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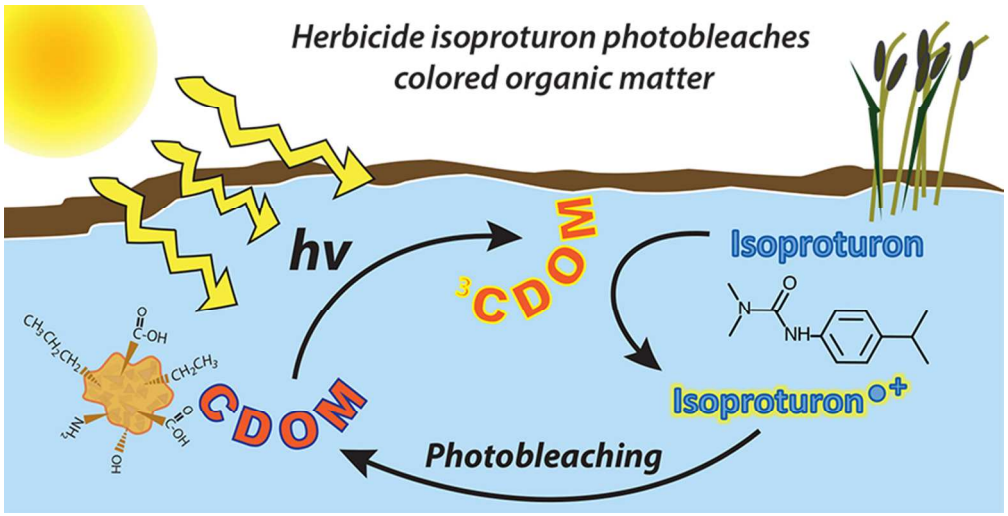

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Environmental Impact Statement:

This contribution examines the role of herbicides on the alteration of chromophoric dissolved organic matter (CDOM) by sunlight in wetland surface waters. Our paper is the first to show that organic compounds that can undergo oxidation by excited CDOM triplets can also catalyze the destruction of chromophores capable of absorbing photons found in sunlight. We also demonstrated that conventional photolysis experiments conducted in sealed phototubes in simulated or natural sunlight resulted in the depletion of dissolved oxygen within the reactor. Thus, this second phenomenon may have ramifications with respect to how photochemical experiments are designed and executed as well as the data that is generated.

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Contaminant-Mediated Photobleaching of Wetland Chromophoric Dissolved Organic Matter

Maureen Langlois[†], Linda K. Weavers[‡], Yu-Ping Chin *[§]

[†] Environmental Science Graduate Program, [‡] Department of Civil, Environmental, and Geodetic Engineering, [§] School of Earth Sciences, The Ohio State University, Columbus, OH 43210

*To whom correspondence should be made: Tel. +1-614-292-6953: yo@geology.ohio-state.edu

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Abstract

Photolytic transformation of organic contaminants in wetlands can be mediated by chromophoric dissolved organic matter (CDOM), which in turn can lose its reactivity from photobleaching. We collected water from a small agricultural wetland (Ohio), Kawai Nui Marsh (Hawaii), the Everglades (Florida), and Okefenokee Swamp (Georgia) to assess the effect of photobleaching on the photofate of two herbicides, acetochlor and isoproturon. Analyte-spiked water samples were irradiated using a solar simulator and monitored for changes in CDOM light absorbance and dissolved oxygen. Photobleaching did not significantly impact the indirect photolysis rates of either herbicide over 24 hours of irradiation. Surprisingly, the opposite effect was observed with isoproturon, which accelerated DOM photobleaching. This phenomenon was more pronounced in higher-CDOM waters, and we believe that the redox pathway between triplet-state CDOM and isoproturon may be responsible for our observations. By contrast, acetochlor indirect photolysis was dependent on reaction with the hydroxyl radical and did not accelerate photobleaching of wetland water as much as isoproturon. Finally, herbicide indirect photolysis rate constants did not correlate strongly to any one chemical or optical property of the sampled waters.

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Introduction

Wetlands have the potential to attenuate mobile contaminants transported by runoff associated with agriculture. Relatively long retention times (compared to streams) and a favorable aspect ratio with respect to sunlight exposure make wetlands well suited as photoreactors for contaminant degradation via direct or indirect photolysis. Direct phototransformation of organic contaminants can occur in wetland waters, but many of these substances lack the chromophores capable of absorbing photons present in sunlight. A more likely pathway occurs when sunlight activates other wetland water constituents (photosensitizers) that in turn react with contaminants via indirect photolytic pathways. These photosensitizing species include nitrate/nitrite, iron and chromophoric dissolved organic matter (CDOM), which lead to the formation of reactive oxygen species (ROS) such as the hydroxyl radical (OH•), singlet oxygen ($^1O_2$), and superoxide (O_2^-/HO_2^-) as well as other excited species including triplet-excited state dissolved organic matter (^{3}DOM) and organic radicals. These species are unstable and quickly react with other water constituents including DOM (which includes CDOM and non-chromophoric molecules), carbonate species, water, and contaminant molecules.

Photobleaching, i.e., the alteration of CDOM composition by both direct and indirect photolysis, is an important physicochemical process in wetland chemistry and contributes to the cycling of organic matter in watersheds. For this reason, CDOM is depleted in sunlit waters more rapidly than DOM in general (1-4). Over time, sunlight exposure decreases the average size of DOM molecules, measured both in terms of lower molecular weight and changes in light absorbance (5). In wetlands the processing of DOM into smaller components has been attributed more to photolytic than microbial processes (6) and has been shown to affect the subsequent bioavailability of DOM to heterotrophic microorganisms (7-9).

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The extent to which CDOM photobleaching influences the transformation of organic contaminants depends on the chemical and optical properties of the wetland in addition to its hydrology, location, and morphology. Attempts have been made to model these processes using the chemical (10-12) and optical (13, 14) properties of the surface waters, but much is still unknown about the responsible pathways, particularly in wetlands (15-18). Finally, recent research has demonstrated that DOM can inhibit the transformation of contaminants known to react readily with ^{3}DOM (19, 20). One implication of these studies is the possibility that contaminant molecules can act as reactive species capable of *transforming* CDOM in irradiated waters, which to our knowledge has not previously been explored.

For this study we investigated 1) the role of various wetland water chemical constituents and DOM optical characteristics on the photodegradation of two herbicides isoproturon (IP) and acetochlor (AC), and 2) the link between contaminant degradation and the coincident CDOM transformation. Both of our target compounds are pre-emergent broadleaf herbicides used in large-scale agriculture and they have chemical properties that make them suitable for use in laboratory studies (low volatility, negligible hydrolysis rates at ambient temperatures, etc.). The objectives of the current study, therefore, are 1) to quantify the rates of change of CDOM and of the probe compound herbicides AC and IP during the course of solar irradiation in various wetland waters, 2) to relate these changes to water chemistry and optical characteristics, and 3) to determine the extent to which light-induced changes in CDOM and in the herbicides are interconnected.

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Materials and Methods

Site descriptions:

Water was collected from four freshwater wetland sites in the U.S. between June 2010 and January 2011 to capture the greatest diversity of natural photosensitizers. Yocom Farm wetland, Champaign County, Ohio (YCF) is a small (<1 ha) modified forested wetland receiving tile drainage from corn and soybean fields in central Ohio. Kawai Nui Marsh (KNM) is a restored freshwater marsh on Oahu, Hawaii (335 ha). The Everglades Wildlife Management Area Water Conservation Area 2B (EVG), located near Ft. Lauderdale, FL, is positioned at the upstream end of the Okeechobee/Everglades system that covers much of southern Florida. Samples were taken from a channel emerging from an expansive stretch of vegetated marsh (USGS EDEN station S11A-H, upstream). The Okefenokee Swamp (OKS) is a 1.77×10^5-ha, peat-filled "blackwater" swamp that is the source of the Suwannee River. Samples were taken from the edge of designated open marsh area accessed from the eastern entrance to the Okefenokee National Wildlife Refuge, Georgia. In all cases, samples were taken from the shore of inundated wetland areas with minimal emergent plant shading. Samples were collected with a glass container on a 3-m extender rod from a depth of 30-50 cm and were vacuum-filtered as soon as possible (< 2 h) with pre-combusted Gelman A/E (1 μm) glass filters and stored in the dark on ice until being refrigerated at 4°C. In the case of OKS samples, high turbidity of the water necessitated splitting the sample and filtering only half of the sample in the field (split OKS_{FF}) and the remaining half in the lab two days later (split OKS_{LF}).

Water chemical characterization:

Parameters measured in the field at each sampling time include water temperature and dissolved oxygen (YSI EcoSense DO200, YSI Environmental, Inc. Yellow Springs, OH). The

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pH and conductivity of the filtrate were measured immediately after filtering (Thermo Orion model 130 conductivity meter, Beverly, MA). Laboratory characterization of the samples included UV-visible (UV-Vis) absorbance (Varian Cary 13 UV-visible spectrophotometer, Agilent Technologies, Santa Clara, CA, U.S.A.), dissolved organic carbon (DOC) analysis (Shimadzu TOC-V CPN, Columbia, MD, U.S.A.), total iron (Varian Vista AX CCD ICP-AES, Agilent Technologies, Santa Clara, CA, U.S.A.) and inorganic ions (Dionex DX-120, Sunnyvale, CA, U.S.A. and Skalar San++ Nutrient Analyzer, Breda, Netherlands).

Optical characterization of water samples:

UV-visible absorbance values were corrected for the absorbance of water (Millipore Milli-Q water purification system, Billerica, MA). Specific UV absorbance ($SUVA_{254}$) values were calculated in the manner of (21) using equation (1),

$$SUVA_{254} = A_{254} / [DOC] \qquad (1)$$

where A_{254} is the absorbance of the wetland water at $\lambda = 254$ nm measured in a 1 cm path-length cuvette and [DOC] is expressed in moles C per L (M) and/or mg C per L (mg-C/L). Samples were diluted if their absorbance were greater than 1 and DOC was re-measured for the diluted samples.

To calculate spectral slope, Napierian absorption coefficients for $\lambda = 250$-500 nm were calculated as follows for each water,

$$a_\lambda = (2.303\ A_\lambda) / l \qquad (2)$$

where a_λ = the absorption coefficient (m^{-1}) at λ, A_λ = corrected UV-visible absorbance at λ, and l = path length (1 cm for our instrument). A plot of ln a as a function of λ yields a relatively linear curve whose slope (S) in various ranges were determined; here $S_{275\text{-}295}$, $S_{350\text{-}400}$ and S_R, the ratio of $S_{275\text{-}295}/S_{350\text{-}400}$ were calculated in the manner of Helms *et al*. (5).

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Absorbance was also used to calculate a screening factor (SF) for each water sample. Briefly, SF at any given λ is calculated as follows,

$$SF = (1-10^{-A\,l})/(2.303Al) \quad (3)$$

where the variables are the same as defined above. SF is plotted as a function of wavelength and fitted to a fourth-order polynomial ($R^2 > 0.98$), which is then integrated over the wavelengths of interest and subtracted from the value without light screening (22).

Photolysis experiments:

Herbicides were obtained from Chem Service (West Chester, PA) at the highest available purity. Wetland water samples were adjusted to the field-measured pH using HCl or NaOH of highest available grade (iron free), spiked with aqueous stock solutions of IP or AC to form a 5 μM reaction solution, and stirred open to air at room temperature for 2-3 hours. Fulvic acid solutions containing Suwannee River or Pony Lake fulvic acids (SRFA or PLFA) were prepared at pH 8 in a 1 mM bicarbonate solution.

Quartz photoreaction tubes (path length = 0.9 cm, volume = 8 mL) were filled with reaction solution and sealed with airtight caps in the dark. Reactors were irradiated in a solar simulator fitted with a collimating lens (Suntest CPS+, Atlas MTT LLC, Chicago, IL). Samples were irradiated for at least one half-life for both analytes. Dark controls consisted of foil-wrapped tubes were placed concurrently within the solar simulator. Direct photolysis rates were determined by irradiating analyte solutions in the absence of DOM and other photosensitizers.

Overall light intensity of the solar simulator was determined using both *p*-nitroanisole/pyridine and *p*-nitroacetophenone /pyridine actinometry (23), which is calibrated to the known quantum yield of the reaction at 313 and 366 nm. The light emitted by our solar simulator (on the manufacturer's 550 W/m^2 setting) was determined to be ~ 2.0 times as strong

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as the summer sun at 40°N latitude (24). Irradiance over the course of experiments was continuously monitored using a UV-light radiometer (VWR International, Bridgeport, NJ) that integrates signal over λ = 320-390 nm. The temperature of the solar simulator was maintained at 27± 3°C.

For a subset of photolysis experiments, UV-Vis absorbance and dissolved oxygen (DO) were measured at time-points during irradiation. DO was determined using a micro-DO probe (Lazar Research Laboratories, Inc., Los Angeles, CA) dry-calibrated in air and wet-calibrated using air-saturated water. DO was measured in most cases within 1 hour of removal from the solar simulator and after the tubes had equilibrated to room temperature. Influx of atmospheric O_2 into the tubes during measurement was determined to be minimal during initial readings (acquisition time 2-3 min), but interfered with measurements over longer spans of time, precluding multiple readings of each sample tube. Herbicide concentrations were analyzed using a Waters reversed-phase HPLC (Milford, MA) equipped with a Nova-Pak C18 column (3.9 x 150 mm). With a mobile phase of 55:45 ACN:H_2O (v:v), detection parameters were as follows: for IP, λ = 240 nm, retention time. ≈ 4.7 min; and for AC, λ = 220 nm, retention time ≈ 6.5 min.

We made amendments to the indirect photolysis experiments with EVG samples to elucidate reaction mechanisms. To assess the role of OH•, *t*-butanol was added to EVG water spiked with AC such that the final concentrations were 25 mM and 5 μM, respectively. Another set of mechanistic experiments involved bubbling EVG with argon (1 min/mL solution) to displace atmospheric gases and then preparing photolysis solutions in a glovebox filled with N_2/H_2 (95%/5%). Initial readings on these low-O_2 solutions showed that this treatment yielded DO of 35-40% of atmospheric O_2 saturation.

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Kinetic Modeling:

The observed rate of loss in complex mixtures such as natural waters is attributed to both direct and indirect photolysis. To determine the rate constant that describes direct photolysis occurring in a given wetland water (k_{dir}), the rate constant for direct photolysis in water was multiplied by the appropriate screening factor (Table 1). Indirect reaction rate constants (k_{ind}) were then calculated by subtracting k_{dir} from k_{obs} (equation [4]),

$$k_{ind} = k_{obs} - k_{dir} \quad (4)$$

where k_{obs} is the overall rate constant from each experiment.

Results

Chemical and optical characteristics of wetland waters:

The four wetlands sampled in this study represent a broad range of chemical composition, from the relatively low-DOC, moderately alkaline YCF to the turbid, acidic OKS (Table 1). The heterogeneity of CDOM composition precludes a simple chemical quantification of the colored fraction presumed to dominate photochemical activity. Accordingly, UV-visible absorbance spectra for each water sample were used to indirectly characterize CDOM optical properties. Screening factors for all sampled waters aligned inversely with [DOC], with the highest [DOC] sample (OKS_{LF}) absorbing nearly 50% of ambient sunlight (Table 1). $SUVA_{254}$ values (an estimate of aromaticity) of the wetland waters fell roughly into two categories, with YCF and EVG at ~360 M^{-1} cm^{-1} (~2.95 L mg C^{-1} m^{-1}) and KNM and OKS_{FF} at ~225 M^{-1} cm^{-1} (~1.85 L mg C^{-1} m^{-1}). High aromaticity has been reported in the northern Everglades previously (25).

Changes to CDOM during light exposure:

During the course of irradiation experiments in the solar simulator, EVG and OKS water samples were periodically monitored for UV-visible absorbance and DO. In all cases, the

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absolute UV-Vis absorbance of the samples decreased with light exposure, indicating loss of chromophores over time. This trend is consistent with numerous previous observations of photobleaching (1, 6, 8).

$S_{275-295}$ increased steadily with light exposure for all waters tested, implying greater loss of absorbance at the higher λ (lower energy) end of this range (Table 2). Increases in $S_{275-295}$ for our samples corroborate previous studies of photobleaching in natural waters and is indicative of the production of lower molecular weight moieties (5, 26). While $S_{275-295}$ changed at similar rates among measured waters (mean rate of change = 1.39×10^{-3} hr^{-1}), the $S_{350-400}$ parameter was more variable (Table 2). Helms et al., (5) also observed both phenomena for various DOM samples with increasing $S_{275-295}$ as a function of irradiance and variability in $S_{350-400}$.

Water samples spiked with AC or IP (5 μM) affected the rate of spectral slope change during the irradiation of EVG water (Table 2). Dark controls showed that the initial spectral slopes for EVG water in the presence and absence of the herbicides were identical, indicating that the contribution of analyte light absorbance to the total absorbance of the sample is negligible. Further, the presence of each herbicide caused a different effect on spectral slope with time. With AC, $dS_{275-295}/dt$ and $dS_{350-400}/dt$ changed slightly compared to no herbicide; however, the slope ratio S_R remained constant. By contrast, the presence of IP considerably accelerated the rate at which $S_{350-400}$ decreased, causing a rate of change of S_R *over twice* that of no-herbicide or AC-containing solutions. Therefore, the presence of herbicides alters the way in which the CDOM changes over the course of irradiation. We believe that this has not been observed in previous DOM mediated herbicide photodegradation studies.

Reducing the initial DO concentration to sub-oxic levels (defined here as argon purged solutions) in our experiments slightly lowered the rate of change in $S_{275-295}$, for AC spiked

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solutions perhaps implying that photobleaching of chromophores absorbing lower-wavelength photons is more due to direct photolysis as oppose to the presence of reactive oxygen species. The opposite occurred for the rate of change in $S_{275\text{-}295}$, for IP spiked solutions whereby we observed a slight increase. Additional experiments would be necessary to determine the effects of low-O_2 conditions in the presence of herbicides. Our results corroborated those reported by Gao and Zepp (27), who observed some photobleaching in anoxic Satilla River water.

In OKS water, all experiments were performed in the presence of herbicides. Compared to irradiation with AC, for both OKS_{FF} and OKS_{LF} the presence of IP resulted in more rapid absorbance changes than those observed in EVG (Table 2). In both OKS splits, the presence of IP caused dS_R/dt to double relative to AC. The factor of two increases in S_R rate of change caused by the presence of IP was consistent among EVG, OKS_{FF} and OKS_{LF} waters *despite* their disparate water characteristics.

Changes in oxygen levels during light exposure:

Irradiated EVG and OKS waters were monitored for changes in DO over the course of irradiation (Table 2). O_2 is a participant in many known indirect photolysis reaction pathways including the photobleaching of CDOM (4, 9), the formation of singlet oxygen (28) and photo-Fenton reactions (29) such that photobleaching has been shown to be largely due to indirect photo-oxidation. From a starting value of 100% atmospheric saturation, we observed steady decreases in DO during all irradiation experiments relative to dark controls. Further, the rate of DO loss was relatively consistent for each water sample over successive trials.

Changes in spectral slope in the presence of AC or IP were mirrored by accelerated DO loss relative to wetland water in the absence of the analytes (Table 2). With AC, DO decreased ~30% faster than in wetland water alone, while changes in the presence of IP, the effect was even

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larger (~70%). Experiments conducted in EVG water under low-O_2 conditions resulted in little change in DO level over the course of the irradiation, although readings exhibited a greater standard deviation compared to air-saturated irradiations. The rate of DO loss was correlated to both DOC and total iron (Fe_{tot}) for the wetland waters, consistent with direct and Fenton-mediated photo-oxidation (Figure 1).

For all waters, the presence of IP caused substantially (1.3 to 2.5 times) higher rates of DO loss compared to AC. This enhancement mirrors the increased photobleaching of waters containing IP versus AC described above. Interestingly, the same pattern emerges in the dependency of DO loss rate on DOC and Fe_{tot} shown in Figure 1 *i.e.*, twice the DO loss per unit DOC or Fe_{tot} occurred for solutions containing IP versus AC.

Rates of contaminant loss during light exposure:

Direct photolysis. The rates of direct photolysis of AC and IP were measured by irradiating the herbicides in water. The direct photolysis reaction rate constant for AC in water was 7.5 ± 0.6 x 10^{-3} hr^{-1} (half-life: ~ 3.9 d) and is consistent with a previously measured value (8.2 x 10^{-3} hr^{-1}) (35). The k_{dir} for IP was smaller at 2.7 ± 0.9 x 10^{-3} hr^{-1} (half-life: ~ 10.6 d). The lower k_{dir} of IP versus AC cannot be explained by their respective absorbance spectra at wavelengths present in sunlight (Figure 2), but is consistent with previous observations (30).

Indirect photolysis. Observed herbicide loss rate constants (k_{obs}) were measured in irradiated wetland waters (Figure 3) and in buffered fulvic acid solutions. For AC, wetland water accelerated photodegradation over water by a factor of 2-3 even when corrected for light screening (Table 3). Indirect photolysis of AC proceeded with nearly identical k_{ind} for almost all the sampled wetlands (including YCF, KNM, EVG and OKS_{LF}), with a mean of 1.2 ± 0.1 x 10^{-2} hr^{-1}. We also observed increasing k_{ind}, for PLFA solutions as DOC concentrations increased (7,

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14 and 21 mg C/L, pH = 8) whereby the range of k_{ind} is similar to those measured for our wetland samples (~1.1 x 10^{-2} hr^{-1}, data not shown). In contrast SRFA solutions (pH = 8) at low (2.5 mg-C/L) concentrations caused little or no enhancement over direct photolysis. One dramatic exception to this pattern was the field-filtered Okefenokee sample (OKS_{FF}) whereby k_{ind} was 4-5 times higher than all other waters. All dark controls showed negligible (<1%) herbicide loss.

IP photolysis was enhanced by a factor of 30-200 in wetland waters compared to water alone (Table 3). These results agree with previously reported ratios of direct to sensitized photolysis for IP (12). Similar to our observations for AC the irradiation of IP in PLFA solutions with increasing DOC yielded linearly increasing rate constants (Figure 4), consistent with the involvement of ^{3}DOM in IP photolysis as shown by others (12, 30). However, as shown in Figure 4 the correlation between PLFA concentration (as DOC), and IP k_{obs} was not observed for our wetland waters.

Probing mechanisms of indirect photolysis:

Low-O_2 conditions. To determine the extent to which O_2 was involved in indirect photolysis, we purged solutions to about 35-40% of atmosphere-equilibrated DO. For AC, low DO conditions did not significantly alter k_{ind}, although deviations from pseudo-first order kinetics occurred (Fig. 3a). For IP, this deviation from pseudo-first order behavior was even more pronounced (Fig. 3b), and the initial rate of degradation was clearly enhanced under low-O_2 conditions.

Addition of t-butanol. Indirect photolysis for AC was shut down in EVG spiked with *t*-butanol, a known OH• scavenger (Figure 3a). The observed reaction rate constant was actually *lower* than k_{dir}, suggesting that the quencher shut down the indirect OH• mediated pathway and possibly influence AC. DO loss in the *t*-butanol-spiked solution was lower than an identical

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solution without the quencher, and more closely approximated the DO loss of EVG water alone (Table 2). Although $dS_{275-295}/dt$ was nearly the same as with non-quenched AC solutions, the S_R rate of change was somewhat lower than even wetland water alone, suggesting some inhibition occurred in photobleaching in the presence of *t*-butanol (Table 2).

Discussion

Establishing likely pathways of contaminant degradation:

The herbicides used as probe compounds in this study were chosen because they are known or suspected to have different dominant pathways for indirect photolysis. For AC, no previous data is available for indirect photolysis in sunlit natural waters, but the primary indirect photolytic pathway for other chloroacetanilide herbicides including metolachlor (31, 32), alachlor (16), and propachlor and butachlor (33) involves non-specific ROS species, particularly OH•. Our results, using the OH• quencher *t*-butanol (Figure 3a), confirm that this radical is important in AC indirect photolysis in wetland waters.

The major formation pathways of OH• in sunlit waters include (1) photolysis of NO_3^- and NO_2^- (2) the reaction of sensitized CDOM with H_2O, and (3) photo-Fenton reactions mediated by Fe (III) and DOM, which becomes important under acidic conditions. Major sinks for OH• are DOM, carbonate, and, to a lesser extent bicarbonate (34). Given the second-order rate constant between AC and OH•, ($k_{OH\cdot} = 7.5 \times 10^9\ M^{-1}\ s^{-1}$) (35), a steady state hydroxyl radical concentration ($[OH\bullet]_{ss}$) on the order of 10^{-16} M would be required to achieve the average k_{ind} of $1.2 \pm 0.1 \times 10^{-2}\ hr^{-1}$ that we observed for AC. This is a plausible scenario given that $[OH\bullet]_{ss}$ of this magnitude has been observed in various wetland waters (36).

Iron-rich, acidic, highly colored waters such as OKS are known to undergo photo-Fenton OH• production (2, 27), which may help to explain why AC photolysis was three times faster in

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OKS_{FF} than in any other water. Alachlor, which is structurally similar to AC, was shown to photodegrade much more rapidly in acidified (pH = 4) wetland waters versus unacidified (16), and the same mechanism may be at work with AC. Although OKS_{LF} water was at the same pH as OKS_{FF}, it also had nearly three times the DOC. Both OH• quenching and significant inner-filter effects associated with this high DOC may in part explain the slower AC kinetics in OKS_{LF}. Finally, it is possible that the iron speciation between OKS_{FF} and OKS_{LF} may have also been altered over the intervening two days, which could also affect the reactivity of the two samples.

The primary reactive species responsible for IP transformation in natural waters appears to be ^{3}DOM (12, 37) and possibly DOM-derived organic radicals (38), although IP oxidation has been observed with other reactive species including OH• (39). The increased rate of IP photolysis in low-O_2 conditions observed by us corroborates this pathway as dissolved oxygen can compete with IP for ^{3}DOM (Figure 3b). We observed a linear increase in k_{ind} with increasing concentration of PLFA (Table 3, Figure 4) and corroborate the results reported by Gerecke et al., (12). Surprising there was no linear dependence of k_{ind} on DOC (Figure 4) for any of the wetland waters.

We observed no strong correlations between IP k_{ind} and water properties such as absorbance, DOC, or pH, but our results revealed trends. The highest k_{ind} value occurred for EVG (pH = 7.9) while the slowest kinetics was observed for OKS (pH = 3.5). While differences in DOM composition will in part explain our observations these results also support previous findings whereby the rates of triplet-induced degradation increase with pH (37). For example Bruccoleri et al., (40) demonstrated that the quantum yield for the formation of triplet DOM increases significantly with increasing pH. Stosser et al., (38) reported a similar phenomenon for

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the production of organic radicals. The idea that pH is correlated with greater IP phototransformation is supported by Figure 4, whereby the two high-pH water samples with similar $SUVA_{254}$ values (EVG and YCF) fall close to the trend created by PLFA (buffered at pH 8). With respect to the influence of DOM composition Guerard et al. (41) observed that photodegradation of the antibiotic sulfadimethoxine (also primarily degraded by ^{3}DOM in sunlight) occurs most quickly in PLFA solution and is not photosensitized by SRFA. We believe that this is partly due to the different antioxidant properties of the fulvic acids whereby the more terrestrially derived SRFA possesses antioxidant poly-phenolic moieties that are not present in PLFA, which is derived from microbial organic matter precursors (20).

Contaminant acceleration of photobleaching with IP:

DOM photobleaching by both direct and indirect photolysis has been attributed to the loss of chromophores. Surprisingly, both AC and IP influenced photobleaching by changing spectral slope and DO beyond the photolytic rates observed in wetland water alone (Table 3). To date we are unaware of any previous study that showed the effect of pesticides on DOM photobleaching. This suggests that the herbicides themselves are involved in the formation of an additional pool of reactive species that can oxidize CDOM. For AC, the change in photobleaching and DO loss compared to solutions in its absence was small. Conversely, IP accelerated the rate of DOM photobleaching substantially. This effect was minimized under low-O_2 conditions, suggesting involvement of DO.

We hypothesize that IP and other compounds susceptible to oxidation by triplets may form radical cations ($IP\bullet^+$) through reaction with triplet aromatic ketone moieties in ^{3}DOM as shown in eq. 5 (42, 43). Others have demonstrated that the triplet-sensitized oxidation of phenylureas and other aniline-containing compounds, decreases in the presence of DOM (19,

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20). The proposed mechanism of this inhibition is DOM-induced reduction of $IP\bullet^+$ back to the parent *IP* (eq. 6) as opposed to the continued reaction of $IP\bullet^+$ with other unknown species (M) to form other products (denoted here as IP_{ox}).

$$^3\text{DOM} + IP \longrightarrow \text{DOM}\bullet^- + IP\bullet^+ \quad (5)$$

$$IP\bullet^+ + \text{DOM} \longrightarrow IP + \text{DOM}\bullet^+ \quad (6)$$

$$IP\bullet^+ + \text{M} \longrightarrow IP_{\text{ox}} + \text{M}\bullet^+ \quad (7)$$

Our observation of increased photobleaching of CDOM in the presence of IP is consistent with reduction of the radical cation $IP\bullet^+$ by CDOM as shown in eq. 6. In high-DOC solutions OKS_{FF} and OKS_{LF}, the presence of IP increased both spectral changes and consumption of O_2 compared to AC. However, the rate of IP degradation itself is *lowest* in both OKS samples (Figure 5), which is contrary to the observation that IP reaction rate roughly increases with increasing DOC (12). The fact that IP increases photobleaching without being rapidly degraded suggests a pathway similar to eq. 6 as opposed to eq. 7.

Our work has identified aspects of these photochemical interactions that merit further work in order to understand the fate of compounds that predominantly undergo oxidation through reactive triplets and their possible role in photobleaching. In particular, the role of DOM chemical composition has not yet been fully investigated. DOM with higher aromatic carbon moieties is both more likely to inhibit triplet-mediated contaminant oxidation (due to the presence of naturally occurring anti-oxidant compounds present in the higher plant precursors) (20) and these substances are more likely to form $^1O_2$ (14, 18). Our findings imply that for more aromatic (allochthonous) DOM, we would expect to see a greater reduction in IP k_{ind} and possibly a more rapid decrease in DO. Finally, ^{3}DOM moieties may have a range of redox

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potentials. For example recent studies have suggested the presence of multiple triplet pools with varying susceptibility to reduction by borohydride (18, 42).

Methodological implications of photochemical experimental design:

Changes in DO over the course of a long (8-30 hr) irradiation experiment reveal issues in the application of closed-tube photoreaction experiments. Photochemical experiments often use airtight, capped phototubes (e.g., 16, 44 and others referenced therein). While studies have compared solar simulators and natural sunlight (45, 46), little attention has been devoted to issues regarding the use of sealed phototubes to determine natural water photoreactivity given the potential for artifacts caused by O_2 depletion. Our observations of herbicide degradation kinetics in this study show that later samples deviate somewhat from pseudo-first order kinetics, with more parent compound left than would be predicted by the kinetic model. This deviation is more pronounced in solutions such as OKS that contain high [DOC] and occurs more frequently with IP than AC, which correlated to higher rates of O_2 consumption as discussed above. This occurred even though IP irradiations were consistently shorter in duration than AC (IP: ~8 hr, AC: ~25 hr). Whatever the source of the O_2 depletion, further study of this phenomenon is warranted, as the fundamental chemical reactivity of photosensitizers including ^{3}DOM are altered in the presence of lower DO (14, 18).

While we observed a strong correlation between DO depletion and spectral slope changes over the experimental timeframes in this study, it can be argued that low-O_2 conditions may not be representative of shallow wetland waters (assumed to be well-mixed and aerated at the top layers where photoreactivity is most relevant). Comparative studies between closed and open solar simulation experiments are needed in order to determine whether differences in the

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mechanisms and rates of contaminant phototransformation exist and if they point to a preferred set of photofate testing procedures in natural waters.

Acknowledgements

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Table 1: Chemical constituent concentrations and optical characterization of collected wetland water samples

Water Sample	Date collected	pH	$[Fe_{tot}]$ (μM)	$[NO_3/NO_2]$ (μM N)	Total [N] (μM N)	[DOC] (mg C/L)	$SUVA_{254}$ (M^{-1} cm^{-1})	$SF_{(290-370)}$ [a]	$S_{(275-295)}$ [b]	$S_{(350-400)}$ [b]	S_R [b]
YCF	07/01/10	8.9	3.6	1.55	586	7.20 ± 0.2	372	0.921	0.015	0.015	1.02
KNM	12/18/10	6.1	29	bdl[c]	119	32.2 ± 0.2	221	0.780	0.012	0.015	0.81
EVG	12/31/10	7.9	1.1	0.68	118	25.0 ± 0.1	351	0.814	0.020	0.020	0.99
OKS_{FF}	01/01/11	3.5	4.3	2.64	73.7	52.5 ± 0.7	230	0.687	0.014	0.013	1.04
OKS_{LF}	01/01/11	3.5	6.8	7.50	510	139 ± 0.7	174	0.513	0.014	0.015	0.93

[a] Screening factor calculated over λ = 290-370 nm.
[b] Spectral slope of linearized UV-vis absorbance over the ranges λ = 275-295 nm, λ = 350-400 nm, and the ratio of the two, after [5].
[c] Below detection limit (~10 ppb N = 0.7 μM)
EVG = Everglades water; OKS = Okefenokee Swamp water ($_{LF}$ = lab-filtered, $_{FF}$ = field-filtered); YCF = Yocom Farm water (Ohio)

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Table 2: Rates of change in optical characteristics and dissolved oxygen of wetland waters during irradiation

	Rates of change of photobleaching parameters				Correlation between DO and spectral rates of change [a]		
Wetland Waters	DO [b]	$S_{275-295}$ [c]	$S_{350-400}$ [c]	S_R [d]	$S_{275-295}$	$S_{350-400}$	S_R
EVG							
alone	-1.04 ± 0.3	1.08 ± 0.01	-0.263 ± 0.01	68.5 ± 0.1	0.81	0.74	0.87
AC only	-1.35 ± 0.3	1.34 ± 0.01	-0.303 ± 0.04	70.9 ± 0.2	0.83	0.14	0.93
IP only	-1.71 ± 0.1	0.94 ± 0.02	-1.77 ± 0.07	143 ± 0.5	0.36	0.45	0.46
AC, Low-O_2	0	0.97 ± 0.03	-0.446 ± 0.04	74.1 ± 0.3	0.07	0.20	0.18
IP, Low-O_2	0	1.09 ± 0.01	-0.463 ± 0.05	81.2 ± 0.2	0.03	0.00	0.06
AC, t-butanol	-1.06 ± 0.3	1.42 ± 0.01	0.348 ± 0.01	52.0 ± 0.1	0.93	0.72	0.95
OKS_{FF}							
AC only	-2.96 ± 1.0	1.78 ± 0.02	1.07 ± 0.04	43.7 ± 0.1	0.74	0.77	0.55
IP only	-5.76 ± 1.4	2.10 ± 0.02	0.033 ± 0.01	83.0 ± 0.1	-	-	-
OKS_{LF}							
AC only	-3.74 ± 1.7	1.32 ± 0.02	1.14 ± 0.03	15.1 ± 0.1	0.70	0.80	0.08
IP only	-9.42 ± 1.6	2.63 ± 0.04	2.34 ± 0.03	29.4 ± 0.1	0.97	0.96	0.97

[a] Coefficient of determination (R^2) for rates of change of spectral parameters (S) indicated as function of DO.
[b] Rate of change of DO (x 10^{-2} % $hr^{=1}$) compared to 100% atmospheric saturation.
[c] Rate of change of spectral slope (S) region indicated (x 10^{-3} hr^{-1})
[d] Rate of change of spectral slope (S) ratio (x 10^{-2} hr^{-1})
AC = Acetochlor (5 μM); DO = Dissolved oxygen; EVG = Everglades water; IP = Isoproturon (5 μM); OKS = Okefenokee Swamp water ($_{LF}$ = lab-filtered, $_{FF}$ = field-filtered)
Errors represent 95% confidence intervals.

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Table 3: Reaction rate constants for the photodegradation of AC and IP in various waters under simulated sunlight

Water Sample	k_{obs} ($\cdot 10^{-2}$ hr^{-1}) [a]		k_{dir} ($\cdot 10^{-2}$ hr^{-1}) [b]		k_{ind} ($\cdot 10^{-2}$ hr^{-1}) [c]	
Wetland Waters [d]	*AC*	*IP*	*AC*	*IP*	*AC*	*IP*
YCF	1.9 ± 0.1	12.7 ± 0.4	0.69 ± 0.06	0.25 ± 0.09	1.2 ± 0.1	12.4 ± 0.8
KNM	1.6 ± 0.1	16.4 ± 0.9	0.58 ± 0.06	0.21 ± 0.09	1.0 ± 0.1	16.2 ± 0.7
EVG	1.8 ± 0.1	30 ± 3.0	0.61 ± 0.06	0.22 ± 0.09	1.2 ± 0.2	30 ± 2.0
OKS_{FF}	5.4 ± 0.5	6.7 ± 0.7	0.51 ± 0.06	0.19 ± 0.09	4.9 ± 0.5	6.5 ± 0.7
OKS_{LF}	1.7 ± 0.1	4.1 ± 0.4	0.38 ± 0.06	0.14 ± 0.09	1.3 ± 0.1	3.9 ± 0.4
PLFA [5]						
7 mg C/L	1.6 ± 0.1	20.6 ± 1.8	0.75 ± 0.06	0.27 ± 0.09	0.9 ± 0.1	20 ± 2.0
14 mg C/L	2.0 ± 0.2	25.5 ± 3.3	0.75 ± 0.06	0.27 ± 0.09	1.2 ± 0.2	25 ± 3.0
21 mg C/L	2.2 ± 0.1	31.9 ± 3.7	0.75 ± 0.06	0.27 ± 0.09	1.4 ± 0.1	32 ± 4.0

[a] Observed experimental reaction rate constant

[b] Direct photolysis rate constant corrected for light screening by $k_{UP} \cdot SF_{290\text{-}370}$; where $k_{UP,\,AC}$ = 7.5 ± 0.6 x 10^{-3} hr^{-1}; $k_{UP,\,IP}$ = 2.7 ± 0.9 x 10^{-3} hr^{-1}

[c] Indirect photolysis rate constant $k_{ind} = k_{obs} - k_{dir}$

[d] Unless otherwise noted, experimental conditions: field pH, atmospheric gas saturation before photolysis, 5 μM herbicide

[e] Fulvic acid solutions diluted from stock solution, distinguished by final [DOC]
AC = Acetochlor (5 μM); EVG = Everglades water; IP = Isoproturon (5 μM); OKS = Okefenokee Swamp water ($_{LF}$ = lab-filtered, $_{FF}$ = field-filtered); YCF = Yocom Farm water (Ohio)

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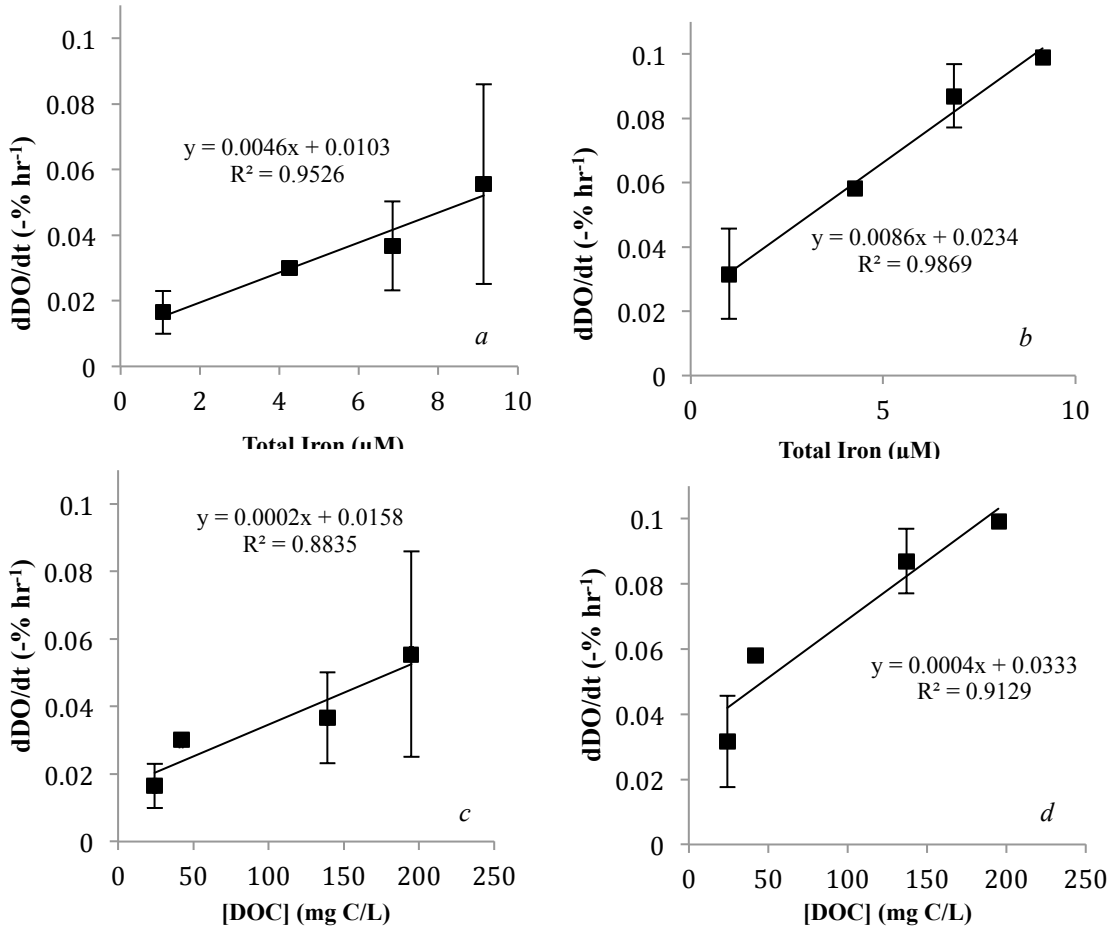

Figure 1: DO loss rate as a function of concentration of dissolved organic carbon ([DOC]) or total iron ([Fe]) in irradiated wetland waters spiked with either acetochlor (AC; a, c) or isoproturon (IP; b, d). Points represent average of all trials. Error bars indicate standard deviation. Samples stored in acidified conditions, but brought to field pH for experiment were included in this regression (6 acidified out of 19 total) to have access to more points.

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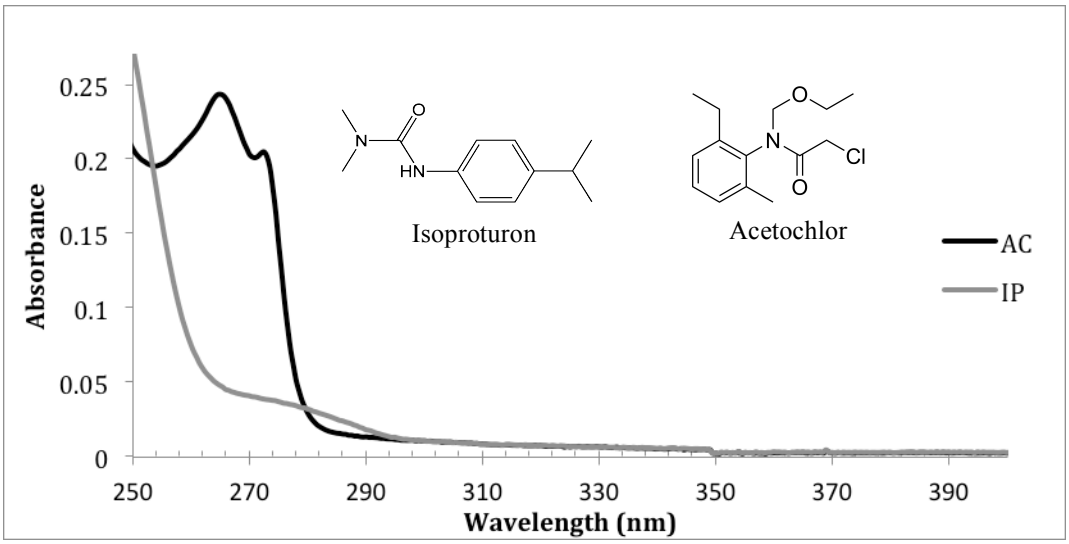

Figure 2: UV-visible absorbance spectra and chemical structures for the herbicides acetochlor (AC; black line) and isoproturon (IP; gray line).

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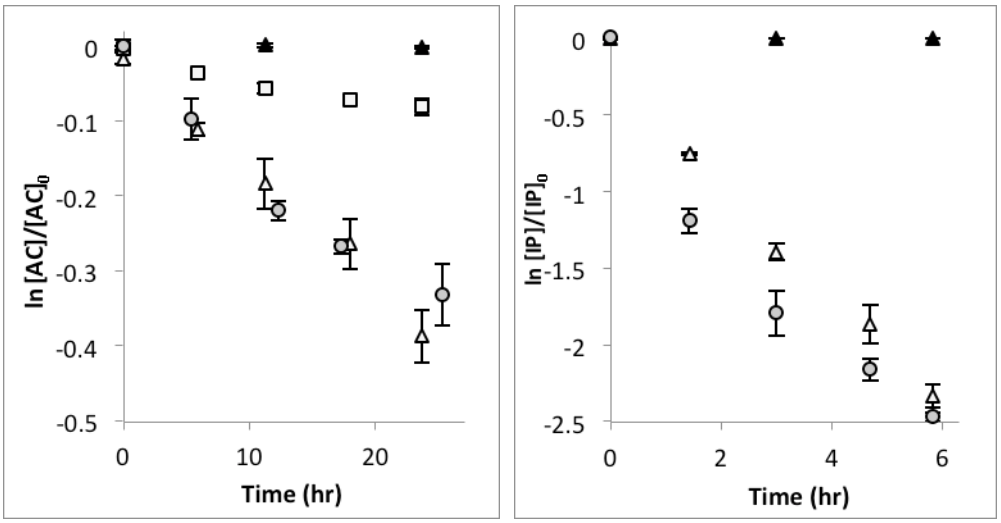

a *b*

Figure 3: Change in herbicide concentrations (a: acetochlor, AC b: isoproturon, IP) during light exposure in Everglades (EVG) water under three conditions: standard (equilibrated in air, Δ), low-O_2 (**O**), or with 25 mM t-butanol (AC only, □). Dark symbols indicate dark controls. Error bars represent 95% confidence interval.

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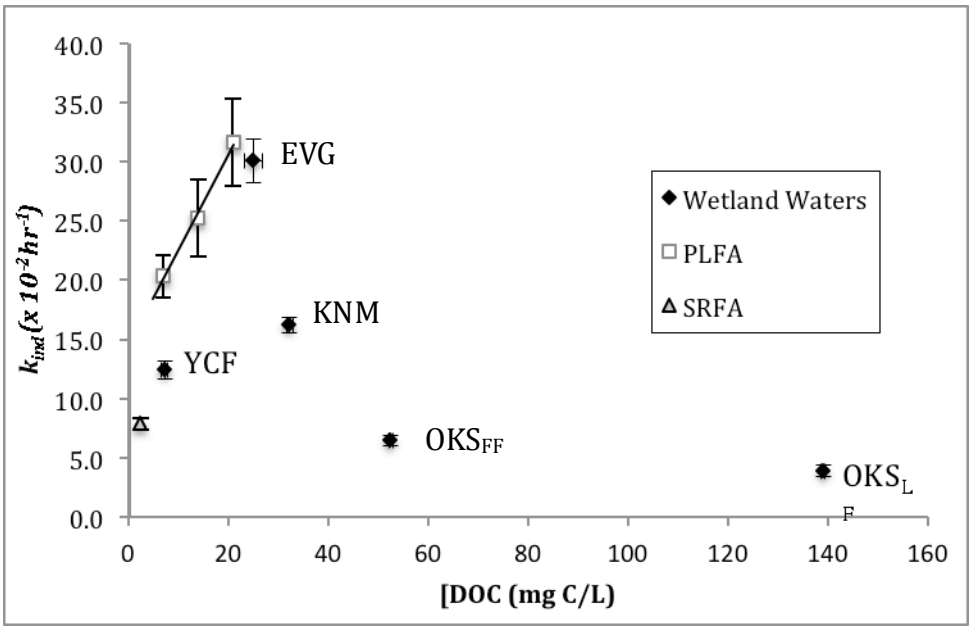

Figure 4: Indirect photolysis reaction rate constants for isoproturon (IP) as a function of dissolved organic carbon concentration ([DOC]) in various wetland waters (filled markers; field pH, see Table 1) and fulvic acid solutions (open markers, Δ = Suwannee River FA, □ = Pony Lake FA; pH = 8.0). Error bars represent 95% confidence interval.

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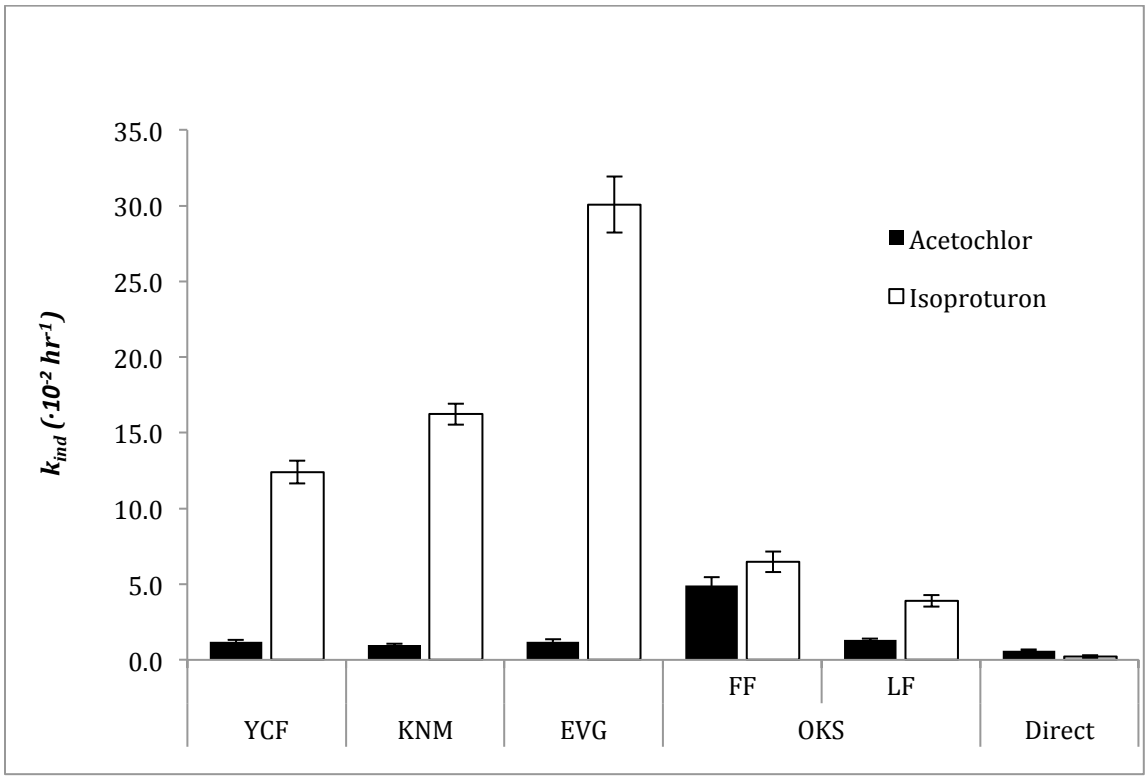

Figure 5: Indirect photolysis reaction rates (k_{ind}) for isoproturon and acetochlor in wetland water samples used in this study**.**

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