactions have been observed. Exposure to UVR caused the photochemical degradation of DOC in humic lake water, converting organic C to inorganic C (Salonen and Vahatalo 1994; Lindell et al. 1995; Morris and Hargreaves 1997). This effect has been described as the photochemical decarboxylation of DOC (Chen et al. 1978; Miles and Brezonik 1981; Budac and Wan 1992) and a major reaction producing this effect is the 'photo-Fenton' reaction caused by reduction of ferric iron to ferrous iron (Zepp et al. 1992). Redox cycling of iron between Fe(III) and Fe(II) has been reported for numerous surface waters (Mcknight et al. 1988; Voelker et al. 1997; Barbeau et al. 2001; Emmenegger et al. 2001), and a specific photochemical pathway involving carboxylate moieties has been determined. Numerous studies have shown that iron is highly correlated with color in water samples (Carpenter and Smith 1984; Pennanen and Frisk 1984; Heikkinen and Ihme 1995) and when in complexation with organic compounds absorbs light in the UVR range. Thus, dissolved Fe may be an overlooked source of dissolved absorbance in lake ecosystems with appreciable humic content.

Humic substances (HS) have been shown to maintain Fe solubility in aqueous environments (Shapiro 1964, 1966; Ghassemi and Christman 1968; Wetzel 2001). HS and Fe interact to form complexes, which allow Fe to remain in solution under conditions out of which it would otherwise precipitate. Shapiro (1964, 1966) first showed that HS form such complexes with Fe. His findings were further supported by studies showing that iron forms complexes with various measurements of DOM: (1) HS, chemically isolated by resin chromatography (Peuravuori and Pihlaja 1997), (2) high molecular weight DOM, isolated by tangential flow filtration (Benner et al. 1997), and (3) DOC, measured with a TOC aqueous analyzer (Benner and Hedges 1993). There appears to be ample evidence that Fe and DOC form complexes that remain in solution and affect water color, thus absorbing UVR.

In mid-latitude, dimictic lakes, Fe-humic compounds may be transported from the lake's bottom to the lake's surface by advective mixing. During warm summer months, when these lakes are stratified, the deep layer (hypolimnion) may accumulate high concentrations of nutrients and ions, mainly from the microbial respiration of organic matter and from sediment release (Wetzel 2001). Often the hypolimnion of these lakes goes anoxic where reduced species are entrained in the hypolimnion due to thermal stratification. In these anoxic waters, iron occurs as Fe(II) due to the reducing environment. When the epilimnion deepens, oxic waters mix with the anoxic hypolimnion, oxidizing dissolved Fe(II), which may precipitate out of the water column into the sediments (Hamilton-Taylor et al. 1996). Some Fe, however, may remain in solution by its continued complexation with HS (Shapiro 1964, 1966; Ghassemi and Christman 1968; Heikkinen and Ihme 1995). Eventually, fall turnover creates a well-mixed water column that is completely oxygenated.

This study reports results from two laboratory experiments, and one *in situ* experiment in a humic lake in northeastern Pennsylvania, designed to investigate the effects of reoxygenation of anoxic hypolimnetic waters rich in iron on dissolved absorption. The first laboratory experiment examined the effect of oxygenation on initially anoxic hypolimnic water, in effect a simulation of fall turnover in dimictic lakes. The second laboratory experiment involved the addition of ferrous Fe to deoxygenated lake water to determine the effects of iron on UVR absorbance. The third experiment used experimental chambers, *in situ*, to follow release of UV-absorptive species from sediments in the hypolimnion of our study lake.

Methods

The study lake was Lake Lacawac, a humic, mesotrophic lake located in the Pocono Plateau Region of northeastern Pennsylvania (41°22′57″ N 75°17′35″ W). Lake Lacawac has a drainage area of 0.70 km^2, surface area of 0.214 km^2, volume of 4.88×10^6 m^3, and maximum depth of 13.0 m (Moeller et al. 1995, unpubl.). The lake has an average epilimnion DOC value of 4.8 mg C l^{-1} and a pH of 5.8–6.4 (Moeller et al. 1995, unpubl.). The hypolimnion starts to form in mid to late June and remains stable through early October, prior to fall turnover.

Oxygenation experiment

Three replicate water samples from 2 and 11 m were collected with a Van Dorn water sampler on 16 October 1999. Each sample was placed into an acid-washed, pre-combusted (450 °C, 5 h minimum) 310 ml biological oxygen demand (BOD) bottle that was filled from the bottom and allowed to overflow for approximately 10 s and then sealed. This procedure ensured that each sample was not affected by aeration during sample transfer. The 2-m sample was representative of oxic, epilimnetic water from the mixing layer and the 11-m sample represented anoxic, hypolimnetic water. Samples were transported on ice to the laboratory. A subsample was immediately drawn into a 10-cm^3 syringe from the bottom of each BOD bottle. The syringe was fitted with a Whatman GF/F glass fiber filter (effective mesh size, 0.7 μm) to maintain anoxic conditions and mechanical sterilization. After initial measurements of dissolved absorption (average of 10-nm bandwidths around 320 nm, $a_{d,320}$), the samples were gently aerated for 2 h. Subsamples were taken hourly and absorption and dissolved oxygen (DO) values were recorded. Dissolved absorption was measured on a Shimadzu PC-160 PLS UV–vis spectrophotometer with a 1 cm quartz cuvette. Samples were referenced to air and deionized water blanks were used to correct for scatter by the cuvette. Absorbance scans were made from 200 to 800 nm and raw absorbance units were converted to dissolved absorption coefficients ($a_{d,\lambda}$):

$$a_{d,\lambda} = (A_{\mathrm{sample},\lambda} - A_{\mathrm{water},\lambda}) \times 2.303/l \tag{2}$$

where A denotes raw absorbance, λ denotes wavelength in nm, and l denotes path length (m) in the spectrophotometer cuvette; modified from Kirk (1994).

Addition of known [Fe] to forced anoxic lake samples

On 22 February 2000, we used a peristaltic sampling pump with clean tubing to collect 10 l of water in two 5 l polycarbonate bottles from 1 m depth below ice cover. This water was filtered through a pre-combusted (450 °C for at least 4 h) Whatman GF/F filter. Two liters of this water were deoxygenated by purging with argon gas in two, 1 l beakers for 30 min. One liter of deionized water was deoxygenated by purging with argon for 30 min. Powdered $Fe(II)SO_4$ (2.728 g) was added to deionized water to create a 250 ml, 250 mg l^{-1} Fe(II) stock solution. We then added 10 ml of the stock solution to a 250 ml Erlenmeyer flask and then filled the flask with the anoxic lake water for a 10.0 mg l^{-1} Fe solution. From this solution, we then made treatments of 0.01, 0.1, 1.0, 2.0, and 4.0 mg l^{-1} Fe for the experiment. Three replicates of each experimental solution were placed into 60 ml acid-washed, pre-combusted BOD bottles. Three replicates of the unspiked, forced anoxic lake water were placed into 60 ml BOD bottles as a control. Subsamples were drawn into a 10 cm^3 syringe with a Whatman GF/F filter attached to it at 0, 4.5, 8.5, 19.5, and 43.5 h after the start of the experiment with dissolved absorption and DO values measured as described above. The samples were allowed to reoxygenate by allowing uncapped BOD bottles to equilibrate with the atmosphere.

DOC, total Fe, and dissolved absorption in Lake Lacawac

Thirty-four water samples were analyzed for $a_{d,320}$, DOC, and total Fe concentration. The 34 samples were from two Lake Lacawac profiles that were collected with a Van Dorn water sampler on 12 August 1999 (representing a stratified lake) and on 5 December 1999 (representing a mixed lake) and from two lake bottom experiments of 16 August 1999 and 22 August 1999. For the lake profiles, samples were collected from 0 to 12 m at 1 m intervals (samples were not taken at the 1, 3, and 5 m depths) in August and at 3, 6, and 10 m in December ($n = 12$).

In our lake bottom experiments, designed to mimic formation of an anoxic hypolimnion, we placed four-20-l carboys (with bottom removed) into the bottom sediment of the lake at a depth slightly above the anoxic waters of the lake. We fitted a two-holed rubber stopper in the mouth of each carboy and secured it with electrical tape. Two pieces of Teflon tubing were inserted through the stoppers; one tube was 1 m long and used for sampling by attaching a 60 cm^3 syringe to it, while the other was approximately 10 cm and re-supplied the lake water taken during collection. Two samples were taken, with the first sample used as a rinse and discarded. For the first experiment, we placed the four carboys at 5.2 m (deepest depth with adequate visibility and above the hypolimnion) and the experiment was conducted from 16 August to 22 August 1999. One initial sample was taken from each carboy and two samples were taken outside the carboys as a control. At the end of the 6-day period, each carboy was sampled again along with the two outside (control) samples. Initially we thought a 6 day period was long enough for the water inside the carboy to reach the hypolimnetic $a_{d,320}$, however after 6 days we only reached an average of 9.2 m^{-1}; a subset of samples from only two carboys and the water column samples were used in the survey analysis (n = 6). Unfortunately, we already redeployed the carboys for the second trial. The four carboys were redeployed on 22 August 1999 at 5.2 m for the start of a second trial and we allowed the second trial to run for a 12 day period sampling every 6 days (22, 28 August and 3 September 1999). We reached the range in hypolimnetic $a_{d,320}$ for the 12 August 1999 profile from 10 to 11 m of 26.2–46.1 m^{-1} on the 3 September 1999 sampling date (mean carboy $a_{d,320}$ = 45.2 m^{-1}). Unfortunately as a result of experimental design limitations we could not measure DO concentrations with the carboys. We lost one sample during retrieval and one during laboratory analysis (n = 16). SCUBA equipment was used to deploy the carboys and to collect the samples.

DOC was measured on a Shimadzu TOC-5000 total Organic Carbon Analyzer and $a_{d,320}$ values were measured as described above. In addition to $a_{d,320}$ measures, we also computed spectral slope (S) to examine the relationships between total Fe and DOC and the entire UV range. We calculated S as the slope of the ln transformed values of absorbance for UV-A and UV-B (280–400 nm) vs. wavelength after background correction (background value was the mean absorbance between 750 and 800 nm). Total Fe concentration (Fe(II) + Fe(III)) were measured using inductively coupled plasma atomic-emission spectrometry (ICP-AES) with an ARL 34000 spectrophotometer, where filtered samples and standards were acidified to a pH of approximately 1.5 with HCl.

Results and discussion

The aeration of oxic and anoxic lake samples showed different $a_{d,320}$ patterns (Figure 1). A two-way ANOVA revealed that the average $a_{d,320}$ significantly increased for the 11-m samples from 23.3 to 81.7 m^{-1} over 1 h ($p < 0.0001$,

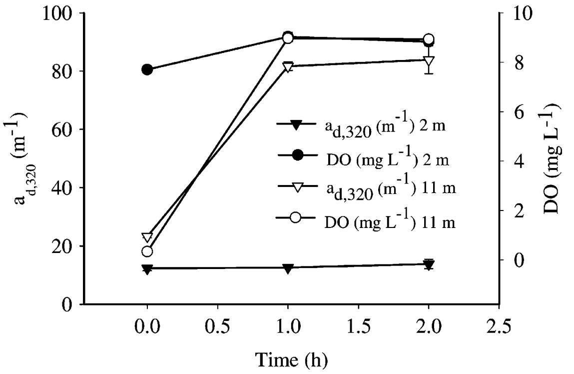

Figure 1. $a_{d,320}$ and dissolved oxygen following aeration of the 2- and 11-m water samples collected on 16 October 1999. The initially anoxic 11-m sample significantly increased in $a_{d,320}$ by 1 h, while the initially oxygenated 2-m sample did not. Error bars are SE's.

$n = 3$), but not for the 2-m sample ($p = 0.92$). In both the 2- and 11-m samples, $a_{d,320}$ did not significantly change from 1 to 2 h ($p = 0.71$ and 0.48, respectively). This suggests rapid oxidation of Fe(II) to Fe(III) of the anoxic lake water accompanied the increases in dissolved absorption and DO.

In all Fe(II)-spiked solutions $a_{d,320}$ increased over time as samples became oxygenated; the results for the 0.01, 0.1, 1, and 10 mg Fe(II) l^{-1} are shown in Figure 2. A repeated measures analysis performed on SPSS version 10.0.5 (SPSS Inc.) showed that, with addition of Fe(II), there was a significant

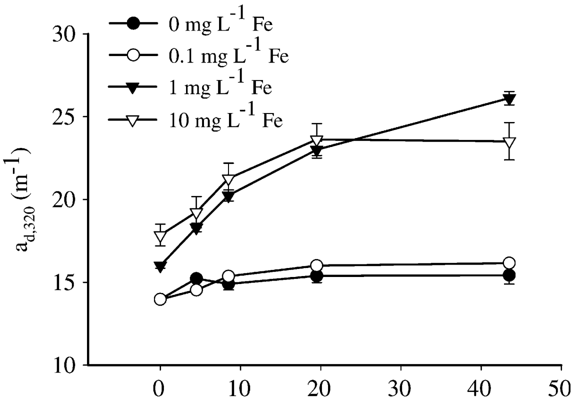

Figure 2. Absorbance increased during reoxygenation of Fe-spiked anoxic lake water. Oxygenated near-surface water low in Fe was initially purged to remove oxygen. Two sets of absorbance classes were shown by a *post hoc* Tukey's analysis, the control, 0.01, and 0.1 mg l^{-1} Fe (represented by the control and 0.1 mg l^{-1}) solutions and the 1.0, 2.0, 4.0, and 10.0 (represented by the 1 and 10 mg l^{-1}) solutions. Error bars are SE's. See Section Results for significance values.

difference in $a_{d,320}$ over time between the samples ($p < 0.05$, $n = 3$). A Tukey's *post hoc* analysis revealed two subsets in the samples. In the first subset, $a_{d,320}$ of the control, 0.01 and 0.1 mg l^{-1} Fe(II) were not significantly different from each other ($p = 0.68$, $n = 3$), and in the second subset the 1.0, 2.0, 4.0, and 10.0 mg Fe(II) l^{-1} were not significantly different from each other ($p = 0.06$, $n = 3$). This analysis seems to suggest a saturation effect on UV absorption of Fe(II) addition above 1.0 mg Fe(II) l^{-1}. It is clear from these experiments that the redox cycling of Fe(II) to Fe(III) coincides with a drastic increase in $a_{d,320}$.

The relationship between total Fe, DOC, and $a_{d,320}$ is apparent when we compared the mid-August and early December 1999 profiles (Figure 3). In August, Lake Lacawac was well-mixed only to about 5 m, and below 8 m the lake was anoxic. Figure 3a shows an increasing total Fe concentration and dissolved absorption below 8 m. Total Fe markedly increased from 0.18 to 2.81 mg l^{-1} (1461%) between 8 and 11 m and $a_{d,320}$ increased from 10.5 to

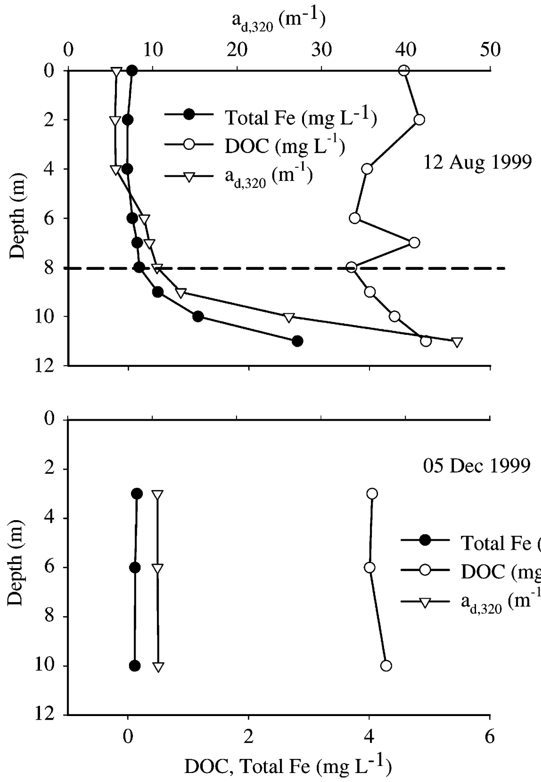

Figure 3. DOC, total Fe and $a_{d,320}$ values vs. depth for 12 August and 5 December 1999 lake profiles, bottom x-axis is total Fe and DOC concentrations and top x-axis is $a_{d,320}$ for both panels. In the 12 August 1999 profile, total Fe and $a_{d,320}$ increased below 8 m (depth of anoxic layer, indicated by dashed line) while DOC remained relatively constant. This trend was not apparent in the 5 December 1999 profile of the well-mixed lake.

46.1 m^{-1} (339%); whereas DOC concentration remained relatively constant (3.7–4.9 mg C l^{-1}, 32%). The increase in $a_{d,320}$ was most likely due to the oxygenation of anoxic waters during sample transport and processing, as were observed in the carboy experiments. This relationship was not seen in the 5 December profile and we suggest this is due to lake turnover, which had occurred in October and had eliminated the anoxic layer (Figure 3b). Total Fe, $a_{d,320}$, and DOC exhibit equal distributions throughout the water column, indicating the lake was well-mixed. An interesting feature of the December profile is that $a_{d,320}$ is approximately 10 m^{-1}, although total Fe was near zero.

The strong correlation between total Fe and $a_{d,320}$ was also seen in the 22 August to 3 September 1999 lake bottom experiment designed to simulate anoxia and release of dissolved Fe from the sediments. Unfortunately, we were unable to measure DO concentration inside the carboys to confirm anoxia, but we did observe trends indicating release of iron from the sediments. From subsamples collected inside the carboys, $a_{d,320}$ increased with total Fe while DOC remained relatively constant (Figure 4). We did not detect any change in total Fe, $a_{d,320}$, nor DOC in subsamples collected outside the carboys. Because we did not keep the subsamples anoxic, the increases in $a_{d,320}$ we measured were likely due to the oxidation of Fe(II) to Fe(III) in our subsamples prior to measurement.

These results provide circumstantial evidence that oxidized iron is contributing to the dissolved absorption in Lake Lacawac. Note that the minima of $a_{d,320}$ in the near surface waters (< 4 m) of the 12 August profile (Figure 3a) is suggestive of CDOM photobleaching, a phenomenon documented previously for this lake (Morris and Hargreaves 1997, but see Osburn et al. 2001b). An alternative interpretation of this profile is a tight coupling between total Fe and $a_{d,320}$ rather than photobleaching. Moreover, prior work in Lake Lacawac by Morris et al. (1995) showed that DOC was strongly coupled to dissolved absorption.

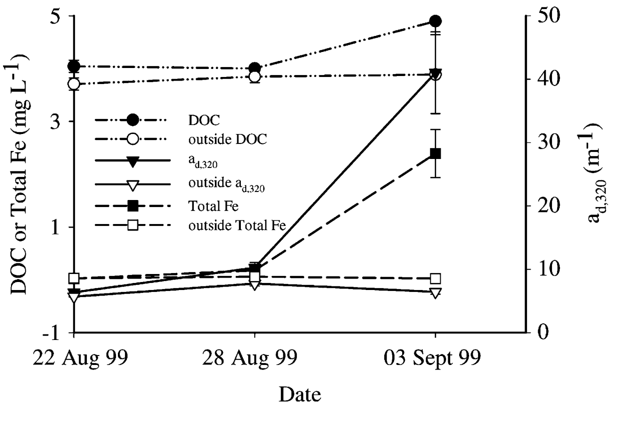

Figure 4. DOC, total Fe and $a_{d,320}$ values vs. time for the *in situ* lake bottom experiment. Error bars are SE's.

Therefore, we tested whether DOC or total Fe was a better predictor of $a_{d,320}$. Figure 5 shows two approaches to this analysis. In Figure 5a, we examined the relationship between $a_{d,320}$ and total Fe and DOC in an attempt to partition dissolved absorption into its DOC and total Fe components. Nearly all the variability in $a_{d,320}$ was explained by total Fe concentration ($r^2 = 0.99$, $n = 34$) as opposed to DOC concentration ($r^2 = 0.60$, $n = 34$). From this analysis, we conclude that total Fe, likely in complexation with DOC, is controlling UV absorption more so than DOC. Furthermore, our analysis suggests that total Fe exerts a remarkable control on water column dissolved absorption – as evidenced by the water column profiles shown in Figure 3.

Similarly, we found a strong correlation between carbon specific $a_{d,320}$, $a_{d,320}$ divided by the DOC concentration, and total Fe ($r^2 = 0.99$, $n = 34$; Figure 5b). This correlation is compelling; although total Fe was highly

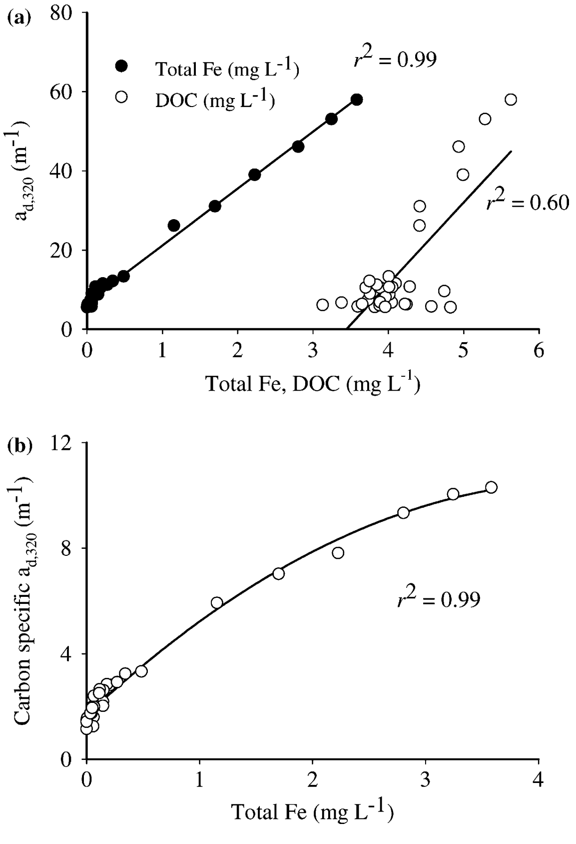

Figure 5. (a) Correlation between total Fe and carbon specific $a_{d,320}$ from the 34 samples analyzed. Total Fe and carbon specific $a_{d,320}$ shown a high correlation $r^2 = 0.99$ following the quadratic equation, $a_{d,320}/\mathrm{DOC} = 1.66 + 4.01([\mathrm{Fe}]) - 0.45([\mathrm{Fe}])^2$. (b) Total Fe was more highly correlated with $a_{d,320}$ than was DOC.

correlated with $a_{d,320}$ (r^2 = 0.99), it did not account for the entire range of carbon specific $a_{d,320}$, which is evident by the trend line not passing through the origin (Figure 5b). This predicted 'Fe-free' carbon specific $a_{d,320}$ (1.66) is residual absorption and falls near values reported previously for Lake Lacawac (1.23, Morris et al. 1995) and for other humic, northeastern US lakes (1.69, L. Waynewood and 1.48, L. Wallenpaupak; Morris et al. 1995). Thus our results suggest that DOC played a large role in $a_{d,320}$ when total Fe concentration was <0.1 mg l^{-1}, however $a_{d,320}$ was largely controlled by total Fe at concentrations >0.1 mg l^{-1}.

Total Fe was related to the spectral slope from 280 to 400 nm ($S_{280\text{–}400}$) following a logistic model:

$$S_{280\text{-}400} = 0.0116 + \frac{0.0067}{1 + \left[\frac{[Fe]}{0.2368}\right]^{0.858}} \tag{3}$$

where [Fe] is the concentration of total iron (r^2 = 0.93, $p < 0.0001$). This relationship reached a minimum near 1 mg l^{-1} Fe suggesting a threshold was reached whereby increased total Fe had no further effect on spectral slope (Figure 6a). This implies that as total Fe increases, up to ~1 mg l^{-1} Fe, UV absorbance increases. This trend was not evident with DOC (Figure 6b).

The decrease in S with increasing total Fe suggests a major control on visible light (PAR) penetration in the water column of Lake Lacawac. In general, spectral slopes are useful for distinguishing source and reactivity of CDOM in natural waters. Steeper slopes (increasing S values) are often interpreted as resulting from autochthonous DOC production or prior photobleaching (Morris and Hargreaves 1997; Vodacek et al. 1997). In Figure 6b, S decreases with increasing DOC concentration, though much scatter exists in the data. An interpretation of this trend could be that lower DOC concentrations corresponding to higher S values may indicate photooxidation of DOC in surface waters. Figure 6a, however, offers a very different interpretation. The most dramatic increase in S is between a total Fe concentration of 0–0.5 mg l^{-1}, and corresponds to a range of S values normally encountered in fresh waters (Markager and Vincent 2000). Above a concentration of 1 mg l^{-1} total Fe, S decreases monotonically to a value of ca. 0.0135 nm^{-1} and the amount of variance in S explained by total Fe is much higher than explained by DOC. The interpretation of these data thus suggests a change in S governed by Fe–DOC relationships that were observed experimentally and not by prior photooxidation of DOC.

We suggest that this Fe–DOC governed change in S is strong evidence for the control of PAR in addition to UVR in surface waters by total Fe, a phenomenon not previously reported to our knowledge. Moreover, availability of PAR to phytoplankton is obviously important for aquatic photosynthesis. Given the importance of Fe availability for photosynthesis, we further suggest a greater importance for Fe in lake ecosystem metabolism than previously recognized.

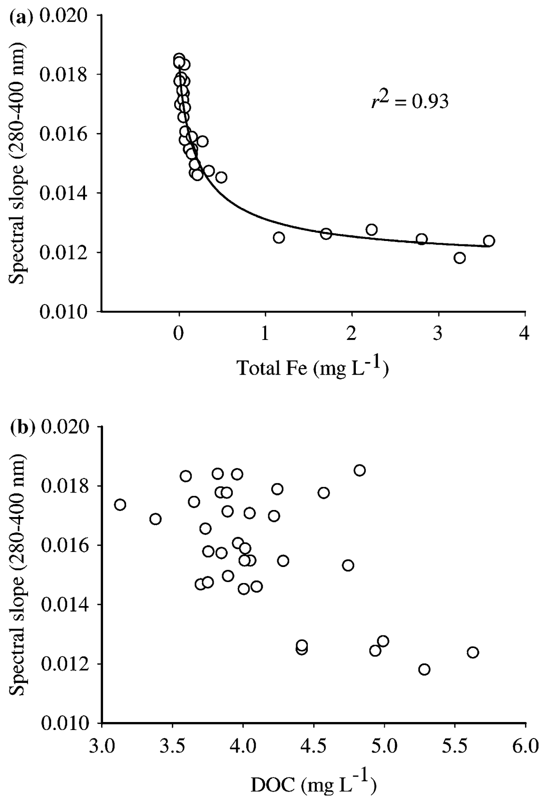

Figure 6. Relationship between total Fe (a) and DOC (b) with spectral slope from 280 to 400 nm. Total Fe was a better predictor of the decrease in the spectral slope, which followed a logistic model (see text), than did DOC, reaching a threshold near 1 mg l^{-1}. DOC was weakly, but not significantly, correlated with spectral slope.

The results from our laboratory and *in situ* carboy experiments suggest that when anoxic hypolimnetic waters reach the epilimnion, existing reduced iron undergoes oxygenation producing an increase in UV absorptivity above that of chromophoric DOC alone. This was evident from our observations that dissolved UV absorption and total Fe concentration increased while DOC remained relatively stable (Figures 1 and 4). Additionally, aeration of the Fe(II)-spiked anoxic water produced increases in $a_{d,320}$ that were initially correlated with Fe concentration but which seemed to reach a threshold above 1 mg l^{-1} total Fe. In addition, total Fe and spectral slope showed tight coupling up to 1 mg l^{-1} in our survey analysis. These results suggest that a solubility saturation concentration was reached, above which the additional Fe might have precipitated and did not affect dissolved absorption. Shapiro (1964) has previously reported reaching a pH dependent solubility saturation threshold with the addition of 2.2 mg l^{-1} Fe at a pH of 5 and 6.1 mg l^{-1} Fe at a pH of 6 in laboratory experiments (but see Drever 1997; Langmuir 1997).

The joint control of $a_{d,320}$ by Fe and DOC that we suspect in Lake Lacawac is a novel assertion, yet inherent in many reports of iron redox cycling in surface waters (Voelker et al. 1997; Gao and Zepp 1998; Emmenegger et al. 2001). For photochemical reactions to occur, photons must be absorbed, thus it is implicit that iron–DOC complexes absorb sunlight, but this does not explain why Fe(III)–DOC complexes are more absorptive than Fe(II)–DOC complexes. However, the ligand–metal charge transfer (LMCT) transitions from organic ligands to Fe(III) do have absorption in the UVR regions found in natural waters (Balzani and Carassiti 1970; Brezonik 1994) and Fe(III) complexes readily with ubiquitous organic acids such as acetic and citric acid. These acids contain carboxylate groups ($-COO^-$), which are the common ligands in Fe–DOC complexes and readily photodecarboxylate upon photolysis due to the LMCT.

Several reports have shown that exposure of DOC to UVR produces low molecular weight organic acids mentioned above (Dahlen et al. 1996; Bertilsson and Tranvik 1998; Bertilsson 2000). Given the ability of these compounds to form metal–ligand complexes, we hypothesize that the relevance of these processes to UV transparency in lakes such as Lake Lacawac lies in two issues that can be tested in future work. First, Fe–DOC complexes may comprise a substantial fraction of UV-absorbing chromophores in the CDOM of Lake Lacawac. Second, a chemical mechanism behind the process of photobleaching (or photochemical 'fading') not yet articulated in the literature may explain our results. In the anoxic hypolimnia of lakes with appreciable iron and DOC, Fe(III) existing as a complex bound to surface sediments is reduced to Fe(II), whereupon it mobilizes into the water column and accumulates in the anoxic hypolimnetic waters. Upon mixing and aeration of the water column, Fe(II) is oxidized to Fe(III) and forms complexes with DOC – the active sites for complex formation being the carboxyl groups. The coordination of the Fe(III) into the organic complex forms a colloid exhibiting UV absorptivity and increasing the overall absorptivity of the lake DOC. Some Fe(III) might precipitate out of the water with other compounds, including organic matter (Pizarro et al. 1995). The remaining iron either may stay in suspension or be held in suspension bound to DOC, thus increasing $a_{d,320}$. Finally, subsequent stratification and surface water mixing exposes some of this colloidal Fe–DOC complex to sunlight whereby photochemical reduction of Fe(III) to Fe(II) generates hydroxyl radicals (through photo-Fenton chemistry) that dissociate carboxyl groups from the larger humic structure. This effect lowers the molecular weight of the DOC and decreases its UV absorptivity, possibly a component of the mechanism that leads to the seasonal increased epilimnial transparency of Lake Lacawac observed previously by Morris and Hargreaves (1997).

Our findings are the first to report that the anoxic layer formation plays an active role in altering water column absorbance via the sediment mediated release of Fe during summer and early autumn in dimictic lakes. Most surprisingly, the spectral slope of CDOM decreased with increasing total Fe, indicating a stronger effect of iron on PAR dissolved absorption than UVR dissolved absorption. Our experimental manipulations suggest that Fe(II) may be transported throughout the water column during fall overturn where it is oxygenated to Fe(III) and complexes with DOC, producing an increase in dissolved absorption. This may, in part, explain the large increases in hypolimnion $a_{d,320}$ observed by Osburn et al. (2001a) for Lake Lacawac. Though our data do not support the chemical reactions mentioned, we find these reactions compelling and deserving of further investigation. In conclusion, we suggest that redox cycling of iron strongly affects UVR and PAR absorption in humic waters such that not all UV absorption in these systems may be attributed, *per se*, to chromophoric moieties of DOC.

Acknowledgments

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