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# Effects of salinity changes on the photodegradation and ultraviolet–visible absorbance of terrestrial dissolved organic matter

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*Abstract*

We performed laboratory studies to determine the effects of salinity on the photodegradation of dissolved organic matter (DOM) from the Great Dismal Swamp, Virginia, an important source of terrestrial DOM to the lower Chesapeake Bay. Samples were created by mixing Great Dismal Swamp water (ionic strength $\approx 0$ mol $L^{-1}$) with modified artificial seawater solutions of differing salinities while keeping the final dissolved organic carbon (DOC) concentration constant. These samples were then irradiated for 24 h in a light box providing ultraviolet (UV) light similar to that of natural sunlight. Light absorbance and DOC concentrations decreased after photoexposure, whereas dissolved inorganic carbon (DIC) concentrations increased. Variations in salinity affected both DIC production and UV absorption, with the higher salinity samples showing lower DIC production and less photobleaching. Addition of an iron chelator eliminated the relationship between photochemistry and salinity by reducing both photobleaching and DIC production at low salinities. As terrigenous DOM transits through an estuary, its photochemical reactivity and optical properties may change significantly as a function of salinity, probably as a result of changes in DOM conformation or changes in iron–DOM photochemistry, or both.

Understanding the cycling of aquatic dissolved organic matter (DOM) is important because DOM is a dynamic component in the global carbon cycle, acts as a nutrient source (either through direct uptake or as a substrate for remineralization), and provides ion exchange capacity within aquatic systems. As an absorber of visible and ultraviolet electromagnetic radiation, DOM can also significantly reduce both photosynthesis and photoinhibition of biota in surface waters. Photochemical processes resulting from this light absorption result in significant carbon remineralization (Miller and Zepp 1995) and transformation of organic matter (Mopper and Kieber 2002 and references therein). Photochemical alteration of DOM has been shown to affect the microbial bioavailability of DOM (e.g., Kieber et al. 1989), and coupled photochemical/microbial degradation is believed to be a major sink for terrestrial, microbially refractory DOM carried by many rivers (Kieber et al. 1990; Mopper and Kieber 2000). This coupled degradation mechanism could largely explain the low abundance of identifiable river-delivered terrestrial DOM within oceanic DOM (Hedges et al. 1997, and references therein).

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Coupled photochemical and microbial degradation of terrestrial DOM is most likely to occur in estuaries and adjoining continental shelves, where water-column light penetration becomes significant. Variations in the optical properties of DOM along estuarine transects have been noted by many researchers. On a spring transect from the Delaware River to the open ocean, Vodacek et al. (1997) found an essentially linear inverse relationship between salinity and fluorescence (at 355 nm) and attributed it mainly to conservative mixing between river and seawater at that time of the year (in agreement with Kowalczuk et al. 2003). During other seasons, however, Vodacek et al. (1997) observed a nonconservative relationship between fluorescence and salinity, which they attributed to photodegradation of colored DOM on the continental shelf. In a study of the Mississippi and Atchafalaya River systems, Sandvik et al. (2000) observed that very low salinity waters exhibited disproportionately greater production of photogenerated free radicals (normalized to initial absorption). Complicating the applicability of this study to estuarine transects, however, is the fact that the DOM samples were ultrafiltered, lyophilized, and then reconstituted in $Na_2PO_4$ buffer at pH 10.8 prior to photoexposure. Furthermore, since the DOM sources were different between the samples, the observed trends cannot be attributed to salinity alone.

Estuaries are dynamic regions characterized by changes in salinity, DOM (both sources and sinks), the physical mixing regime, and light penetration. While the relative influences of these factors are difficult to resolve in natural systems, previous studies have shown that ionic strength can play an important role in affecting DOM molecular conformation (e.g., Chin and Gschwend 1991) as well as the complexation and solubility of trace-metal species (Liu and Millero 1999).

To our knowledge, the role of such ionic-strength variations on DOM photoreactivity has not yet been explicitly addressed. In this work, we conducted a series of experiments to determine whether salinity changes affect organic matter photodegradation when the initial natural-water input of dissolved organic and inorganic material is the same. Our motivation was to isolate and evaluate the role of salinity in the photoreactivity and potential fate of organic matter from a terrestrial source as it travels down an estuarine transect.

## Materials and methods

To determine the effects of salinity in the absence of other variables, laboratory experiments were conducted in which DOM-rich freshwater was mixed with varying concentrations of artificial seawater (ASW). The DOM-rich freshwater was collected in summer (09 June 2004) and winter (25 February 2005) via stainless steel bucket from Portsmouth Ditch in Great Dismal Swamp, Virginia. This site represents the freshwater end member of the Elizabeth River, which is a tributary of the lower Chesapeake Bay. After collection, the surface-water samples were transported to the laboratory (less than an hour away) and immediately filtered using 0.2-$\mu$m cartridge filters (Whatman Polycap) in order to remove microbes.

ASW was created by mixing combusted (organic free) NaCl and $MgSO_4$ with Elga Maxima ultrapure deionized water (DI; >15.0 M$\Omega$). Our artificial seawater composition is a compromise between experimental constraints (we must combust our salts to remove organic contaminants) and an attempt to mimic natural salt distributions (we want to have divalent cations, known to be important in flocculation processes). Owing to this compromise, our experimental "transect" has lower pH values than would be found in natural estuaries, especially at sites with high salinity. It also lacks $Ca^{2+}$ ions, known to be important in the coagulation/flocculation of organic matter. These caveats must be considered when comparing results from this study to natural systems in the literature; on the other hand, the between-treatment constancy in organic matter source and concentration allows for a simplified interpretation of ionic-strength effects on photodegradation that is not possible with field-based sampling regimes.

Experimental estuarine transects were generated by diluting Great Dismal Swamp water with mixtures of ASW and DI to create the desired salinity gradient (measured via refractometer). For the summer and winter experiments the dilution was one part Dismal Swamp water to one part ASW–DI. For the iron-chelator experiment, the dilution was one part Dismal Swamp water to three parts ASW–DI. These "transects" covered an ionic-strength range of ~0 to 0.56 mol $L^{-1}$ (a salinity range of 0 to 30). The pH of archived summer samples (dark storage at 4°C) was measured for salinities of 0 and 15 and found to be 4.4 and 4.5, respectively. The pH was measured for all winter sample treatments and fell within the range of 3.7 to 4.2 (mean = 4.0).

Following mixing, samples were allowed to flocculate overnight. The next day, approximately half of the water from each treatment was filtered through precombusted glass fiber filters (Whatman GF/F, nominal pore size = 0.7 $\mu$m) to remove flocculates. Filters from the summer experiment were saved for particulate organic carbon (POC) analysis. Aliquots of both filtered (Fil) and unfiltered (Floc) treatments were placed into 500-mL round bottom flasks. Quartz flasks were used for photoirradiated samples, and foil-covered borosilicate glass flasks were used for dark controls. With the exception of Floc controls from the summer samples (owing to sample volume constraints), all flasks were completely filled to eliminate headspace.

All flasks were irradiated for 24 h in a light box equipped with 12 Q-panel UV340 bulbs and a rotating table (1 rpm) to ensure even light exposure. The light box provides a spectral shape similar to that of natural sunlight from 295 to 365 nm (Q-panel) but underestimates ultraviolet (UV) light at wavelengths greater than about 365 nm. We compared our irradiations with natural sunlight by splitting a natural-water sample into aliquots and comparing the photobleaching (integrated over 250 to 400 nm) that occurred in the two light treatments. In this comparison 5 h in the light box provided 127% of the photobleaching occurring during 5 h of winter midday sunlight at 36°89′N latitude.

Following irradiation, aliquots were taken for UV–visible (UV–vis) spectroscopy, dissolved organic carbon

(DOC) and dissolved inorganic carbon (DIC) analyses, and bacterial counts.

UV–vis spectroscopy was performed using a Cary 3 Bio spectrophotometer (summer experiment) or a Hitachi U-2010 spectrophotometer (winter and desferrioxamine mesylate [DFOM] experiments). The absorbance spectra from wavelengths from 800 to 190 nm were measured using a 1.00 cm path length and were then blank corrected relative to DI water and background corrected using the wavelength range 700–800 nm.

DOC data were collected as nonpurgeable organic carbon performed on acidified samples using high temperature combustion on a Shimadzu TOC-5000 total organic carbon analyzer. Concentrations were determined from a four-point calibration curve and blank corrected against low-DOC DI water (Milli-Q). Periodic blanks and standards were used to monitor instrument performance. Peak areas were taken from the closest three of five replicate injections; the average coefficient of variation for replicate injections of the same sample was less than 2%.

For DIC analysis, sample was drawn into a 50-mL glass syringe from the bottom of the flask immediately after the flask was opened to minimize exposure to atmospheric $CO_2$. The syringe was wrapped with foil to avoid further light exposure and was connected directly to the sample inlet of a Shimadzu TOC-5000 total organic carbon analyzer configured for DIC analysis by acidification and sparging. Sample analyses were calibrated against a mixed standard (20 ppm C) of sodium carbonate and bicarbonate (1:1 mole ratio). In order to minimize error caused by instrumental variations, a standard was run immediately before and after each sample and the reported DIC concentration is based on the average of these two standards. Instrument precision (based upon replicate injections of the same sample) was less than $\pm 2$ $\mu$mol $L^{-1}$.

Potential bacterial contamination was monitored on formalin-preserved samples using an adaptation of the DAPI staining protocol (Porter and Feig 1980) followed by bacterial enumeration on a Zeiss Standard 16 epifluorescence microscope using an Omega bandpass 4′,6-diamidino-2-phenylindole (DAPI) filter set and $\times$1,000 magnification.

For the summer experiment, POC analysis was performed on replicate slices (0.6 cm diameter) taken from the GF/F filters and pelletized in tin cups. Prior to splitting and pelletizing, the GF/F filters were fumed over 12 mol $L^{-1}$ HCl for 24 h and dried at 100°C to remove carbonates. POC analysis was performed on a PDZ-Europa ANCA-GSL elemental analyzer with a 20-20 stable isotope analyzer. Owing to the small amounts of carbon detected, isotope values are not reported.

To evaluate the potential effects of iron on DOM photodegradation, an additional irradiation experiment was performed using DFOM, an Fe(III) chelator (Hudson et al. 1992). DFOM is reported to form a photochemically inert complex with Fe(III) that lacks light absorption at wavelengths greater than 295 nm and exhibits no Fe(II) photoproduction upon irradiation in a solar simulator (Gao and Zepp 1998). To determine the amount of DFOM necessary to complex Fe based on thermodynamic calculations (Morel and Hering 1993), the iron and copper concentrations within the winter Dismal Swamp sample were measured using a nitric acid–hydrochloric acid digestion and inductively coupled plasma–mass spectrometry. Aliquots of the sample were then diluted (one part Dismal Swamp water to three parts ASW–DI) and allowed to sit overnight, after which they were equilibrated with DFOM (10 $\mu$mol $L^{-1}$ final concentration) for 80 h; previous studies have used DFOM equilibration times ranging between 12 h (Gao and Zepp 1998) and 1 week (Brinkman et al. 2003). For comparison, salinity 0 and 5 samples without DFOM were also prepared and were included in the irradiation experiment. Because our previous experiments showed little to no difference between Floc and Fil samples, the DFOM experiment consisted of Floc samples only. At the end of the experiment, samples were taken for DIC, UV–vis, and bacterial analyses.

## Results and discussion

Flocculation did not appear significant in our experimental "transect." For most of the summer samples, salinity changes did not lead to the generation of POC at levels significantly above that of the filter blank. However, the highest salinity sample, prior to the placement in the solar simulator, did have measurable POC (128 $\mu$mol $L^{-1}$), and the corresponding dark and light samples (Floc) also had measurable, albeit lower, POC concentrations (47.3 and 41.5 $\mu$mol $L^{-1}$, respectively). Although these POC concentrations were measurable, they are quite small relative to DOC (which averaged 3,040 $\mu$mol $L^{-1}$ within the diluted dark controls).

Bacterial degradation was probably not an important factor during the experiments. Bacterial counts showed that initial 0.2-$\mu$m filtration removed 93% of the bacterial population in the summer sample and that there was no measurable growth of bacteria in any subsequent treatments. For the winter experiment, filtration removed more than 80% of the bacterial population, and the greatest regrowth of bacteria was seen in the salinity 30 sample (to 41% of the original bacterial population in the light-exposed sample and 42% in the dark control). Although there was bacterial regrowth in the winter experiment, trends seen in this experiment mirror those of the summer samples (Fig. 1) and imply that this regrowth did not significantly impact the photochemical results. For the DFOM experiment, initial filtration removed 77% of the bacteria. The greatest regrowth was seen in the salinity 5 samples unamended with DFOM (with cell counts reaching 47% of initial whole water in the light-exposed sample and 57% in the dark control) and the salinity 30 DFOM samples (46% of the initial whole water in the light-exposed sample and 44% in the dark control).

In both the summer and winter experiments, light exposure led to significant production of DIC; concentrations in photoexposed samples are more than 100 $\mu$mol $L^{-1}$ higher than in dark controls. The concentration of DIC produced photochemically decreases as salinity increases (Fig. 1a,b) and does not appear to be significantly affected

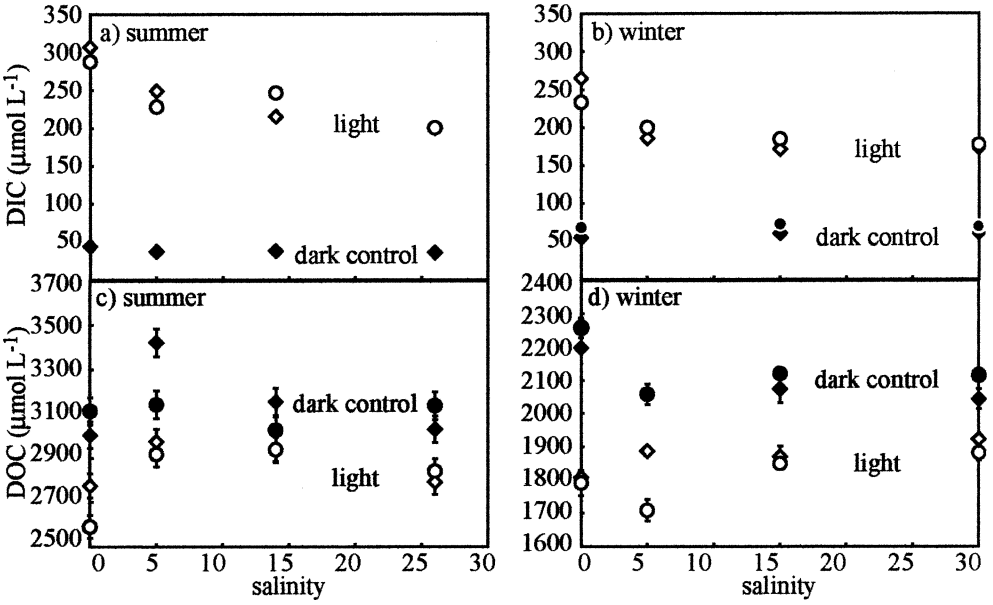


Fig. 1. (a, b) DIC concentration of Fil samples (diamonds) and Floc (circles) as a function of salinity in the summer and winter experiments, respectively. (c, d) DOC concentration of Fil and Floc samples as a function of salinity in the summer and winter experiments, respectively. Note the varying scales of the *y*-axes for the DIC and DOC concentrations. Error bars are for replicate injections of the same sample, DIC error bars are smaller than the symbol.

by filtration of samples to remove potential flocculates resulting from salinity changes.

DOC concentrations decreased in light-exposed samples relative to the corresponding dark controls (Fig. 1c,d). In general, DIC production is similar in magnitude to the DOC consumption in these experiments; however, the larger uncertainty in DOC measurements prevents us from performing a satisfying mass balance.

Light-exposed samples showed a loss in absorbance (i.e., photobleaching) relative to the dark controls, as typified in Fig. 2. In general, the Floc and Fil absorbance spectra overlap (Fig. 2a), though presence of flocculate did affect the absorbance spectrum for the highest salinity summer sample (Fig. 2b). The degree of photobleaching was affected by salinity, with the greatest impact occurring at low salinities; e.g., photobleaching at 280 nm was approximately 20% greater at salinity 0 than at salinities $\geq$14 (Fig. 2c).

The relationships between photobleaching, DIC photoproduction, and salinity have not, to our knowledge, been studied previously in a system where the DOC concentration and composition are the same across the salinity gradient. The fact that we observed greater photobleaching and DIC photoproduction at lower salinities when the initial DOM pool is the same indicates the importance of ionic-strength regulated factors such as DOM conformation and/or trace-metal availability in determining the photochemical fate (i.e., rate of photodegradation) of terrestrial organic matter. Evidence that DOM conformation influences DOM reactivity has been seen in previous studies of organic contaminant sorption to humic substances (Salloum et al. 2001 and Simpson et al. 2003).

The presence of photoreactive trace metals, especially iron (present at a concentration of 29.0 $\mu$mol $L^{-1}$) and, to a lesser degree, copper (0.10 $\mu$mol $L^{-1}$), in Great Dismal Swamp water will likely enhance DOM photodegradation. To test the role of iron, we added the photochemically inert chelator DFOM to aliquots of sample prior to irradiation and compared the results to non-DFOM and to dark controls (both with and without DFOM). The addition of DFOM to the winter samples caused a small decrease in absorption from 270 to 370 nm (as measured in the salinity 0 dark controls; data not shown), perhaps because of the loss of Fe(III)–DOM complexes. It also eliminated the salinity-related trends in photobleaching and DIC photoproduction, primarily by reducing these processes at low salinities. This reduction can be seen by comparing Fig. 1b (which shows DIC concentrations along a "transect" in which one part winter sample was mixed with one part ASW–DI) and Fig. 3 (which shows photoproduction of DIC, i.e., the difference between DIC concentrations in light and dark samples, along a "transect" in which one part of the same winter sample was mixed with three parts ASW–DI).

The fact that iron plays a significant role in our system is not surprising; photochemical interactions between iron and DOM have been seen by numerous researchers (e.g., Gao and Zepp 1998). It is not generally clear, however, where the balance falls between direct interactions between iron and DOM and indirect interactions between the products of iron photochemistry (reactive oxygen species) and the DOM. While at the pH range of our experiments, Fe(III) hydroxide solubility does not appear strongly dependent upon ionic strength (Liu and Millero 1999),

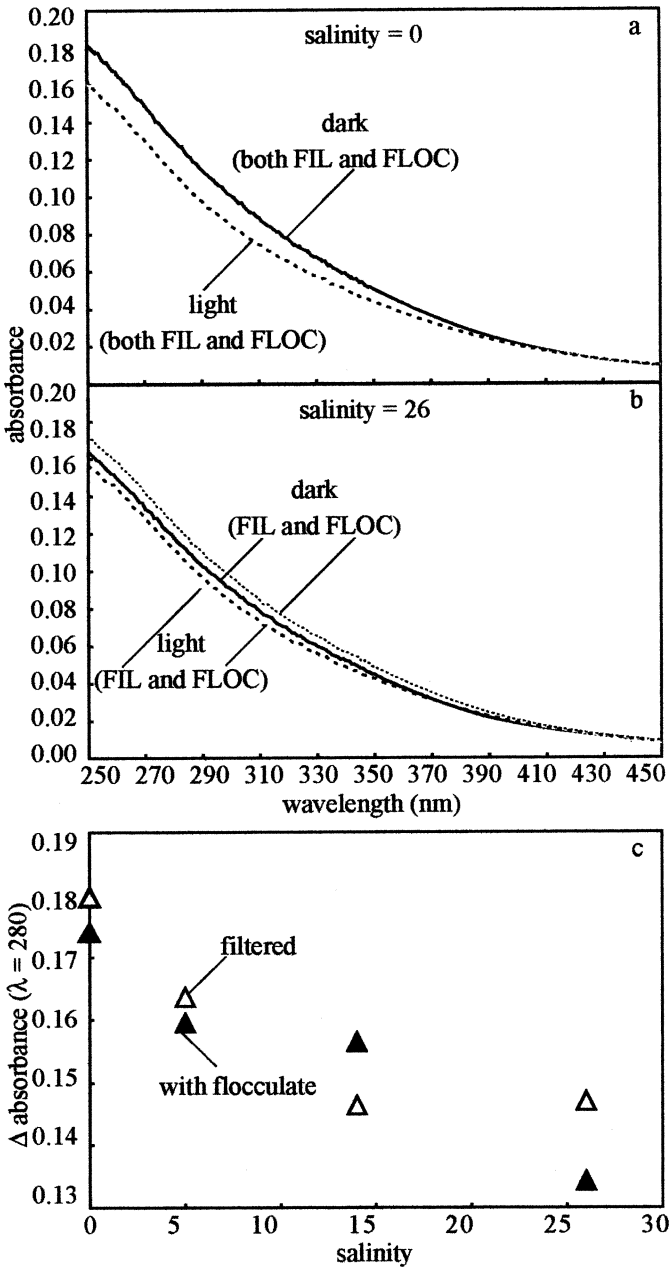


Fig. 2. (a) Absorbance versus wavelength for the summer Fil and Floc samples with a salinity of 0. (b) Same as in (a) but for salinity 26. (c) Photobleaching at 280 nm as a function of salinity (all summer samples, Floc and Fil).

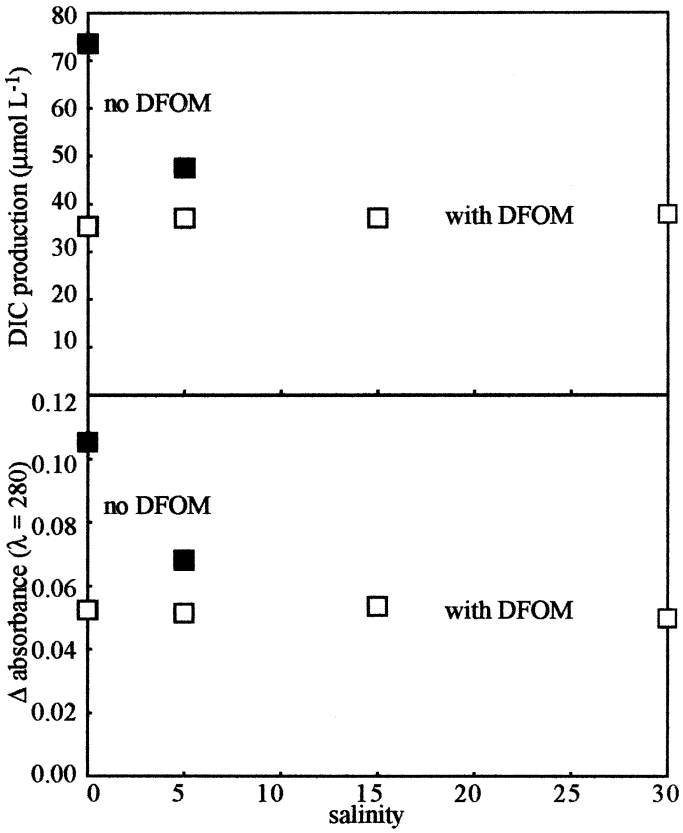


Fig. 3. (a) DIC photoproduction (the difference in DIC concentration between light-exposed and matching dark-control samples) and (b) photobleaching (difference in absorbance between dark-control and light samples) at 280 nm for samples amended with DFOM (open symbols) and samples of the same salinity without DFOM (closed symbols).

ionic-strength variations may still affect iron availability for photochemical reaction, perhaps through changes in chloride complexation (Byrne et al. 2005). It is also possible that iron is more strongly bound to DOM at low ionic strengths, thus leading to enhanced ligand to metal charge transfer reactions. Such a hypothesis is consistent with the studies of Meunier et al. (2005), which indicate that iron(II) results mainly from photolysis of iron(III) complexes in samples from the Mediterranean Sea and from a Swiss lake. The above arguments concern iron and DOM, but it must be remembered that changes in ionic strength (in other words, changes in the concentration of major ions) may affect the stability of reactive products of photochemistry rather than the photochemistry itself (e.g., Zafiriou et al. 1987).

Iron photochemistry is enhanced at low pH ranges such as those in our experimental system (e.g., Molot et al. 2005). Therefore, our experiments (where low pH reflected the Great Dismal Swamp source water) cannot be directly extrapolated to most natural estuaries. However, our results clearly indicate the importance of ionic strength as a factor in the photochemistry of natural waters and suggest that further research into the effects of salinity and pH upon DOM and iron photochemistry is warranted.

Our experiments were designed to give insights into how changes in ionic strength affect DOM photoreactivity and optical properties during estuarine transport. After photoexposure, all light-exposed samples (relative to the dark controls) exhibited photobleaching, organic carbon losses, and photoproduction of DIC. At higher salinities there is less photobleaching of chromophoric DOM and less photoproduction of DIC. For our samples, the loss of DOC roughly accounts for production of DIC.

The fact that we see ionic-strength–related differences, even though the initial natural water (including DOC) in each treatment was the same, may be explainable in terms

of conformational changes in the DOM and/or changes in iron photochemistry. The addition of an iron chelator (DFOM) reduces DIC photoproduction and eliminates the inverse relationship between DIC and salinity, thus indicating the importance of iron in the system. However, it is unclear whether the ionic-strength effects are changing the availability of iron for photochemical reaction (e.g., displacement of the iron from DOM complexes), the availability of reactive products of iron photochemistry for reaction with DOM, or the ability of the DOM to generate DIC upon interaction with iron or the products of iron photochemistry.

Based upon our results, increased salinity decreases the sensitivity of terrestrial DOM to photoremineralization and photobleaching by UV light. This decreased sensitivity indicates that the region (i.e., salinity range) of the river in which dilution leads to significant light penetration may be an important factor in determining the fate of terrestrial DOM. This photochemically optimal riverine–estuarine region probably varies not only from river to river but also within each river–estuary system as a function of freshwater input.

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