Long-term photochemical and microbial decomposition of wetland-derived dissolved organic matter with alteration of $^{13}C:{}^{12}C$ mass ratio

Anssi V. Vähätalo[1]

Department of Biological and Environmental Sciences, University of Helsinki, P.O. Box 65, FI-00014 University of Helsinki, Finland

Robert G. Wetzel

Department of Environmental Sciences and Engineering, University of North Carolina, Chapel Hill, North Carolina 27599-7431; deceased 18 April 2005

Abstract

We investigated the long-term photochemical and microbial decomposition of biologically recalcitrant humic-like dissolved organic matter (DOM) leached from a vascular wetland plant, the common rush (*Juncus effusus*). Although the leachate would have been characterized as biologically recalcitrant by short-term (<14 d) bioassays, microbes decomposed 51% of its organic carbon in 898 d with a first-order biological decomposition coefficient of 0.0008 d^{-1} in darkness. Solar radiation exposure accelerated the decomposition of leachate. Under 459-d exposure to surface solar radiation, up to 90% of organic carbon was mineralized. During the exposure, the photochemical reactions preferentially mineralized the ^{12}C fraction of organic carbon and enriched the ^{13}C of organic carbon by 6‰ in the residual leachate. Solar radiation also decomposed nearly completely (up to 99.7%) chromo- and fluorophores of DOM. A 439-d bioassay following the solar radiation exposure resulted in up to 97.3% mineralization of organic carbon. Solar radiation together with microbial metabolism can completely mineralize at least some forms of wetland-derived DOM in surface waters with sufficiently long residence times.

In freshwaters and coastal waters, imported (allochthonous) organic carbon contributes much to the composition of dissolved organic carbon (DOC; Wetzel 2001). Major sources of allochthonous DOC are vascular plants in the littoral zone, wetlands, and terrestrial environments, which are hydrologically connected to open-water regions (Wetzel 1992). Because decomposers consume quickly the bioavailable parts of plant-derived DOC, biologically recalcitrant humic substances dominate the allochthonous DOC in open-water environments (Thurman 1985).

Aquatic microbes consume typically only a small portion (<5%) of humic-like allochthonous DOC in ≤2 weeks, a time typically used to test the biological lability of DOC (Moran and Hodson 1990). Such short-term bioassays dominate the literature (Søndergaard and Middelboe 1995; del Giorgio and Davis 2003) but provide little insight regarding the fate of the >95% biologically recalcitrant allochthonous humic-like DOC in the receiving lakes and ocean. Biologically recalcitrant DOC contributes much to the DOC transported to lakes, rivers, and finally to the ocean with annual loads of 0.25×10^{15} g C (Hedges et al. 1997). Molecular tracers of terrestrial organic carbon such as lignin and ^{13}C-depleted terrestrial-like organic carbon, however, are scarce in oceanic waters and marine sediments (Hedges 1992). This suggests that decomposition rather than sedimentation must be a major sink for terrestrial DOC. In addition to biological mineralization, photochemical reactions can mineralize at least a portion of terrestrial humic-like DOC and can potentially explain the decomposition of allochthonous DOC (Mopper and Kieber 2002). Previous photochemical experiments have been typically short (a few hours to weeks) and do not provide direct evidence for the long-term photodecomposition of allochthonous DOC in the receiving lakes or ocean with the water residence times lasting years or longer.

In this study we hypothesize that long-term (years) microbial and photochemical decomposition is responsible for the disappearance of biologically recalcitrant allochthonous DOC in lakes and marine waters. Our experimental work simulates the long-term fate of wetland-derived humic-like DOM in the surface waters of a receiving open-water environment. We generated humic-like DOM from common rush (*Juncus effusus*), an emergent vascular wetland plant with a widespread distribution throughout the northern hemisphere, and exposed it to solar radiation (for 459 d) and to heterotrophic microbes for up to 898 d. These exposures are longer than the times typically used for testing the biological lability or the photochemical decomposition of DOC but similar to or shorter than the residence time of water in lakes and ocean.

Material

Preparation of leachate—Chlorophyllous (green) and senescent leaves of *J. effusus,* a C_3 plant fixing its CO_2 by the Benson–Calvin pathway, were collected from Talladega

[1] Corresponding author (anssi.vahatalo@helsinki.fi).

(Alabama) Wetland Ecosystem on 18 June 1998 (Wetzel and Howe 1999). About 30 liters of plant biomass (50% green and 50% senescent standing leaves) were placed in a container and inundated with deionized water (38 liters). The decomposition of plant biomass rapidly consumed dissolved oxygen, and most of the decomposition was anaerobic. After 19 weeks, water was collected and gravity filtered first through Whatman 50 low-ash filter paper and later vacuum filtered through Whatman GF/F (0.7-μm nominal pore size) filters. The collected filtrate (8 liters) was lyophilized.

Exposure to solar radiation—Lyophilized leachate (dry mass 6.7 g) was dissolved in water from Lake Tuscaloosa with DOC of 2.8 mg C L^{-1} (3,050 mL filtered through Whatman GF/F, <0.7-μm; Vähätalo and Wetzel 2004). The leachate was distributed in seven quartz flasks and one glass flask with ground-glass stoppers and autoclaved. Autoclaving evaporated water increasing the concentration of total organic carbon (TOC) 1.07-fold and generated some chromophores because the absorption coefficient of chromophoric dissolved organic matter (CDOM) at 300 nm increased more (1.13-fold) than TOC. Each 700-mL quartz flask (56 mm in diameter, 284 mm in length) received leachate (350 mL) and an O$_2$ headspace (350 mL). An aliquot of autoclaved leachate was lyophilized for the determination of δ^{13}C. Seven quartz flasks were positioned horizontally under ambient solar radiation without cooling for 459 d on the rooftop, first at the University of Alabama (Tuscaloosa, Alabama; 33°12′59″N, 87°32′36″W) from 23 June 2001 to 29 July 2001 and then at the University of North Carolina (Chapel Hill, North Carolina; 35°54′21″N, 79°03′16″W) from 08 August 2001 to 25 September 2002. For the dark treatment, the glass flask was wrapped in aluminum foil but treated otherwise similarly to the quartz flasks. The headspaces of flasks were purged with O$_2$ gas on 26 September 2001 and 11 March 2002 so that the introduced O$_2$ (43 mmol O$_2$ flask^{-1}) was large enough to decompose TOC (25 mmol C flask^{-1}). During winter (26 October 2001–10 April 2002), the flasks were taken inside on 45 d when temperatures were below or near 0°C.

Four quartz flasks became turbid from microbial growth during the exposure, while two quartz flasks did not exhibit visible microbial turbidity, although little precipitated matter was present in the bottom of flasks (barely visible in the left flask of Fig. 1). This precipitate was Gram stained, but microscopy revealed no bacteria-like particles. Precipitate (0.5 mL) was also plated on tryptic soy agar. After a weeklong incubation both at room temperature and at +37°C, the plates showed one to four colonies with different morphologies (i.e., 0.5–8 colony-forming units mL^{-1}). Thus, even the flasks without obvious microbial turbidity contained viable bacteria.

Bioassay of treated leachates—After the solar radiation exposure, a microbial bioassay was used to measure the biological mineralization of TOC of treated leachates. The leachates were diluted with deionized water to the concentration of ~10 mg TOC L^{-1} and received a 5% (vol:vol) microbial (<10-μm filtrate) inoculum collected

Fig. 1. The leachate after 459 d of exposure to solar radiation on a roof (left) and the dark control leachate treated similarly except wrapped in aluminum foil (right). The absorption spectra of CDOM are shown in Fig. 2.

from Bolin Creek, Chapel Hill, North Carolina, along with nutrients (NH$_4$Cl and KH$_2$PO$_4$) to the final concentration of 1.7 mg N L^{-1} and 0.24 mg P L^{-1}. The leachates with microbes were sealed into 20-mL glass ampoules with 5 mL of headspace (O$_2$ gas in excess for full decomposition of TOC) and incubated in darkness at 20–25°C for 439 d. In order to describe an overall development of TOC during the whole experiment (roof exposure + bioassay), the decrease (%) in the concentration of TOC (diluted) during the bioassay was combined with the decrease in the concentration of TOC (undiluted) during the roof exposure. During the bioassay, the decrease in TOC (% ± coefficient of variation, $n = 3$) was the concentration of TOC at the end of bioassay divided by the concentration of TOC at the beginning of bioassay.

Chemical and physical measurements—Absorption by chromophoric dissolved organic matter (CDOM) was determined from 0.22-μm-filtered (Millex-GV) waters with a Beckman DU 650 spectrophotometer against deionized (Milli-Q) water blank. For quantitative measurements, the absorbance of samples was adjusted to the absorbance (A) <1 by selecting cuvettes of 1- or 10-cm path lengths or diluting the sample with Milli-Q water. The absorption spectrum of each sample was scanned two to five times with a new blank each time at 0.5- or 1-nm intervals through 800 to 200 nm. Absorbance was converted into absorption coefficient ($a_{CDOM,\lambda} = 2.303 A_{CDOM,\lambda}$ path length^{-1}) at those wavelengths where the mean A was >3 times the standard deviation of replicates. The spectral slope coefficient of $a_{CDOM,\lambda}$ (S) was calculated by a nonlinear regression for a spectral region starting at 300 nm and ending at the lowest detectable $a_{CDOM,\lambda}$.

The excitation emission matrix fluorescence spectra of leachates were measured with a Jobin Yvon SPEX FluoroMax-3 spectrofluorometer. The leachates were filtered (0.22 μm, Millex-GV) and diluted with Milli-Q
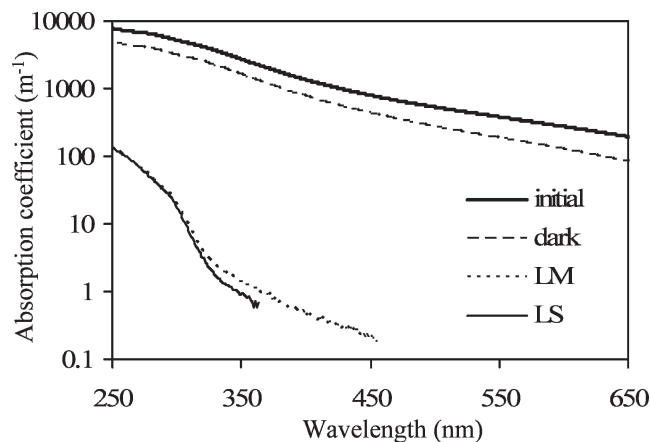
Fig. 2. Absorption spectra of chromophoric dissolved organic matter in the leachates of *Juncus effusus* initially and after treatments. Initial = in the beginning of experiment, dark = dark treatment after 459 d, and LM and LS = solar radiation exposed samples after 459 d with and without microbial turbidity, respectively.

Table 1. Spectral slope coefficients (S, $nm^{-1} \times 10^3$) for leachate initially and after treatments. Initial = in the beginning of experiment, dark = dark treatment after 459 d, and exposed LM and LS = solar radiation exposed samples after 459 d with and without microbial turbidity, respectively. The spectra are shown in Fig. 2.

Treatment	S
Initial	13
Dark	13
Exposed turbid (LM)	76
Exposed nonturbid (LS)	84

water to the absorbance of <0.02 cm^{-1} at 350 nm. The details of the measurement procedure and the elimination of Rayleigh and Raman scattering are described by Kovalczuk et al. (2005). We calculated the intensity of fluorescence for common DOM fluorophores, that is, the fluorophores A, C, and M associated with humic substances and the fluorophore T associated with aromatic amino acids (Coble 1996) as described by Kovalczuk et al. (2005).

The concentration of TOC was measured by high-temperature catalytic oxidation followed by infrared detection for CO_2 with a TOC 5000 or a TOC-V$_{CPH}$ instrument (Shimadzu). For the determination of the $^{13}C:^{12}C$ ratio of organic carbon, lyophilized leachates (3–20 mg, depending on the organic carbon content) were mixed with 50–75 μL of 2 mol L^{-1} HCl for the effective removal of inorganic carbon. The introduced solution of HCl was evaporated at room temperature overnight. Stable carbon isotope ratios ($^{13}C:^{12}C$) of samples and peptone standard ($\delta^{13}C$ of -17.25) were measured with a Micromass Optima isotope ratio mass spectrometer. Results were reported as per mill (‰) difference relative to the Pee Dee Belemnite:

$$\delta^{13}C = \left[sample(^{13}C:^{12}C)/standard(^{13}C:^{12}C) - 1\right] \times 1,000 \quad (1)$$

Results

The leachate of *J. effusus* was initially visually black and had a high concentration of CDOM (Fig. 1). The absorption coefficient of CDOM, for example, at 300 nm ($a_{CDOM,300}$) was 5200 m^{-1} (Fig. 2). After 459 d of exposure to solar radiation, the $a_{CDOM,300}$ of leachate was 18 m^{-1} (0.3% of initial; Figs. 1, 2). The CDOM absorption of photobleached leachate was below the detection limit at the visible range of the spectrum, and the leachate was visually as transparent as pure water. The dark control leachate looked still visually

black after the 459-d incubation on the roof, although $a_{CDOM,300}$ had decreased to 3,111 m^{-1} and 60% of the initial concentration of CDOM (Figs. 1, 2). These results show that natural solar radiation decomposed the $a_{CDOM,300}$ of leachate nearly completely (99.7%) in 459 d.

The spectral slope coefficient of CDOM (S) was initially low and did not change during the 459-d incubation in the darkness (Table 1). In the solar radiation–exposed leachates, S was much higher than initially or in the dark control leachate. Thus, solar radiation exposure increased the spectral slope coefficient of residual CDOM to very high values.

The excitation emission matrix of fluorescent DOM (FDOM) showed the presence of typical fluorophores in the dark control leachate on day 420 (Fig. 3A; the fluorophores A, C, M, and T described by Coble 1996). At the same time, in the solar radiation–exposed leachate without microbial turbidity, the fluorescence of A, C, and M fluorophores related to humic substances was 0.1–0.3% of that found in the dark control leachate (Fig. 3). The fluorescence of fluorophore T related to aromatic amino acids, which has an excitation wavelength below the solar UV range, was 4.3% of that in the dark control leachate. These results indicate that the solar radiation exposure decomposed FDOM nearly completely, in particular when the excitation wavelengths of FDOM overlapped with solar UV radiation.

The concentration of TOC decreased during the course of experiment (Fig. 4). In the dark treatment, the first-order decay coefficient for TOC (k_{bio}) was 0.00080 d^{-1} (r^2 = 0.97, $n = 3$), and after 898 d, the concentration of TOC was 49% of the initial concentration, indicating a half-life of 2.4 yr. Under solar radiation exposure, the concentration of TOC decreased to 10% and 28% of the initial in the leachates with (LM) and without (LS) visible microbial turbidity, respectively (Fig. 4). After the following bioassay, the concentration of TOC decreased to 2.3% and 4.0% of the initial in the LM and LS treatments, respectively. Thus, solar radiation–induced photochemical reactions, together with microbial metabolism, mineralized TOC nearly completely (up to 97.7%).

The $\delta^{13}C$ of TOC was -29.9 in the initial leachate (Fig. 4). The incubation in the darkness did not change the $\delta^{13}C$ of TOC. The solar radiation exposure enriched the ^{13}C of TOC by 5‰ and 6‰ in the leachate with (LM) and without (LS) microbial turbidity, respectively. These results
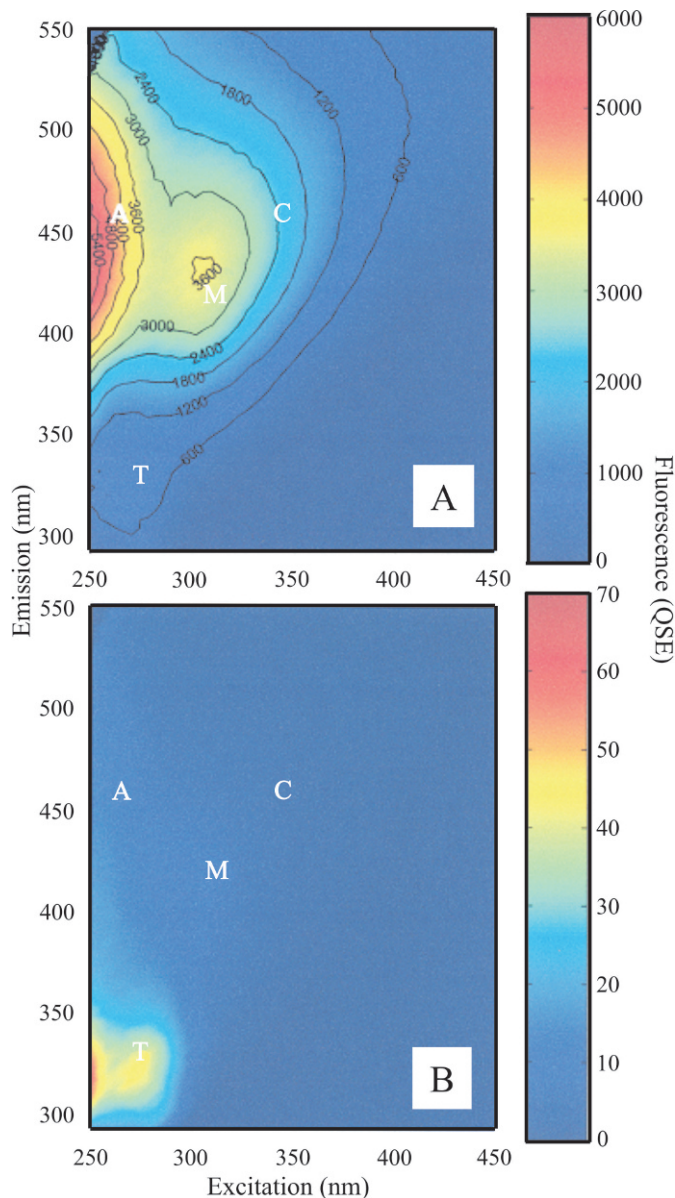
Fig. 3.   Excitation emission matrices of fluorophores in the treated leachates expressed as quinone sulfate equivalents in μg L^{-1}. (A) Dark treatment after 420 d. (B) Solar radiation exposed sample after 420 d without microbial turbidity. A, C, M, and T show typical fluorophores in DOM described by Coble (1996). Note different scales in (A) and (B).

Fig. 4.   Concentration of organic carbon and its $\delta^{13}C$ values (mean $\pm$ SD) in treated leachates during the exposure to solar radiation (0–459 d) and the following bioassay (460–898 d). Dark = dark treatment, and LM and LS = solar radiation exposed samples with and without microbial turbidity, respectively. SD is typically lower than the size of symbol.

indicate that solar radiation–induced photochemical reactions preferentially mineralized ^{12}C over ^{13}C.

Discussion

Photobleaching of CDOM and FDOM—The specific absorption coefficient at 450 nm (0.94 m^{-1} mg C^{-1} L) of initial leachate is similar to 1.15–1.36 of humic substances isolated from Orinoco River plume, 0.62–0.91 of soil fulvic acids, or 0.95 of reservoir DOC (Zepp and Schlotzhauer 1981; Blough et al. 1993; Vähätalo and Wetzel 2004). Thus,
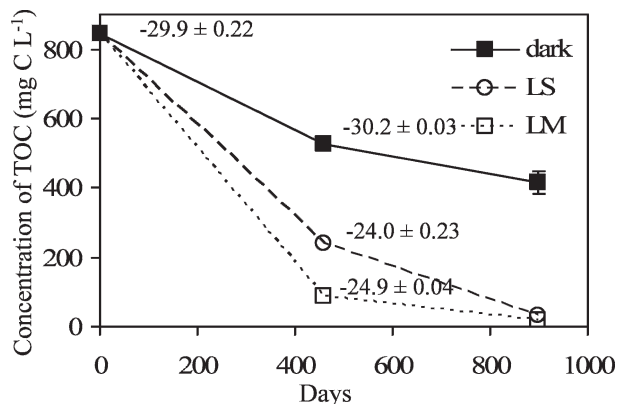
despite the high concentration of our leachate, its specific absorption coefficient is similar to DOC in soils and freshwaters and terrestrial colored organic matter discharged to ocean.

The photobleaching of CDOM and FDOM in our study agrees with numerous earlier studies showing partial photobleaching of CDOM (Coble 2007). Our study provides additional evidence that solar radiation can photobleach CDOM completely. Because of the high initial concentration, the absorption coefficient at 300 nm of our residual (0.3% of initial $a_{CDOM,300}$) leachate after photobleaching was comparable to that found in many freshwaters and estuaries. However, the spectral slope coefficient of photobleached leachate was very high, and the TOC-specific UV absorption (SUVA) was very low. The lowest SUVA in natural surface waters has been reported in high-DOC saline lakes. In saline Manito Lake, $K_{d,UV-B}$ was 11.6 m^{-1}, and DOC was 114.7 mg C L^{-1}, indicating that DOC-specific absorption of CDOM at ~315 nm was around 0.1 m^{-1} mg C^{-1} L, which is higher than the 0.019 m^{-1} mg C^{-1} L of the exposed leachate in this study (Arts et al. 2000). In the clearest surface marine waters, SUVA(315) is around 0.13–0.19 m^{-1} mg C^{-1} L when calculated according to the lowest reported $a_{CDOM,315}$ in the Atlantic Ocean (0.14 m^{-1}) and typical concentrations (0.72–1.08 mg C L^{-1}) of DOC in surface ocean (Kitidis et al. 2006). One of the largest spectral slope coefficients found in natural surface waters (0.037 nm^{-1} in the Atlantic Ocean by linear fitting for 290–350 nm) is less than 0.065 nm^{-1} of photobleached leachate calculated for the same spectral range with the same method (Kitidis et al. 2006). Our results show that solar radiation can photobleach wetland-derived CDOM completely, below SUVAs and above spectral slope coefficients found for CDOM in the clearest natural surface waters.

Organic carbon—In our study, microbes decomposed >50% of leachate TOC in 898 d, providing evidence that

the biological decomposition of *Juncus*-leachate TOC continues beyond the times used for short-term bioassays. The k_{bio} of leachate TOC is similar to that of 0.00083–0.0013 d^{-1} and 0.00069 d^{-1} found for the microbial decomposition of reservoir CDOM in a 500 d (Vähätalo and Wetzel 2004) and Mississippi River plume DOC in 620 d (Hernes and Benner 2003), respectively. In the present study, the biological decomposition of leachate TOC resembled that of CDOM or DOM discharged to the ocean and took place at the time scales that are relevant to the residence time of water as well as allochthonous DOM in many lakes and coastal waters. Thus, our k_{bio} for leachate TOC can be applied to estimate roughly the biological decomposition kinetics of wetland-derived DOC in the receiving waters.

In order to test the applicability of our k_{bio} for predicting the fate of DOC, we compare it to the loss rates of allochthonous DOC in lakes. Our k_{bio} of 0.00080 d^{-1} is similar to the first-order loss constant of DOC (0.00085 ± 0.0005 d^{-1}, mean ± SD; range 0.00026–0.00166) in seven Ontario lakes with a water residence time of 3.0 ± 1.4 yr (mean ± SD, range 1.6–5.7; calculated from Dillon and Molot 1997). The loss constant of DOC in lakes includes microbial mineralization, solar photolysis, and sedimentary losses and is influenced by the water residence time (Algesten et al. 2003). From the data set of Swedish lakes (Algesten et al. 2003), it is possible to calculate the loss constant of 0.00067 d^{-1} similar to our k_{bio} for DOC arriving into a typical lake with water residence time equaling the length of our bioassay (898 d). The comparison of our k_{bio} to the loss constants of DOC in lakes suggests that biological decomposition can be potentially responsible for much of the loss of DOC in lakes. However, our or any other k_{bio} needs to be applied with caution because numerous factors (temperature, nutrient availability, community structures, and photochemical transformations) influence the biological decomposition rate of allochthonous DOC.

In our leachate exposed to solar radiation, the photochemical mineralization of TOC to CO_2 and the photochemical production of biologically labile organic compounds must have contributed to the mineralization of TOC (Wetzel et al. 1995; Mopper and Kieber 2002). Because microbes were present during the exposure of leachate in variable degree (turbid and nonturbid treatments), it is not possible to separate direct photochemical mineralization from the microbial mineralization of biologically labile photoproducts. Our TOC results indicate that microbes consumed the biologically labile photoproducts in part already under solar radiation and to a greater extent in the microbially turbid than in the nonturbid leachates. In the bioassay following the solar radiation exposure, the biologically labile photoproducts can explain the extensive (86%) mineralization of photobleached leachate (in nonturbid leachate) in comparison to moderate (21%) mineralization in the dark treatment. The photomineralization of TOC followed by the microbial mineralization of biologically labile photoproducts has been observed in numerous short-term photochemical experiments examining biologically recalcitrant humic-like DOC

(Mopper and Kieber 2002). Our study greatly expands the understanding gained from previous short-term observations by demonstrating that solar radiation exposure followed by microbial metabolism does not mineralize just a portion of DOC but instead can cause virtually complete mineralization of allochthonous humic-like DOC.

The photochemical turnover time of our leachate is not directly applicable for wetland-derived TOC in the receiving waters, where the turnover times vary depending on site and solar radiation dose. Rather, our study demonstrates that extensive solar radiation exposure, together with microbial metabolism, can fully decompose wetland-derived TOC eventually. For example, combined photochemical and microbial processes might be expected to fully mineralize wetland-derived riverine DOC in coastal waters where riverine DOC is trapped into surface lenses and exposed to extensive solar radiation.

Photochemical fractionation of TO^{13}C—Solar radiation mineralized preferentially the TO^{12}C fraction of leachate, and the residual TOC became enriched in ^{13}C, in agreement with solar radiation–induced 1.2‰ and 1.6‰ isotopic fractionation of DOC from *Sphagnum* bog (Osburn et al. 2001) and river water (Opsahl and Zepp 2001), respectively. In the earlier studies, solar radiation, together with microbes, mineralized 16% and 27% of DOC in bog and river water, respectively, in comparison to 72–90% in our study. The extensive solar radiation–induced mineralization of *Juncus* leachate may explain why the fractionation was larger (6‰) in this study than in the earlier studies. Because solar radiation decomposed completely the absorbing components of *Juncus* leachate, the 6‰ photochemical isotopic fractionation represents the maximal fractionation for our leachate. In the tissues of vascular plants, lignin is typically depleted in ^{13}C by about 4–7‰ relative to the δ^{13}C of bulk tissue, whereas carbohydrates are about 1–2‰ enriched in ^{13}C (Benner et al. 1987). Preferential photochemical mineralization of isotopically light lignin phenols may explain the isotopic fractionation of TOC (Opsahl and Benner 1998; Vähätalo et al. 1999; Opsahl and Zepp 2001).

The large (6‰) isotopic fractionation has implications to δ^{13}C as a proxy of terrestrially produced TOC. Because terrestrial TOC (δ^{13}C: −26 to −31) is typically isotopically lighter than TOC produced in the marine environment (δ^{13}C: −18 to −22), the fate of terrestrial TOC can be followed according to the δ^{13}C signature of terrestrial TOC in marine waters (Hedges et al. 1992). After partial photomineralization and isotopic photochemical fractionation by 6‰, the δ^{13}C signature of terrestrial TOC starts to resemble isotopically that of marine TOC. When photochemical fractionation enriches the δ^{13}C signature of terrestrial TOC in coastal waters, the δ^{13}C-based contribution of terrestrial TOC to marine waters becomes underestimated. Our study provides evidence that microbes and solar radiation can completely decompose allochthonous biologically recalcitrant wetland-derived DOM if it remains in the surface waters of receiving lakes or ocean long enough. The selective photolysis of lignin (Opsahl and Benner 1998; Vähätalo et al. 1999), with

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subsequent changes in the $\delta^{13}C$ signature of terrestrial TOC, can explain additionally the disappearance of terrestrial molecular markers (lignin and $\delta^{13}C$ signature) in the ocean.

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