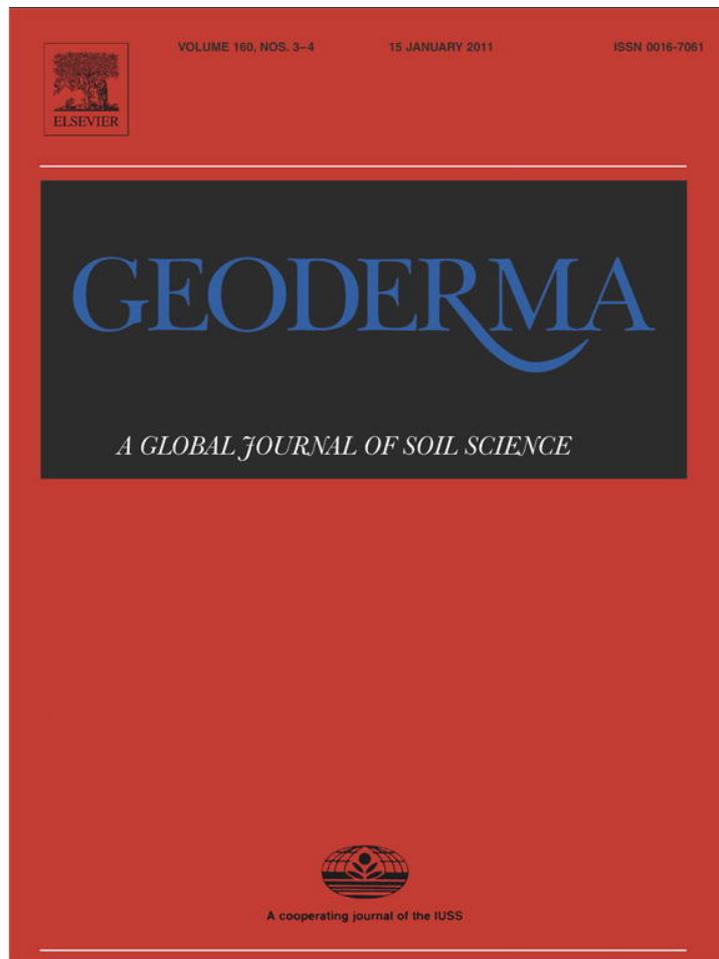


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Photodissolution of soil organic matter

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ARTICLE INFO

Article history:

Received 7 December 2010

Received in revised form 29 November 2011

Accepted 30 November 2011

Available online xxx

Keywords:

Photochemistry

Soil organic matter

Photodissolution

Dissolved organic carbon

Nitrogen

Moisture

ABSTRACT

Sunlight has been shown to enhance loss of organic matter from aquatic sediments and terrestrial plant litter, so we tested for similar reactions in mineral soil horizons. Losses of up to a third of particulate organic carbon occurred after continuous exposure to full-strength sunlight for dozens of hours, with similar amounts appearing as photodissolved organic carbon. Nitrogen dissolved similarly, appearing partly as ammonium. Modified experiments with interruption of irradiation to include extended dark incubation periods increased loss of total organic carbon, implying remineralization by some combination of light and microbes. These photodissolution reactions respond strongly to water content, with reaction extent under air-dry to fully wet conditions increasing by a factor of 3–4 fold. Light limitation was explored using lamp intensity and soil depth experiments. Reaction extent varied linearly with lamp intensity. Depth experiments indicate that attenuation of reaction occurs within the top tens to hundreds of micrometers of soil depth. Our data allow only order-of-magnitude extrapolations to field conditions, but suggest that this type of reaction could induce loss of 10–20% of soil organic carbon in the top 10 cm horizon over a century. It may therefore have contributed to historical losses of soil carbon via agriculture, and should be considered in soil management on similar time scales.

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1. Introduction

Sunlight is a well-known agent in weathering of many forms of organic matter, and is commonly studied in life-cycle analysis for organic materials exposed to it. Field studies have shown that plant litter decay is accelerated by sunlight (Austin and Vivanco, 2006; Henry et al., 2008; Parton et al., 2007). Irradiation of vascular plant detritus and wood accelerates decay and leaching of dissolved organic carbon (Anesio et al., 1999; Denward and Tranvik, 1998; Nemeth and Faix, 1994; Vähätalo et al., 1998) and soil Humic-type materials also show degradation under exposure to ultraviolet and visible wavelengths (Schmitt-Kopplin et al., 1998). Mineral soils contain these materials, and their organic matter should therefore undergo similar reactions.

Sediments in rivers and coastal regions represent largely eroded mineral soil horizons. Riverine and coastal sediments have been shown to undergo photodissolution, in which exposure to sunlight leads to both dissolution of up to tens of percent of the total particulate organic carbon (here termed POC) to dissolved organic carbon (DOC; Kieber et al., 2006; Mayer et al., 2006; Riggsbee et al. 2008) and photooxidation of a lesser amount (Estapa and Mayer, 2010). The organic matter in sediments from riverine and coastal environments

often derives largely from soils (Goñi et al., 1998, 2006; Zhu et al., 2011). Soil organic matter in its terrestrial habitat should hence be subject to similar reactions.

Carbon storage in soils tends to be concentrated in the upper mineral soil horizons that are most likely exposed to sunlight. In addition to sequestering carbon from the atmosphere, this organic matter performs critical functions in soil-based terrestrial ecosystems. Any process with the potential to destabilize significant fractions of soil organic matter and mobilize it from land thus deserves attention. Pauli (1964) and Moorhead and Callaghan (1994) suggested that photochemistry influences soil organic matter, and thus the upper mineral horizons seem important targets for study.

Here we examine the possibility, extent, and several possible control variables for light-induced loss of organic matter in mineral soils, especially photodissolution of organic carbon. To isolate the role of various environmental variables, we employed a laboratory experimental approach to study the influence of light dosage, water content, time, dark rest states, and solution composition, as well as determine the range of reactivities among a small collection of different soils.

2. Methods and materials

2.1. Sample sources

We obtained several A-horizon soils from United States Department of Agriculture (USDA) archives or our own samplings (Table 1). This

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sample set includes tilled and untilled horizons, which may represent histories of more and less previous exposure to sun, and with about an order of magnitude range in organic carbon content. The Albia, Gumz, Satanta, Richfield, Kibler and Howell soils were obtained from USDA National Soil Survey Center (Lincoln, NE, USA). The Tully soil was sampled from never-tilled native tallgrass prairie located north of the campus of Kansas State University in Manhattan, KS, USA. The Marshall soil was sampled from the Dinesen Prairie Profile at Ridgetop Site 2 near Harlan, IA, USA.

2.2. Sample preparation and general experimental conditions

Experimental protocols varied according to goals, and descriptions are headed according to their purpose. Each experiment was designed to focus on the influence of one variable, so that comparisons are largely valid within rather than among experiments.

Soil preparation conditions varied during the ca. 5 y of experiments. For example, to improve homogeneity and light exposure, soils were usually sieved, after drying and lightly disaggregating (no grinding) in a mortar and pestle. Soils in early experiments were sieved at relatively coarse sizes (e.g., 500 μm) and, as our appreciation for light limitation developed, at progressively smaller sizes (down to 63 μm). It is possible that this evolution led to varying reaction yields among experiments, but this possibility was not systematically tested.

Special flat-bottom glassware or quartzware was used to minimize accumulation of soil particles along edges of beaker bottoms. All irradiations were carried out in Suntest XLS + and/or CPS + instruments (Atlas Materials Testing Technology). These units use a Xenon lamp whose output is filtered to simulate noon sunlight in a subtropical latitude with total output of 765 W m^{-2} . Temperature in the sample containers was controlled by immersing sample holders (e.g., beakers) in a water-filled tray inside the Suntest, through which flowed water from an external, temperature-controlled, water bath and circulator.

We tested for the effect of stirring on photodissolution yield in several soil suspensions. Reaction conditions among these experiments varied, because they were often conducted in the context of an experiment designed for other reasons. Results varied among experiments, but generally showed little to no effect of stirring (<25% enhancement). The one exception was an early experiment involving Tully 15–30 cm soil sieved at 500 μm , which showed a threefold enhancement of DOC yield in stirred relative to unstirred suspension.

2.2.1. Varying light intensity

To vary incident light intensity in the Suntest, we adjusted the lamp voltage, as per manufacturer's instructions. We did not test for proportionality of irradiation with voltage. Albia 1138 and Kibler soils, sieved at 212 μm , were added to 5 mM CaCl_2 solution to a level of 1 g-soil L^{-1} and the resultant suspensions in quadruplicate were stirred

and irradiated at 19–20° for 48 h. Dark controls were incubated without irradiation for the same time, stirring and temperature conditions. "t=0" suspensions were similar except for sampling within 5 min of stirring in the dark. After irradiation, the suspensions were filtered through pre-muffled Whatman GFF filters, and the filtrates analyzed for DOC.

2.2.2. Effect of solution composition

We used deionized water or 5 mM CaCl_2 solution for various experiments, with the latter intended to improve sample handling of some soils. To test for differences in photodissolution extents between these two solutions, we performed one experiment that varied only in this solution composition. The Tully and Albia 1138 soils were sieved at 63 μm , and the Albia 1131 soil was run without sieving. We made 40 mL suspensions (1 g-soil L^{-1}) in both deionized water and 5 mM CaCl_2 solutions, and then irradiated them under 765 W m^{-2} for 4 h at 19–20°. After irradiation, the suspensions were filtered through pre-muffled Whatman GFF filters, and the filtrates analyzed for DOC.

2.2.3. Kinetics and extent of reaction for different soils

To assess the range of reaction extents and kinetics of reaction for a variety of soils under identical experimental conditions, we selected the Albia 1131, Albia 1138, Tully, Gumz, Kibler, Howell and Richfield soils. Each was sieved at 212 μm . These samples were then dried at 60° for 2 h, 40 mg of each soil quadruplicate added to a 250 mL beaker and 40 mL of 5 mM CaCl_2 added along with a glass stir bar. Premuffled quartz plates were placed over each beaker and the irradiation under 765 W m^{-2} carried out for 4 d at 19–20°. After 1, 2, 3, and 4 d of irradiation, we sacrificed aliquots and filtered the suspensions through Whatman GFF filters. The filters were analyzed for POC and particulate nitrogen (PN) and the filtrates for DOC. Dark controls consisted of each soil under the same stirring and temperature conditions but without irradiation.

2.2.4. Release of nitrogen

To examine the extent and forms of nitrogen release, the Tully soil was disaggregated and sieved at 250 μm . Triplicate suspensions of 1 g-soil L^{-1} in deionized water were made in beakers, covered with quartz plates and irradiated under 765 W cm^{-2} at 22° without stirring. At 24 and 48 h, suspensions were removed and filtered through Whatman GFF filters. Filters were analyzed for POC/PN and the filtrates analyzed for DOC, dissolved organic nitrogen and various inorganic forms of dissolved nitrogen.

2.2.5. Alternate light–dark, longer-term incubation

Light can inhibit microbial activity (Sommaruga et al., 1997), so we don't know if or how organisms affected organic matter dynamics during irradiation. In aquatic systems, photo-inhibited microbial activity rapidly recovers (Kaiser and Herndl, 1997). We therefore conducted experiments with short irradiations interrupted with longer dark incubations, to allow microbial populations to recover and possibly contribute to overall organic matter losses. Such combined irradiation and dark incubation experiments have been shown to maximize light-mediated loss of DOC in aquatic samples (Miller and Moran, 1997).

We added 40 mg of the Richfield soil, sieved at 212 μm , to 38 mm i.d. glass tubes in quadruplicate and added 10 mL of deionized water to each. The slurries were shaken and then allowed to settle, and irradiated at 765 W m^{-2} for 8 h at 20°. The light was then turned off and the tubes incubated in the dark at ca. 20° for 64 or 88 h, in alternating sequence. The irradiation was then repeated for 8 h, followed by another dark incubation. After every third irradiation and incubation, a set of tubes was sacrificed and sampled by filtering through a Whatman GFF filter. Samples were thus taken at 24, 48, and 72 h of cumulative irradiation, plus their associated dark incubation periods. The filtrates and filters were analyzed for DOC and POC, respectively.

Table 1

Soils used in this study. Ap horizons have been tilled, while A horizons have not. Organic carbon concentrations refer to parent sample; the sievings used in various experiments led to slightly different concentrations for different experiments.

Soil series, order (USA state of origin)	Description	Horizon (depth, cm)	Organic carbon (mg g ⁻¹)
Albia 1131 Alfisol (NJ)	Mesic, Aric Fragiaqualf	Ap (0–13)	13.5
Albia 1138 Alfisol native (NJ)	Mesic, Aric Fragiaqualf	A (0–6)	78.0
Gumz Mollisol (IN)	Mesic, Typic Endoaquoll	Ap (0–23)	79.6
Satanta Mollisol (KS)	Mesic, Aridic Argiustoll	Ap (0–12)	4.0
Richfield Mollisol (KS)	Mesic, Aridic Argiustoll	Ap (0–13)	16.2
Kibler Ultisol (VA)	Mesic, Typic Dystrudept	Ap (0–20)	59.6
Howell Ultisol (MD)	Mesic, Typic Hapludult	Ap (0–13)	43.3
Tully Mollisol (KS)	Mesic, Pachic Argiustoll	A (15–30)	20.4
Marshall Mollisol (IA)	Mesic, Typic Hapludoll	A (20–40)	21.0

2.2.6. Varying moisture

Albia 1138 soil was sieved at 212 μm and dried at 60° for 3 h before irradiation. After sprinkling 50 mg-soil into shallow aluminum dishes (approximately 3.7 cm diameter \times 1.2 cm depth), varying amounts of 5 mM CaCl_2 solution were added to make roughly three levels of moisture. For the air-dry treatment there was no solution added, for conditions approximating field-moist states we added small amounts of mist with an atomizer, and for full immersion we added 1.5–1.6 mL-solution using a pipette. The upper rims of the dishes were then covered with a precut gasket made of Parafilm, to ensure a seal, and overlain with a quartz or glass disk (for irradiated or dark controls, respectively). The dishes were weighed at each step to determine exact added amounts of soil and water. The dishes were then placed in bottom contact with water from a temperature-controlled water bath, and placed in the Suntest for irradiation. Irradiated samples were subjected to 765 W m^{-2} of simulated sunlight for 48 h at 20 °C. After irradiation, the outsides of the dishes were carefully dried with a Kimwipe and reweighed to determine water loss. For the full immersion treatments there was <1% water loss, for the field-moist treatments water losses ranged 7–20%, and there was no weight change for the air-dry treatments. To extract photodissolved material using the same solid:water ratio, we then added 1.5 mL of CaCl_2 solution to the 50 mg of soil in the air-dry and field-moist treatment dishes. From each dish, we then stirred the water–soil mixture, removed 1 mL of the suspension with a 1 mL pipette, and filtered it through a Whatman GFF filter. Each filter was then rinsed with a further 4 mL of CaCl_2 solution into the ca. 1 mL initial filtrate, and this solution was analyzed for DOC. Blanks of CaCl_2 solution in dishes without soil were run, and their DOC values subtracted from all treatments. As a $t=0$ control, we made triplicate dishes with 1.5 mL- CaCl_2 solution added to 50 mg of dry soil and immediately subjected it to the removal and filtration steps.

2.2.7. Effect of soil depth

Albia 1138 soil was sieved at 63 μm and dried at 60° for 1 h before irradiation. Soil was weighed out into reaction vessels, either beakers or glass tubes, to achieve depths equivalent to 30, 60, 120, and 600 μm , based on an assumed bulk density of 1.3 g-soil cm^{-3} (discussed below). We tested and found that reaction extent was independent of beaker vs. tube. We added 0.5 or 2.5 mL of 5 mM CaCl_2 to tubes and beakers, respectively, to create triplicate slurries that could then be swirled to evenly distribute the soil, and then dried each vessel at 40°. The vessels were then separated into two sets for irradiation. One set of reaction vessels was kept dry, and to the second set we added 5 mM CaCl_2 solution at a ratio of 20 mL g-soil^{-1} prior to irradiation. A set of tubes of each “depth” was sacrificed immediately to obtain a $t=0$ release of organic matter, another set of the thinnest “depth” was maintained as a dark control, and the rest of the vessels were irradiated for 72 h at 765 W m^{-2} at 20°. The dry irradiation treatments were extracted immediately after the irradiation with the same ratio of 5 mM CaCl_2 solution as those to which the solution had been added prior to irradiation, to equalize the extraction step water:solid ratios for wet and dry treatments. In other words, they differed only in whether irradiated in wet or dry state. The resultant slurries were then filtered through precombusted Whatman GFF filters, and the filtrates analyzed for DOC.

2.3. Analyses

Particulate organic matter was measured as organic carbon and total nitrogen using a Perkin-Elmer 2400B Elemental Analyzer. Carbonate minerals were removed prior to analysis by gas-phase exposure to concentrated HCl (Mayer, 1994). Dissolved organic carbon and nitrogen were analyzed on a Shimadzu TOC-V CPH analyzer that combines high-temperature combustion with non-dispersive infrared detection for carbon and chemiluminescence detection for nitrogen. We

used the non-purgeable organic carbon (NPOC) option for DOC. Dissolved ammonium concentrations were determined on a Lachat QuikChem FIA+ analyzer, using the alkaline, phenol-hypochlorite spectrophotometric method as described in the instrument manual (Method #31-107-06-1-B). Nitrite plus nitrate concentrations were measured spectrophotometrically on the Lachat analyzer after cadmium reduction of nitrate to nitrite, followed by determination of the nitrite as diazo dye formed with sulfanilamide (Method #31-107-04-1-C).

3. Results

3.1. Varying light intensity

We verified the potential for light to cause photodissolution of organic carbon under varying irradiation intensities that represent a range from darkness to mid-day, subtropical solar irradiance. DOC release over 48 h was roughly proportional to the irradiation intensity (Fig. 1). Dark controls, incubated for the same 48 h as the irradiations, showed small release of DOC, which was similar in magnitude to release found within minutes (“ $t=0$ ”) under dark conditions. This similarity was found in many experiments, although both $t=0$ and dark controls were not run for every experiment. The release of DOC above the release found for the dark control or $t=0$ values, then, is considered to represent net photodissolution of organic matter. Subtracting the $t=0$ value indicates changes during an irradiation, but does not account for changes that would occur in the absence of light. Subtracting a dark control indicates such changes, but removal of dissolved organic carbon by processes such as biological uptake or remineralization will not be necessarily equal to those occurring under irradiation. Our findings of similar differences using $t=0$ or dark controls indicates that these dark processes have, on the time scales of the irradiation experiments, negligible effect on desorbed organic matter in the absence of light.

3.2. Effect of solution composition

There was generally little difference in yield of dissolved organic carbon irradiated in deionized water vs. 5 mM CaCl_2 solution (Fig. 2). Of the three samples, only the Tully sample showed a significant but small deviation from the 1:1 line. This finding is in keeping with the results of Mayer et al. (2006) who found little difference among solutions ranging from deionized water to seawater.

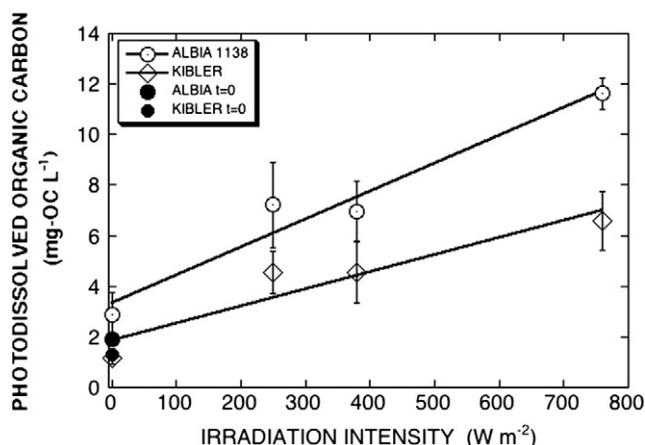


Fig. 1. Release of DOC from Albia 1138 and Kibler soils under varying irradiation intensities. Stirred soil suspensions consisted of 1 g-soil (L-5 mM CaCl_2) $^{-1}$ irradiated at 19–20° for 48 h. Soils were sieved at 212 μm . Dark controls (i.e. Irradiation intensity = 0) were identical except incubated in the dark under similar times, stirring and temperature conditions. “ $t=0$ ” suspensions were similar to dark controls except for sampling within 5 min of stirring in the dark.

3.3. Kinetics and extent of reaction for different soils

Most of the POC loss in this kinetics experiment appeared as an increase in DOC; in other words, particulate organic matter largely photodissolved as organic matter (Fig. 3) rather than being oxidized. Most data have sufficient variance after error propagation to show indistinguishable POC loss and DOC gain; nevertheless, most data pairs show greater POC loss than DOC gain. This trend implies loss of some POC into a phase not detected as DOC. Similar budget short-falls between DOC gain and POC loss for marine sediments (Mayer et al., 2006) have been accounted for by measured carbon dioxide production via photooxidation (Estapa and Mayer, 2010), which seems likely here as well. The discrepancies between POC loss and DOC gain for many of these soil samples appear higher than observed for marine sediments, suggesting greater susceptibility to photooxidation. Indeed, photochemical alteration of terrestrial plant detritus has been shown to be largely photooxidative in nature (Brandt et al., 2009). Explicit measurement of dissolved inorganic carbon production will be necessary to confirm this possibility.

Over 4 d of irradiation, loss of POC reached extents of 3–35% for the seven soils under identical experimental conditions. Reaction proceeded to asymptotic values for some soils and continued at a slow rate in others. Averaged across these soils (Fig. 4), the POC loss slowed considerably after a few tens of hours. Longer time spans were not explored because the closed system, batch nature of these experiments is unrealistic for many field situations (see Discussion below). There was no relationship between initial organic matter content and either reaction extent or kinetic behavior. The range of photodissolution extents found for this set of seven soils encompasses results found with other soils irradiated under slightly different conditions during this study.

3.4. Release of nitrogen

Nitrogen photodissolved from soils in generally similar proportions as carbon. For example, the C:N ratio of six of the seven soils in the kinetics experiment above (Figs. 3 and 4) remained constant during the irradiation, implying similar losses of carbon and nitrogen. It decreased from 11.3 to 7.1 in the Richfield soil, indicating preferential loss of carbon over nitrogen. We examined the dissolution of organic vs. inorganic forms of nitrogen for only the uncultivated Tully and Marshall prairie soils. Irradiation produced dissolved organic nitrogen to a much greater extent than dissolved in the dark control (Fig. 5). We observed light-induced production of ammonium in these two experiments; this photoammonification reaction accounted for 7

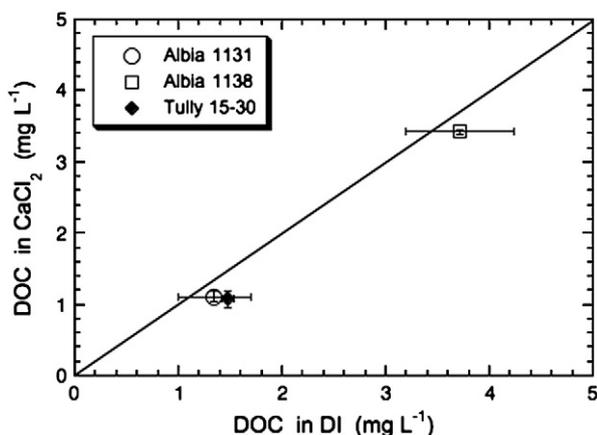


Fig. 2. Concentration of dissolved organic carbon from three soils (Albia 1131, Albia 1138, and Tully) from a 1 g-soil L⁻¹ suspension after 4 h irradiation, in either deionized water (DI) or 5 mM CaCl₂ solution. Diagonal line represents equal concentrations.

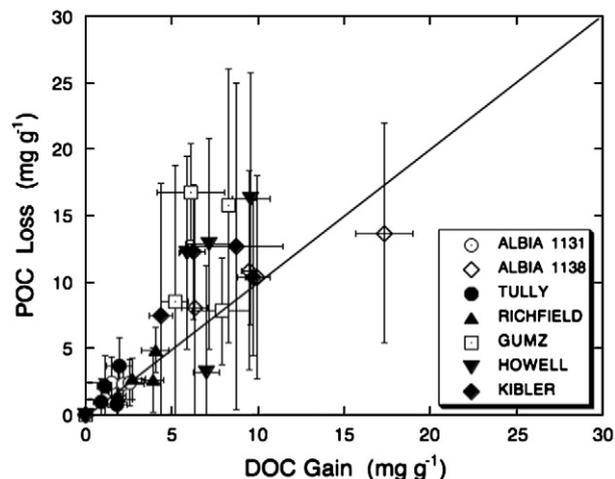


Fig. 3. POC loss vs. DOC gain for seven soils irradiated continuously for 4 d in stirred suspensions, normalized to g-dry weight of soil. Soils include Albia 1131 and 1138, Tully, Richfield, Gumz, Howell, and Kibler (see Table 1). Multiple symbols for each soil represent sampling times of 1, 2, 3 and 4 d. Propagated errors lead to high variances in POC gain due to relatively small differences between initial and irradiated soils. Diagonal line represents equal POC loss and DOC gain.

and 23% of the total, light-induced dissolution of N for the Tully and Marshall soils, respectively. These ratios are similar to findings for aquatic sediments (Mayer et al., 2011; Southwell et al., 2010). There was negligible change in nitrite plus nitrate concentrations. The C:N of the photodissolved organic matter therefore was somewhat higher than that of the original particulate organic matter (15.5 vs. 11.1 for the Marshall soil and 13.4–15 vs. 11.0 for the Tully soil, respectively). These higher C:N ratios in the photodissolved organic matter are presumably due in part to photoammonification of the dissolving organic matter as ammonium, leaving dissolved organic matter with higher C:N (Mayer et al., 2009). Studies with sediments have shown that the dissolved phase C:N ratio changes strongly with irradiation time (unpubl. data), but that possibility was not examined here.

3.5. Alternate light–dark, longer-term incubation

To further enhance the possibility of remineralization, we conducted experiments with sequential short irradiation times and longer intervening dark incubation times to allow microbial recovery and possible remineralization. These experiments also increased

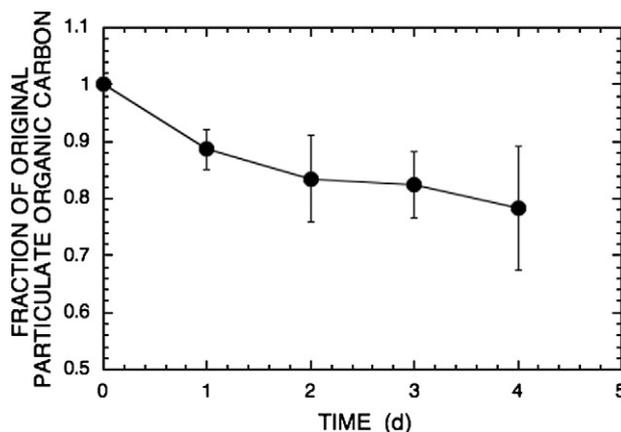


Fig. 4. Time course of mean POC loss for seven soils under continuous irradiation over 4 d. Soils include Albia 1131 and 1138, Tully, Richfield, Gumz, Howell, and Kibler (see Table 1). Error bars represent variance (1 SD, after error propagation) among the seven soils.

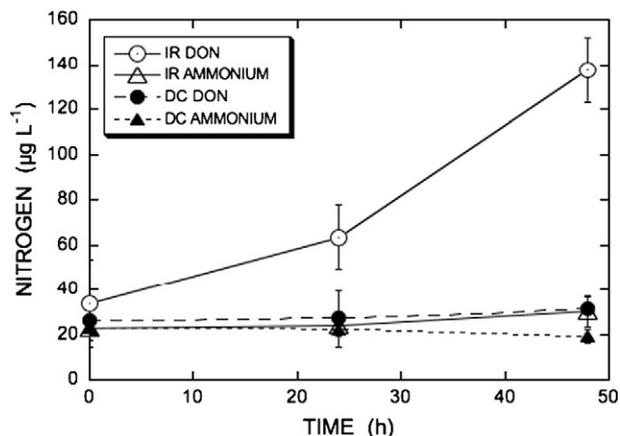


Fig. 5. Photodissolution of nitrogen as dissolved organic nitrogen (DON) and ammonium from the Tully soil. IR refers to irradiated treatment while DC refers to dark control.

replication to discern differences between loss of POC and appearance of DOC. Results showed a clear difference, with POC losses exceeding DOC appearance (Fig. 6) by roughly a factor of three. These differences were apparent by the 24 h cumulative irradiation time, which would include an additional 216 h of dark incubation. The experimental design differed from the kinetics experiments described above, and hence do not shed light on whether the less clear discrepancies between POC loss and DOC gain (Fig. 3) in that experiment were due to remineralization. The lack of change in the dark controls implies more clearly that some light-mediated remineralization occurred, presumably due to some combination of photochemical and microbial reactions. Different experimental design would be necessary to assess the relative responsibilities of each.

3.6. Varying moisture

Photodissolution was markedly lower if irradiation was conducted under drier conditions, followed by rinsing to dissolve liberated organic matter. For the Albia soil, the yield of photodissolved DOC after 48 h of irradiation was roughly 3–5 times higher (after subtracting the $t = 0$ control) under a fully immersed state relative to air-dry

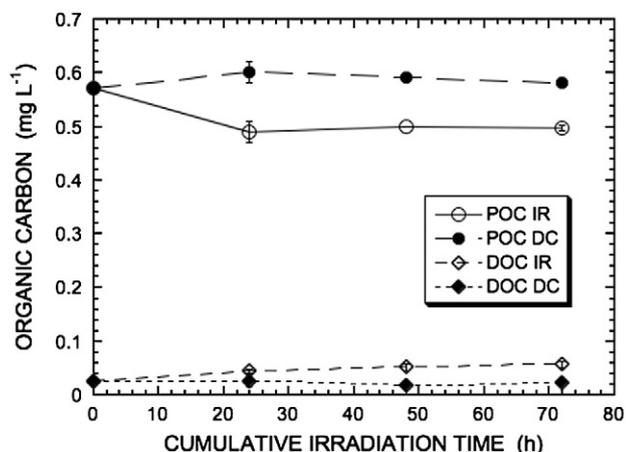


Fig. 6. Loss of particulate organic carbon (POC) and appearance of dissolved organic carbon (DOC) over alternating periods of irradiation (IR) and dark incubation of the Richfield soil. Irradiation periods of 8 h were followed by dark incubations of 64 or 88 h, and the cycle repeated; samplings were taken after every third irradiation–dark incubation cycle. Dark controls samples (DC) were incubated under same conditions except without irradiation.

conditions (Fig. 7). Intermediate states of moisture, with gravimetric water contents of 0.35–0.86 g-water g-dry soil⁻¹ that are roughly equivalent to field-moist conditions, showed intermediate yields of photodissolution. We have found strong enhancement of photodissolution of organic matter by water in four other soils, including two depth horizons of the Tully soil and two Maine soils (unpubl. data), with magnitudes similar to that of the Albia soil.

3.7. Effect of soil depth

We assessed the depth dependence of photodissolution by placing varying amounts of soil per irradiated area in dishes, and calculating an equivalent depth of soil by assuming bulk density of 1.3 g cm⁻³. It is of course unlikely that this bulk density applies to either the top mm of soil in the field, where microtopography is considerable, or to our thin experimental treatments, but this conversion does allow for scaling to thicker soil columns. This experiment used soil sieved at 63 µm, rather than coarser sizes, in order to minimize self-shading by aggregates larger than 63 µm. For the Albia 1138 soil, we found that discernible amounts of photodissolved organic carbon were observable at equivalent depths of hundreds of µm (Fig. 8). Wet soils yielded more photodissolved organic carbon, albeit with a similar depth dependence. The photodissolution yield also increased roughly twofold by increasing the ratio of rinse solution to dry soil after the irradiation roughly tenfold (data not shown). A pair of slurry treatments, stirred and unstirred, with the ~1 g-soil L-water⁻¹ loading similar to experiments reported above, were run simultaneously with the same soil sample. They yielded higher photodissolution extents of 16.2 and 12.7 mg-DOC g-soil⁻¹ for the stirred and unstirred treatments, respectively (data not shown). The equivalent depth of total soil in these slurries, if the particles were deposited as dry soils with bulk density of 1.3 g cm⁻³ as calculated for the other treatments, would be 13 µm. It's not clear if greater photodissolution in these slurries was due to less light limitation in these optically thinner configurations or higher water:soil ratios.

The differences in yield of DOC between the irradiated and either dark control or $t = 0$ treatments are roughly in inverse proportion to the calculated depth of the soil. In other words, Fig. 8 data approximate a dilution plot, although propagation of errors creates too much variance for a strong test of this inverse proportionality. Hence the effective photic zone for this reaction – the depth by which the majority of forward reaction has occurred – is at the lower end of the size range, likely in the tens of micrometers. Similar results were obtained for the

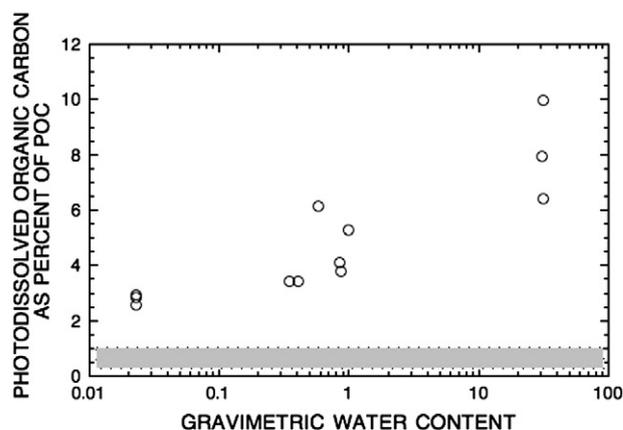


Fig. 7. Photodissolution of organic carbon from Albia 1138 soil under varying moisture states. Gravimetric water contents are mass of CaCl₂ solution per mass of dry soil at the start of the irradiation. Each point is a singlicate. Photodissolution is expressed as percentage of original particulate organic carbon appearing as DOC. Stippled area represents range of triplicate values at $t = 0$.

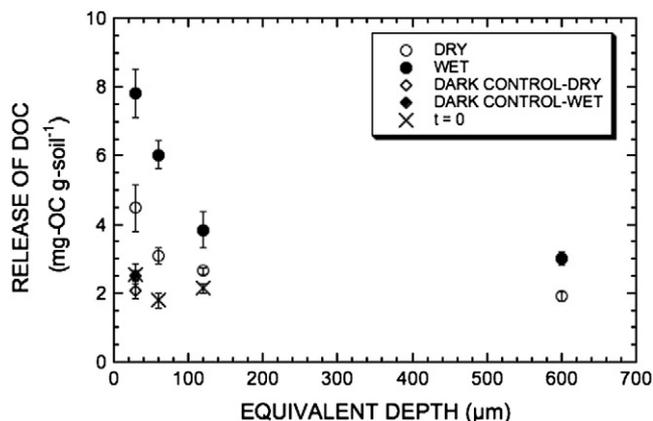


Fig. 8. Amount of original particulate organic carbon appearing as dissolved organic carbon upon irradiation of Albia 1138 soil, under dry and wet states, as a function of the equivalent depth of soil. Irradiation was for 72 h. Also shown are dark controls, performed only for the 30 μm -equivalent depth, and the $t=0$ controls, performed only for the 30, 60, and 120 μm -equivalent depths.

Tully soil (data not shown). Such a shallow photic zone is consistent with previous studies. Hebert and Miller (1990) found >90% of ultraviolet light to attenuate by 200 μm in four soils, and Ciani et al. (2005) found consistent loss of 99% of light by soil depths of 30–200 μm for light wavelengths of 300–500 nm in twenty soils examined. These wavelengths comprise the range important for the bulk of photodissolution in marine sediments that contain mostly terrestrial organic matter (Mayer et al., 2006; Estapa, unpublished data), and hence are likely as important for soils.

4. Discussion

4.1. Controls on reaction extent

Our results show that fractions of up to a third of total soil organic matter are susceptible to loss from the solid phase under simulated solar irradiation, largely to photoproduction of dissolved organic matter. Thus, under similar experimental conditions of stirred suspensions of soil, these mineral soil horizons respond similarly to sunlight as river and coastal sediments (Kieber et al., 2006; Mayer et al., 2006; Riggsbee et al. 2008). This finding is not surprising given that soil organic matter can dominate the total organic matter in those other environments. Further, there is little effect of solution composition on photodissolution yield (Mayer et al., 2006), so that the CaCl_2 solutions generally used here gave similar results as seawater solutions in other studies.

This range of susceptibilities was found in suspensions that were relatively thin in an optical sense. The slurries for kinetic experiments (Figs. 3 and 4), for example, had depth-integrated soil that would be equivalent to a thickness of 14 μm if they were settled into a deposit with bulk density of 1.3 g cm^{-3} . It is likely, therefore, that the variance among photodissolution susceptibilities is due to properties of the soils. Some candidate properties include chemical nature of the organic matter, optical properties of the soils (e.g., aggregate size), and presence of minerals that may catalyze the reaction. We generated no data to test these possible intrinsic controls on photodissolution extent.

Our experiments used soils in a static condition, in the sense that the experiments were largely closed with respect to reactant input or product output. If, for example, photodissolution derives most strongly from the younger fractions of soil organic matter – as appears to be the case for sediments (Mayer et al., 2009) – then continuous input of litter detritus with a higher reactivity might lead to a greater

importance of these photochemical reactions on a time-integrated basis. On the product output side, most of our experiments kept photodissolved organic matter in contact with the solid phase throughout the experiment, so that sorption or solubility equilibrium might have restricted further dissolution of organic matter.

Our exploration of environmental parameters relevant to the field – e.g., time and water content – provides only initial explorations of their potential importance. They are not intended to allow accurate simulations of photodissolution extents to be expected in the field, nor do they provide mechanistic explanations for relationships. For example, the observed dependence of reaction on the moisture state could be due to chemical, optical or other factors, and we have not identified if the functional relationship is with water content or water activity.

The tilling of landscapes for agriculture likely has enhanced exposure of mineral soil horizons to sunlight. We found no effect of untilled vs. tilled history on the extent of photodissolution or POC loss upon irradiation. The pair of Albia soils tested represents tilled and untilled versions of the same soil series, and differed greatly in their organic matter content, but showed similar proportions of organic matter loss upon irradiation. The Marshall soil from Iowa and Tully soil from Kansas were also untilled soils, and their photodissolution losses fell within the range of values found for other, tilled soils. While this preliminary comparison is not statistically strong because of the small number of soils tested, there does not appear to be a major impact of tilling history on photochemical susceptibility.

Photodissolution is defined operationally as the appearance of organic matter in the filtrate passing a glass fiber filter of nominal pore size 0.7 μm . The range of possible materials in these filtrates is large, from small organic molecules to larger colloids. Our only characterization of this material is that it generally has a C:N ratio somewhat higher than that of bulk soil organic matter.

These filterable materials likely have greater mobility and/or biological availability than the originating soil organic material. Photodissolved material, which would include dissolved organic carbon and nitrogen plus other compounds such as the ammonium found here or phosphorus found in other studies (Southwell et al., 2010), should be amenable to leaching from the horizon in which it was liberated. These exported materials may be chemically read-sorbed or biologically utilized in subsurface soil horizons as is other DOC released from surface layers by non-photochemical processes (e.g., Lilienfein et al., 2004). Readsorption and/or microbial utilization may be partly responsible for the decrease in net photodissolution extent with increasing soil depth (Fig. 8). These outcomes were not investigated in this study and need attention.

4.2. Roles of water and aggregation

Soils are not normally exposed to sunlight as a stirred suspension, with some exceptions such as puddled rice paddies. Thus, we also studied physical conditions closer to normal soil states of variable water content and physical agitation.

Our experiments with varying water content show that water status likely has a major control on photodissolution in field situations. The endmember cases of field-dry conditions versus immersion (e.g., rice paddies) may lead to 3–5 fold variations in photodissolution rates. Similar relative rates of photooxidation – as CO_2 production – under dry vs. wet conditions were found for detritus from aquatic plants (Anesio et al., 1999), though water content in combination with microbial activity can lead to significant changes in litter degradability after irradiation (Foeroid et al., 2010). Unfortunately, despite an extensive literature on bulk soil water content, there is little information on the depth dependence of moisture over the top tens to hundreds of μm in which the reaction will take place, especially during changing states such as dew drying under morning sunlight.

The influence of water in our experiments may derive from various possible mechanisms, including optical and chemical ones. In an unstirred field setting, it is likely that light is both retained and propagates more deeply in wet than in dry soils (Bänninger et al., 2005; Ciani et al., 2005). Water might act as a transport medium in which photoproduced reactive oxygen species (e.g., singlet oxygen – Gohre and Miller, 1983) can be transferred from point of generation to point of reaction with particulate organic matter, to cause a secondary dissolution reaction. Water content affects both production and decay rates of reactive oxygen species in wood (Hon and Feist, 1981).

The aggregation state of soils is likely important in these reactions, because both microaggregates and macroaggregates are of sufficient size to cause light attenuation in their interiors. This effect was shown clearly in a study using high-intensity ultraviolet light to photooxidize soil organic matter (Skjemstad et al., 2008). Water-induced disaggregation (slaking) might expose interior parts of aggregates to more light. Our finding of little effect of stirring on photodissolution yield from soils that had passed sieves finer than 212 μm prior to irradiation, compared with enhancement of OC loss by stirring with a soil sieved at 500 μm , is consistent with an aggregation effect. Too many other variables changed among these experiments to allow strong inference for this aggregation effect from these experiments, and in addition our experiments cannot discern between an optical vs. a surface reactivity explanation for this enhancement.

4.3. Preliminary extrapolation to field conditions

Our experiments into the extent of reaction with soil depth show that photodissolution of organic carbon will proceed to depths of tens to perhaps hundreds of μm , consistent with other work on soil photic depth (Ciani et al., 2005; Hebert and Miller, 1990). More accurate estimates will require further study. The intrinsic susceptibility to photodissolution among soils studied here varied by an order of magnitude. Environmental factors such as moisture content, stirring and solid:water ratios also affected reaction extent up to several-fold. Temperature was not investigated here, but a positive temperature dependence as found with sediments (Estapa, unpubl. data), could cause several-fold variation over environmental ranges. Thus, it is impossible to calculate an effective reaction extent per area of field soil per amount of incident solar irradiance with better than an order of magnitude accuracy with the data at hand.

Nevertheless, such an order of magnitude estimate for field susceptibility of soils for light-induced loss of POC can be made from the experiment that examined alternate light and dark incubations (Fig. 6). In this experiment, the Richfield soil lost 16% of its POC in the first 24 h of irradiation, to some combination of DOC production, photooxidation and biological remineralization. A similar experiment with the Howell soil showed similar results. The mass loading of soil in this experiment was 3.5 mg-soil cm^{-2} , which would be equivalent to a depth of 27 μm assuming bulk density of 1.3 g cm^{-3} . This depth is 1/3700 of the soil in the top 10 cm of A-horizon soil with the same bulk density, so that 8.9×10^4 h would be required to irradiate every particle in the top 10 cm if the soil were well mixed. This irradiation could be achieved in ca 120 y, assuming that suitable radiation was provided for 5 h d^{-1} for 150 d y^{-1} . Upper soil horizons in many landscapes can be well-mixed on such time scales, as evidenced by radionuclide profiles (Kaste et al., 2007; Matisoff et al., 2002; Whiting et al., 2001). This mixing results from physical processes that move soil laterally and vertically, such as wind and rain, as well as bioturbation by humans, other animals, and plants (Gabet et al., 2003; Smith et al., 2001).

Obviously this calculation makes many crude assumptions, and can be refined for many factors such as changing climate, sun angle, and vegetative cover. Shorter term kinetics experiments might show that the reaction proceeds quickly enough as to require less

cumulative irradiance to achieve significant organic matter loss. Loss estimates might therefore shift in either direction with better data. Nevertheless, it does show that sunlight might induce loss of as much as a few percent of the organic matter in the top 10 cm soil horizon on decadal to century time scales. Soil biomes rich in bioturbating animals that bring mineral soil to the surface – e.g. earthworms, termites, gophers, cattle, humans – may be especially susceptible. Photochemical losses of organic matter may thus have played some role in the 20–50% overall losses observed in the decades following introduction of tilling to many landscapes (Mann, 1986; Tiessen et al., 1982), as tilling obviously leads to enhanced mixing and exposure of mineral horizons to sunlight. These losses have been focused in the top 10 cm of soil (Luo et al., 2010), consistent with a role for photodissolution, though also of course with many other organic matter loss mechanisms.

Soil management practices may influence soil organic matter losses to photochemical reactions on multidecadal time scales. In addition to tilling, irrigation may be a particularly important process to manage in this context – e.g., subsurface or night-time irrigation would minimize wetting of irradiated surface mineral horizons.

Obviously, the photochemical reaction in soils will be optimized in bare, moist, warm, low-latitude situations, such as irrigation spraying on unvegetated soils or rice paddies under disturbance. Daytime, summer irrigation during early stage crop growth may enhance photodissolution loss of organic matter. Long-term losses of soil organic matter under irrigation (Nunes et al., 2007) may thus be due in part to this reaction. Temperature and water content might compensate for one another, with wetter soils remaining cooler due to evaporation.

Sunlight may destabilize significant fractions of organic matter in soil mineral horizons on decadal time scales. In the ocean, a similar possibility exists that organic matter from dark subsurface zones is destabilized upon resuspension and irradiation at the ocean's surface. In both soils and oceanic regimes, light limits the photochemical reaction, and quantifying of the extent of these reactions will depend on working out delivery of photons to chromophores, which will be influenced by both the photochemical properties and the vertical mixing of the substrate. The prediction of impacts of land use practices such as day-time irrigation must await such studies.

Acknowledgments

This project was supported by National Research Initiative Competitive Grant #2008-35107-04497 from the USDA National Institute of Food and Agriculture. We thank the National Soil Survey Center, USDA, Lincoln NE for soil samples. J.D.J. was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Biological and Environmental Research under contract DE-AC02-06CH11357 to Argonne National Laboratory.

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