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Review Article

Chemical characterization of dissolved organic matter (DOM): A prerequisite for understanding UV-induced changes of DOM absorption properties and bioavailability

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Abstract. UV-induced transformations of colored dissolved organic matter (CDOM, which is part of dissolved organic matter, DOM) affect CDOM absorption properties resulting in the loss of color (referred to as photobleaching). CDOM photobleaching increases the penetration depths of the damaging UV-B radiation into water bodies and strongly depends on the wavelength of solar radiation and on the pH of aquatic systems. UV-induced transformations also affect DOM availability to bacterioplankton, often enhancing the bioavailability of terrigenous DOM and in turn microbial respiration. The combination of UV-induced enhancement of DOM bioavailability and increased export of terrigenous DOM into estuaries and coastal waters due to climate-related changes in continental hydrology could result in a UV-mediated positive feedback of CO₂ accumulation in the atmosphere.

The extent and type of CDOM photobleaching and of UV-induced changes in DOM bioavailability depend on (C)DOM chemical composition, which in turn undergoes drastic changes upon UV-induced transformations. Therefore, the chemical characterization of (C)DOM is key for rationalizing UV-induced transformations. In the second section (after the “Introduction”), we review important methods for the elucidation of the chemical composition of (C)DOM. However, this article is not intended to be comprehensive regarding (C)DOM chemical characterization. An important purpose is to provide photochemical bases for the understanding of UV-induced changes of (C)DOM absorption properties and bioavailability (mainly discussed in the sections “Pathways of DOM phototransformations” and “UV-induced changes of the absorption properties of CDOM”).

Key words. DOM characterization; DOM phototransformations; CDOM photobleaching; DOM bioavailability; UV-radiation; climate change.

Introduction

One of the most important substances in aquatic systems that absorbs solar UV radiation is the chromophoric dissolved organic material (CDOM).

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Terrestrial ecosystems are significant sources of CDOM (Bracchini et al., 2006; Duan et al., 2007a; Duan et al., 2007b; Sobek et al., 2007), and rivers serve as important reactors as well as transporters of terrigenous CDOM to lakes, reservoirs, and oceans (Algesten et al., 2004; Blough et al., 1993; Cauwet, 2002; Chen et al., 2004; Conmy et al., 2004; Dittmar et al., 2006; Hansell et al., 2004; Hedges et al., 1997; Hopkinson et al., 1998; Kowalczyk et al., 2003; Kowalczyk et al., 2005; Kowalczyk et al., 2006; Opsahl and Benner, 1997; Opsahl et al., 1999; Waiser and Robarts, 2000; Zanardi-Lamardo et al., 2004). Terrigenous CDOM originates from the decomposition of nonliving plant material, and is introduced into aquatic systems via leaching and runoff from land. CDOM also can be produced through the decay of phytoplankton detritus (Biers et al., 2007; Chen et al., 2004; Kowalczyk et al., 2006; Twardowski and Donaghay, 2001). This source of CDOM has been referred to as “microbially derived” CDOM (McKnight et al., 2001). Furthermore, salt marsh cordgrasses and seagrasses are important sources of CDOM in estuarine and coastal ecosystems (Maie et al., 2005; Stabenau et al., 2004; Wang et al., 2007a).

During riverine transport, and in estuaries and coastal waters, CDOM undergoes photochemical transformations, resulting in the loss of color, mainly in the UV region (referred to as photobleaching) (Blough et al., 1993; Del Vecchio and Blough, 2002; Del Vecchio and Blough, 2004a; Gao and Zepp, 1998; Hefner et al., 2006; Kieber et al., 1990; Minor et al., 2007; Molot et al., 2005; Moran et al., 2000; Rodriguez-Zuniga et al., 2008; Stabenau et al., 2004; Stabenau and Zika, 2004; Twardowski and Donaghay, 2002; Vähätalo and Wetzel, 2004; Vähätalo and Wetzel, 2008; Vodacek et al., 1995; White et al., 2003; Xie et al., 2004). CDOM photobleaching also has been demonstrated in lakes (Brinkmann et al., 2003a; Ma and Green, 2004; Morris and Hargreaves, 1997; Obernosterer and Benner, 2004; Reche et al., 1998; Reche et al., 1999; Reche et al., 2000; Scully et al., 2003). As a consequence of CDOM photobleaching, the UV penetration into water bodies increases and enhances the exposure of aquatic organisms to UV radiation. Aquatic organisms that play important roles in carbon cycling such as phytoplankton, bacterioplankton, and coral reefs are damaged by UV radiation. The biological processes known to be affected by UV-B are primary production (Beardall and Raven, 2004; Leu et al., 2007; Wangberg et al., 2006), bacterioplankton growth (Hernández et al., 2007; Herndl et al., 1993; Jeffrey et al., 1996; Langenheder et al., 2006), and coral bleaching (Anthony et al., 2007; Anthony and Kerswell, 2007), enhancing the warming-related stress on corals (An-

thony et al., 2007; Rodriguez-Roman et al., 2006). UV-B damages on algal photosynthesis include inhibitory effects on nutrient uptake and damage to DNA (Beardall and Raven, 2004 and refs. cited therein).

Dissolved organic matter (DOM), which includes CDOM, is a key nutrient and energy source for consumers, including heterotrophic bacteria and metazooplankton (Wetzel, 1992). However, not all chemical forms of DOM are available to these organisms. Photochemical transformations of DOM can increase or decrease DOM bioavailability (Benner and Biddanda, 1998; Bertilsson and Tranvik, 1998; Bertilsson et al., 1999; Biddanda and Cotner, 2003; Brinkmann et al., 2003b; Herndl et al., 1997; Jorgensen et al., 1998; Judd et al., 2007; Kaiser and Herndl, 1997; Kaiser and Sulzberger, 2004; Kieber et al., 1989; Lindell et al., 1995; Mopper et al., 1991; Moran and Zepp, 1997; Obernosterer et al., 1999b; Pullin et al., 2004; Vähätalo et al., 2003; Vähätalo and Wetzel, 2008; Wetzel et al., 1995). The light-induced increase in DOM bioavailability may enhance microbial respiration of DOM with production of CO₂ and consumption of O₂ (Bertilsson and Tranvik, 1998; Obernosterer and Benner, 2004; Pullin et al., 2004; Vähätalo and Wetzel, 2008) or increase microbial biomass through the microbial loop (Bertilsson et al., 1999; Daniel et al., 2006). Furthermore, mineralization of DOM also occurs as a purely abiotic, light-induced process (Anesio and Granéli, 2004; Austin and Vivanco, 2006; Bélanger et al., 2006; Benner and Biddanda, 1998; Clark et al., 2004; Gao and Zepp, 1998; Goldstone et al., 2002; Granéli et al., 1996; Granéli et al., 1998; Miller and Zepp, 1995; Minor et al., 2006; Minor et al., 2007; Mopper et al., 1991; Obernosterer and Benner, 2004; Rodriguez-Zuniga et al., 2008; Vähätalo and Wetzel, 2004; Vodacek et al., 1997; Xie et al., 2004).

The photochemical and biological reactivity of DOM depend on its source and hence its chemical composition. Thus understanding the chemical composition of DOM is a prerequisite for rationalizing UV-induced changes of DOM absorption properties and bioavailability. The molecular-level characterization of what has long been referred to as molecularly uncharacterized carbon has largely improved thanks to modern spectroscopic and spectrometric methods, e.g., multidimensional nuclear magnetic resonance (NMR) spectroscopy, and Fourier transform ion cyclotron resonance mass spectrometry (Mopper et al., 2007). In this article, we review selected literature on the chemical characterization of DOM and on how solar UV radiation affects the chemical composition and thus the optical properties and bioavailability of DOM in marine and freshwater systems, focusing on

dissolved organic carbon (DOC). [Note that in the following text we use “DOM” synonymous to “DOC”.] This review article is not intended to be comprehensive regarding DOM chemical characterization; for example, we have not included studies that used stable isotope or electrochemical methods. An important purpose of this article is to provide photochemical basis for the understanding of UV-induced changes of DOM absorption properties and bioavailability. Many studies that we cite in this review article have used artificial or ambient solar radiation and not specifically UV radiation. Since UV (ranging from 280–315 and 315–400 nm for UV-B and UV-A radiation, respectively) is an important range of the solar spectrum with regard to photochemical processes involving DOM, we refer to these processes in general as UV-induced processes. For convenience we are using the abbreviated notations “UV”, “UV-B”, and “UV-A” for solar UV, UV-B, and UV-A radiation. The following text is divided into five sections, where each section includes up to four subsections:

- (i) Methods for the elucidation of the chemical composition of DOM
- (ii) Pathways of DOM phototransformations
- (iii) UV-induced changes of the absorption properties of CDOM
- (iv) Effects of UV radiation on the bioavailability and mineralization of DOM
- (v) Conclusions

Methods for the elucidation of the chemical composition of DOM

Regarding the utmost complex mixture of chemical compounds contained in DOM, the first question a geochemist asks about DOM pertains to its polydispersity. In the first subsection, we therefore outline methods by which the molecular mass distribution of DOM can be explored.

Molecular mass distribution of DOM

To obtain the dissolved fraction of natural organic matter, sea- or freshwater samples have to be filtered (e.g., through a 0.45 μm filter). Hence “dissolved” organic matter (DOM) is an operational definition. Ultrafiltration then allows the fractionation of DOM into high-molecular-weight (HMW) and low-molecular-weight (LMW) DOM compounds. Ultrafiltration employing a tangential flow ultrafiltration system with a 1 kD nominal weight cutoff membrane was extensively evaluated by Ronald Benner and coworkers (e.g., Benner et al., 1992; Benner et al., 1997) and is

widely used for the chemical characterization of DOM. Ultrafiltration may be followed by C_{18} solid phase extraction (SPE) or XAD chromatography (Brown et al., 2004; Simjouw et al., 2005). It is important to realize that ultrafiltration is based on a physical separation of DOM, whereas SPE and XAD chromatography are based on chemical fractionation, which divide DOM into hydrophilic and hydrophobic compounds.

A widely used method for the elucidation of the molecular mass distribution of DOM at a finer scale, which in addition provides information on the chemical composition of DOM, is size exclusion chromatography (SEC) and high-pressure size exclusion chromatography (HPSEC) (Brinkmann et al., 2003a; Brinkmann et al., 2003b; Brown et al., 2004; Chin et al., 1994; Gaberell et al., 2003; Kaiser and Sulzberger, 2004; Reemtsma and These, 2005; Schmitt et al., 2001; Schwede-Thomas et al., 2005). SEC not only separates DOM compounds based on size (hydrodynamic radii), but also ion-exclusion and hydrophobic interactions of the fractions with the column material can occur (Schmitt et al., 2001). Ideally, both the dissolved organic carbon concentration (DOC) and the absorbance at 254 nm of the eluents with different retention times are detected (Brinkmann et al., 2003a; Brinkmann et al., 2003b; Kaiser and Sulzberger, 2004; Schmitt et al., 2001) since not all DOM compounds, e.g., polysaccharides, absorb UV light at 254 nm. SEC or HPSEC is sensitive enough to delineate changes in the chemical composition of DOM upon irradiation and/or biodegradation (Brinkmann et al., 2003a; Brinkmann et al., 2003b; Kaiser and Sulzberger, 2004). For example, using SEC Brinkmann and coworkers (2003b) demonstrated that irradiation with simulated solar UV light of humic-derived DOM from an acidic lake resulted in a reduction of the mean hydrodynamic radii of the DOM compounds. Furthermore, new fractions appeared in the SEC which were assigned to aliphatic mono- and dicarboxylic acids such as formic and oxalic acid, which were biologically more labile than the reactants (Fig. 1). Some studies have used SEC or HPSEC followed by mass spectrometry (Reemtsma and These, 2005; Schmitt et al., 2001) or nuclear magnetic resonance (NMR) spectroscopy (Brown et al., 2004) (see also below).

Next to SEC, mass spectrometry is an obvious tool to assess the molecular mass distribution of DOM (Kujawinski et al., 2004; Minor et al., 2007; Reemtsma et al., 2008; Seitzinger et al., 2005; Stabenau et al., 2004; Stabenau and Zika, 2004; Tremblay et al., 2007). For example, Stabenau and Zika (2004) applied a combination of a solid-phase extraction method with electrospray ionization (ESI) continuous flowing ion

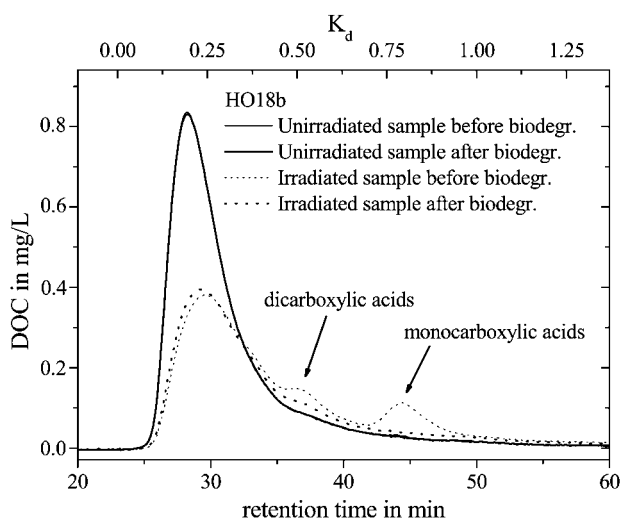


Figure 1. Size exclusion chromatogram of water samples from an acidic lake (Lake Hohloh, Germany; pH ~ 4.2; [DOC]_{initial} = 11.0 mg L⁻¹) before and after irradiation (for 24 h) with simulated solar UV radiation, and before and after incubation (for 100 h) with natural bacterioplankton (reproduced from Brinkmann et al., 2003b, with permission from the authors and from the American Chemical Society).

trap mass spectrometry to compare the mass distribution of a seagrass species to that of coastal DOM. They confirmed earlier findings (Hemminga and Duarte, 2000) that seagrasses are a major source of DOM in the coastal ocean.

Bulk characterization of DOM

The chemical definition of DOM has long relied on elemental analysis (C, H, N, O, and S). The C/N ratio serves as an indicator of the source material of DOM present in aquatic systems. The reason for using the C/N ratio for the elucidation of the origin of aquatic DOM is that vascular plant tissues are typically carbon-rich (C/N = 20–500) compared to phytoplankton (C/N ~ 7) and bacteria (C/N ~ 4), due to the predominance of nitrogen-free bio-macromolecules (e.g. lignin, tannin, hemicellulose, cellulose, cutin, and suberin) over proteins (C/N ~ 3–4) (Hedges et al., 1986).

The introduction of gas chromatography and mass spectrometry (GC/MS) in the 1960s allowed scientists to go beyond elemental analysis of DOM. However, compounds need to be volatile to be characterized by GC/MS. The combination of pyrolytic or chemolytic techniques with GC/MS was a major breakthrough in the analysis of DOM. One of the chemolytic reagents used in combination with GC/MS is tetramethyl ammonium hydroxide (TMAH) (Fimmen et al., 2007; Frazier et al., 2005; Hatcher and Clifford, 1994; Wetzel et al., 1995; Zang et al., 2000). Another chemolytic reagent, which was implemented by John

I. Hedges (e.g., Ertel et al., 1984; Ertel et al., 1986; Goni and Hedges, 1992; Hu et al., 1999) and which allows the detection of methoxylated phenols derived from lignin is CuO. The identification and quantification of trace levels of lignin requires the pre-concentration of these compounds, e.g., by SPE (Louchouart et al., 2000) prior to CuO oxidation and detection of the oxidation products by GC/MS. Lignin phenols are used as molecular tracers of vascular plant sources and have been measured among the basic CuO reaction products in various aquatic environments (Duan et al., 2007a; Ertel et al., 1984; Goni and Hedges, 1992; Hernes and Benner, 2003; Opsahl and Benner, 1997; Opsahl and Benner, 1998).

Another separation method that can be combined with MS is high performance capillary electrophoresis (HPCE). This method allows the separation of biomolecules such as amino acids, peptides, proteins, nucleic acids, and DNA and has been used for the chemical characterization of humic substances and marine DOM (Garrison et al., 1995; Hertkorn et al., 2006; Schmitt-Kopplin et al., 1998b; Schmitt-Kopplin and Kettrup, 2003; Vogt et al., 2004).

The drawback of pyrolytic or chemolytic techniques combined with GC/MS is that they are invasive and selective (i.e., certain compounds react more readily than others). Among non-invasive techniques, nuclear magnetic resonance (NMR) spectroscopy, particularly solid-state ¹³C NMR is frequently used for the identification of the bulk chemical composition of DOM (Baldock et al., 2004; Benner et al., 1992; Brown et al., 2004; Chin et al., 1994; Clair and Sayer, 1997; Cory and McKnight, 2005; Dria et al., 2002; Fan et al., 2000; Fimmen et al., 2007; Gaberell et al., 2003; Hedges et al., 1992; Hertkorn et al., 2006; Kaiser et al., 2003; Kaiser and Sulzberger, 2004; Kulovaara et al., 1996; Maie et al., 2005; McKnight et al., 2003; Mladenov et al., 2007; Novotny et al., 2007; Rodriguez-Zuniga et al., 2008; Schwede-Thomas et al., 2005; Wetzel et al., 1995). ¹³C NMR spectroscopy enables the determination of the relative abundances of differently bound carbons contained in DOM such as aliphatic carbons, carbohydrate carbons, olefinic and aromatic carbons, carboxylic carbons, amide carbonyl carbons, and carbonyl carbons (aldehydes and ketones). For example, in a seminal study by Benner and coworkers (1992), ¹³C NMR spectra of HMW DOM indicated that the relative abundance of polysaccharides was high (~50%) in surface water of the North Pacific Ocean and decreased to ~25% in deeper water samples. This technique also allowed a detailed and critical re-evaluation of the widely recognized Redfield-Ketchum-Richards equation (Readfield et al., 1963) in marine phytoplankton (Hedges et al., 2002). Further, ¹³C NMR spectroscopy

was used to elucidate the difference in the bulk chemical composition of terrestrial- and algal-derived DOM (Gaberell et al., 2003; Maie et al., 2005; Schwede-Thomas et al., 2005). These studies have shown that algal-derived DOM generally exhibits a lower percentage of aromatic compounds than terrigenous DOM.

NMR techniques require that DOM, usually present at low concentrations in natural water samples, is concentrated using isolation methods such as ultrafiltration, SPE, and XAD chromatography, referred to as HMW DOM, C_{18} DOM, and XAD DOM, respectively. These methods also allow recovering DOM as a powder that can be directly analyzed by solid-state NMR or redissolved for solution-state NMR. Each of these methods isolates different fractions of DOM, in terms of both chemical composition and molecular weight. C_{18} DOM is enriched in aromatic compounds (from lignin and/or aromatic amino acids in proteins), whereas HMW DOM comprises proteins, peptides, polysaccharides, and simple sugars such as aminosugars, 6-deoxy- and methyl sugars (Kaiser et al., 2003; Louchouart et al., 2000; Quan and Repeta, 2007; Schwede-Thomas et al., 2005; Simjouw et al., 2005).

Molecular-level characterization of DOM

One-dimensional (1-D) ^{13}C NMR spectroscopy only provides information on the bulk chemical composition of DOM but not on how structures are arranged at the molecular level within DOM. Increasingly, 2-dimensional (2-D) liquid-state multinuclear magnetic resonance techniques are being used (Cook, 2004; Fan et al., 2000; Hertkorn et al., 2006; Kaiser et al., 2003; Kelleher and Simpson, 2006; Lam et al., 2007; Schmitt-Kopplin et al., 1998a; Simpson, 2001; Simpson et al., 2007). The advantage of multidimensional NMR over 1-D methods lies in the much improved spectral resolution and capability of providing information such as ^1H covalent network (with Total Correlation Spectroscopy, TOCSY), ^1H - ^{13}C or ^1H - ^{15}N linkages (with Heteronuclear Single Quantum Coherence (HSQC) spectroscopy), through-space connectivities (with Nuclear Overhauser Enhanced Spectroscopy, NOESY), and exchange dynamics (exchange spectroscopy) (Cook, 2004). These 2-D NMR parameters greatly facilitate the determination of structures and conformations of extended molecular fragments present in complex macromolecules. Studies using multidimensional NMR spectroscopy revealed that humic substance (HS) in soils is a complex mixture of microbial and plant biopolymers (or stably aggregated components) and their degradation products, but not a distinct chemical category such as oxidized

lignin (Kelleher and Simpson, 2006; Simpson et al., 2007; Sutton and Sposito, 2005).

Mass spectrometry (MS) also is used for the molecular-level characterization of DOM, particularly by applying electrospray ionization (ESI), a "soft" technique that ionizes polar compounds from aqueous solution prior to injection into a mass spectrometer (Ashcroft, 1997; Hatcher et al., 2001; Hatcher, 2004; Hertkorn et al., 2006; Kim et al., 2006; Kujawinski et al., 2004; Reemtsma and These, 2005; Reemtsma et al., 2006; Reemtsma et al., 2008; Seitzinger et al., 2005; Stabenau and Zika, 2004; Tremblay et al., 2007; Whitehead and Hedges, 2003). ESI has been combined with various types of mass spectrometry, with ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR-MS) (Hatcher, 2004; Hertkorn et al., 2006; Kim et al., 2006; Kujawinski et al., 2004; Reemtsma et al., 2006; Reemtsma et al., 2008; Sleighter and Hatcher, 2008; Tremblay et al., 2007), tandem mass spectrometry (ESI-MS/MS) (Whitehead and Hedges, 2003), quadrupole time-of-flight mass spectrometry (ESI-QTOF-MS) (Reemtsma and These, 2005), and continuous flowing ion trap mass spectrometry (ESI-cf-MS) (Stabenau and Zika, 2004). The combination of ESI with other ionization techniques, such as chemical ionization and photoionization, would allow an overly improved analysis of DOM compounds (Schmitt-Kopplin, pers. comm.). The advantage of mass spectrometry over NMR spectroscopy is that also LMW DOM compounds at ambient natural concentrations can be identified (Reemtsma and These, 2005; Seitzinger et al., 2005; Stabenau and Zika, 2004; Whitehead and Hedges, 2003).

Several studies have used a combination of separation, spectrometric, and spectroscopic methods for the molecular-level characterization of DOM and the elucidation of its three-dimensional structure (Fan et al., 2000; Fimmen et al., 2007; Hertkorn et al., 2006; Paul et al., 2006; Rodriguez-Zuniga et al., 2008; Schmitt-Kopplin et al., 1998a; Schulten and Schnitzer, 1997; Simjouw et al., 2005). For example, Fan and coworkers (2000) combined one- and two-dimensional NMR spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and pyrolysis GC/MS to chemically characterize forest soil humic substance. They identified the amino acids Gly, Ala, Leu, Ile, Val, Asp, Ser, Thr, Clu, and Pro as peptidic, and analysis with ^1H NOESY, TOCSY, and HSQC indicated that the peptidic side chains were mobile, whereas aromatic groups were relatively rigid. Based on a combination of separation, spectrometric and spectroscopic methods with molecular mechanics calculations, Schulten and Schnitzer (1997) proposed a three-dimensional structure of soil humic acid including 738 atoms ($C_{308}H_{335}O_{90}$

N₅). In a similar fashion, the combination of ultra-filtration, NMR spectroscopy, capillary electrophoresis, and FT-IRC-MS allowed the identification of refractory carboxylic-rich acyclic molecules (CRAM), a component of marine DOM that until recently was recognized to belong to the “molecularly uncharacterized” component of DOM that derives from highly decomposed biomolecules (Hertkorn et al., 2006).

Elucidation of the origin and chemical composition of CDOM with absorption and fluorescence spectroscopy

Since the optical properties and the chemical composition of CDOM are interrelated, absorption and fluorescent spectroscopy can be used in addition to the methods mentioned in the previous subsections to elucidate the chemical composition of CDOM (for a recent review on the chemistry of ocean color see Coble, 2007). The specific UV-absorbance of CDOM (SUVA), which is defined as the UV absorbance of a water sample at a given wavelength in the UV region (usually at 280 nm), normalized to DOC concentration, has been shown to correlate with the fraction of aromatic compounds contained in CDOM (Chin et al., 1994; Gaberell et al., 2003; Hassellöv, 2005; Mladenov et al., 2007; Weishaar et al., 2003).

In addition to UV/VIS absorption spectroscopy, fluorescence spectroscopy has been used to delineate the chemical composition and origin of CDOM, particularly three-dimensional excitation-emission matrix (EEM) fluorescence spectroscopy (Boehme et al., 2004; Boyd and Osburn, 2004; Coble et al., 1990; Conmy et al., 2004; Cory and McKnight, 2005; Fulton et al., 2004; Jiang et al., 2008; Kowalczuk et al., 2003; Kowalczuk et al., 2005; McKnight et al., 2001; Mladenov et al., 2007; Murphy et al., 2008; Stedmon and Markager, 2005a; Stedmon and Markager, 2005b; Vähätalo and Wetzel, 2008; Zepp et al., 2004). The combination of EEM with parallel factor data analysis allows the chemical identification of fluorophores, e.g., quinone-like fluorophores (Cory and McKnight, 2005; Mladenov et al., 2007; Stedmon and Markager, 2005a; Stedmon and Markager, 2005b). EEM also provides information on the redox properties of DOM (Cory and McKnight, 2005).

The fluorescence index (FI), which is the ratio of emission intensity (450 nm / 500 nm) at 370 nm excitation (McKnight et al., 2001), is correlated to the relative contribution of autochthonous versus terrigenous DOM, and therefore a valuable tool for DOM source identification (Battin, 1998; Boyd and Osburn, 2004; Cory and McKnight, 2005; Fimmen et al., 2007; McKnight et al., 2001; Mladenov et al., 2007; Schwede-Thomas et al., 2005). For example, McKnight and coworkers (2001) found a value of

~1.9 for microbial-derived fulvic acid and a value of ~1.4 for terrestrial-derived fulvic acid.

Pathways of DOM phototransformations

There exist several pathways of UV-induced DOM transformations, depending on DOM chemical composition and on environmental factors such as the presence of iron (Fig. 2). The following subsections describe these pathways and discuss how the chemical composition and origin of DOM affect its photoreactivity.

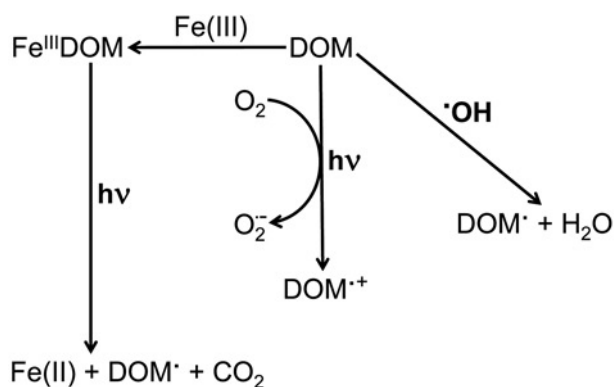
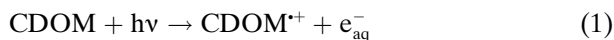


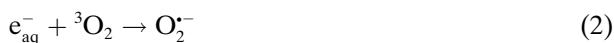
Figure 2. Pathways of light-induced transformations of DOM; from left to right: (i) via photolysis of Fe(III)-DOM complexes, (ii) via direct photochemical transformations of DOM, and (iii) via •OH attack of DOM.

Direct photochemical transformations of CDOM

The fraction of DOM that absorbs solar radiation reaching the earth surface (~65%, Blough et al., 1993) is referred to as CDOM (see also above). During direct photochemical transformations, CDOM itself acts as the primary chromophore. The deactivation of an electronically excited state of CDOM then occurs via, e.g., ionization of CDOM to produce hydrated electrons (e_{aq}⁻) (Blough and Zepp, 1995 and refs. cited therein; Bruccoleri et al., 1993; Wang et al., 2007b; Zepp et al., 1987):



These hydrated electrons further react in various ways, e.g., with molecular oxygen (which is a triplet state in its ground state) yielding superoxide (O₂⁻) (Blough and Zepp, 1995 and refs. cited therein; Bruccoleri et al., 1993):



The organic radical, which may be relatively long-lived (Paul et al., 2006), can add molecular oxygen to form a peroxy radical cation (Bruccoleri et al., 1993),



which undergoes further reactions yielding the final CDOM oxidation product(s). Upon irradiation of CDOM the content of aromatic carbons generally decreases (Kujawinski et al., 2004; Kulovaara et al., 1996; Minor et al., 2007; Opsahl and Benner, 1998; Schmitt-Kopplin et al., 1998a; Scully et al., 2004), so that compounds with low double bond equivalent and high oxygen content remain after phototransformations (Kujawinski et al., 2004).

In oligotrophic water bodies, in which CDOM is the main light-absorbing component, the rate of photochemical CDOM transformation, R_p , can be approximated as,

$$R_p \approx 2.303 \times \int_{\lambda} W(\lambda) a(\lambda) D(\lambda) \Phi_p(\lambda) d\lambda \quad (4)$$

where $W(\lambda)$ is the spectral photon flux that hits the surface of a water body (in einstein $\text{m}^{-2} \text{s}^{-1} \text{nm}^{-1}$ or millieinstein $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$) (also called incident light intensity), $a(\lambda)$ is the decadic absorption coefficient in m^{-1} or cm^{-1} (absorbance of the water body divided by the optical pathlength), $D(\lambda)$ is related to the angle of refraction, $D(\lambda) = (\cos\phi_\lambda)^{-1}$, and $\Phi_p(\lambda)$ is the quantum yield of primary photoproduct formation (see Eq. 1). According to the rate expression given by Eq. 4, the rate of direct photochemical CDOM transformation is linearly dependent on the decadic absorption coefficient $a(\lambda)$, which in turn depends on the concentration and the absorption properties of CDOM.

The absorption properties and thus the reactivity of CDOM toward direct photochemical transformations depend on the chemical composition of CDOM and thus on its origin. A number of studies have shown that terrigenous CDOM exhibits a higher photo-reactivity than algal-derived CDOM (Bertilsson and Jones, 2003; Biddanda and Cotner, 2003; Chen et al., 2004; Clair and Sayer, 1997; Gaberell et al., 2003; Meunier et al., 2005; Minor et al., 2007; Obernosterer and Benner, 2004; Opsahl and Benner, 1998; Scully et al., 2004; Vähätalo and Wetzel, 2004). This phenomenon can be rationalized in terms of the higher percentage of aromatic compounds in allochthonous CDOM as compared to autochthonous CDOM (Chin et al., 1994; Clair and Sayer, 1997; Dittmar et al., 2006; Gaberell et al., 2003; Maie et al., 2005; McKnight et al., 1991; Minor et al., 2007; Reemtsma and These, 2005; Schwede-Thomas et al., 2005; Stubbins et al., 2008). The absorption properties also depend on the molecular weight of CDOM (Blough and Green, 1995; Chin et al., 1994; Del Vecchio and Blough, 2004b; Stabenau et al., 2004; Stabenau and Zika, 2004). For example, the molar absorptivity of aquatic

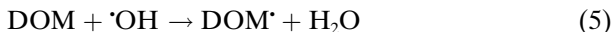
humic substances at 280 nm, ϵ_{280} nm (in L (mole DOC) $^{-1} \text{cm}^{-1}$), has been demonstrated to be linearly correlated with their molecular weight (Chin et al., 1994). Regarding the chemical origin of light absorption by CDOM, Del Vecchio and Blough (2004b) hypothesized that the long wavelength absorption tail of humic substances (>350 nm) arises from coupled intramolecular charge-transfer transitions between hydroxy-aromatic donors and quinoid acceptors formed by the partial oxidation of lignin precursors. This model is in line with the observation that (poly)phenolic structures within CDOM are particularly sensitive to phototransformations (Judd et al., 2007; Opsahl and Benner, 1998; Schmitt-Kopplin et al., 1998a; Scully et al., 2004).

The rate of direct photochemical CDOM transformations also depends on the reaction quantum yield, $\Phi_p(\lambda)$ (Eq. 4). To assess quantum yields of primary photoproduct formation and to elucidate the mechanisms involved in light absorption and in the deactivation of excited states of CDOM, time-resolved spectroscopic methods are required, which so far have been applied in only a few environmental photochemical studies (Bruccoleri et al., 1993; Del Vecchio and Blough, 2004b; Wang et al., 2007b). Many studies have, however, determined apparent quantum yields of photochemical decomposition of CDOM (Vähätalo and Wetzel, 2004) and stable photoproduct formation like dissolved inorganic carbon (DIC) (Gao and Zepp, 1998; Johannessen and Miller, 2001; Miller and Zepp, 1995), CO (Bélanger et al., 2006; Gao and Zepp, 1998; Stubbins et al., 2008; Valentine and Zepp, 1993; Zhang et al., 2006; Ziolkowski and Miller, 2007), and carbonyl compounds (Kieber et al., 1990). Regarding stable photoproduct formation, one has to bear in mind that these can be formed via direct and indirect photochemical transformations of CDOM, e.g., attack of CDOM by reactive intermediates that are produced in primary photochemical processes (Del Vecchio and Blough, 2002) or via iron-catalyzed CDOM transformation (Gao and Zepp, 1998).

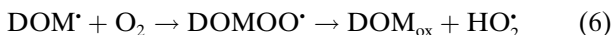
Indirect photochemical transformations of DOM via $\cdot\text{OH}$ attack

If DOM is not colored, i.e., if it does not absorb solar radiation that reaches the Earth surface, it may be transformed via indirect photochemical reactions (also referred to as photosensitized reactions). One important pathway is reaction of DOM with the hydroxyl radical ($\cdot\text{OH}$) (Anesio and Granéli, 2004; Brinkmann et al., 2003a; Brinkmann et al., 2003b; Gao and Zepp, 1998; Molot et al., 2005; Pullin et al., 2004; Schmitt-Kopplin et al., 1998b; Scully et al., 2003; White et al., 2003; Xie et al., 2004), e.g.,

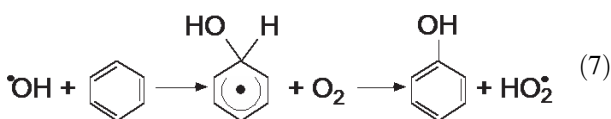
abstraction of a hydrogen atom from DOM by $\cdot\text{OH}$ (Blough and Zepp, 1995 and refs. cited therein):



Oxygen addition then leads to an organic peroxy radical, which may eliminate $\text{HO}_2\cdot$:



Another reaction pathway is addition of $\cdot\text{OH}$ to DOM, followed by oxygen addition and elimination of $\text{HO}_2\cdot$. For example, the addition of $\cdot\text{OH}$ to benzene in the presence of oxygen results in phenol and $\text{HO}_2\cdot$ (Warneck and Wurzing, 1988):



In sunlit aquatic systems, there are several pathways of $\cdot\text{OH}$ formation (Blough and Zepp, 1995; Vaughan and Blough, 1998 and refs. cited in these articles): (i) photolysis of NO_3^- , (ii) H-abstraction from water by ${}^3\text{CDOM}^*$, and (iii) photo-Fenton reactions (Fig. 3), the latter being an important pathway in iron-rich aquatic systems (Anesio and Granéli, 2004; Brinkmann et al., 2003a; Brinkmann et al., 2003b; Gao and Zepp, 1998; Molot et al., 2005; Southworth and Voelker, 2003; White et al., 2003; Xie et al., 2004). White and coworkers (2003) attributed the high rate of photochemical $\cdot\text{OH}$ formation in the acidic Satilla River water (0.4 nM s^{-1}) mainly to the involvement of photo-Fenton reactions. Molot and coworkers (2005) found that the oxidative loss of stream DOM by reaction with photo-produced $\cdot\text{OH}$ was highest at pH 4 but still significant at pH 7. The strong pH-dependence of photooxidation of DOM by $\cdot\text{OH}$ can be interpreted in terms of the pH-dependence of the various reactions involved in photo-Fenton systems (Anesio and Granéli, 2004; Balmer and Sulzberger, 1999; Molot et al., 2005).

Several studies have assessed the relative importance of DOM transformations via reaction with $\cdot\text{OH}$, as compared to other photochemical transformation processes of DOM (Goldstone et al., 2002; Hefner et al., 2006; Minor et al., 2007; Molot et al., 2005; Pullin et al., 2004). Some studies found that reactions with $\cdot\text{OH}$ play a minor role in photobleaching and abiotic mineralization of humic and fulvic substances (Goldstone et al., 2002; Hefner et al., 2006; Minor et al., 2007). On the other hand, Pullin and coworkers (2004) reported that treatment of river water samples with $\cdot\text{OH}$ (produced by gamma radiation) had a larger

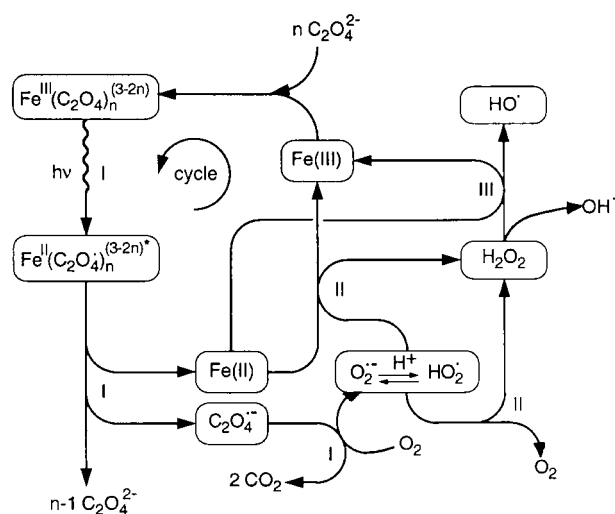


Figure 3. Scheme of hydroxyl radical ($\cdot\text{OH}$) formation in photo-Fenton systems. For simplicity the reactions are depicted with oxalate as a model compound for DOM (modified from Zuo and Holgné, 1992).

effect on the production of LMW organic acids (acetic, formic, malonic, and oxalic acid) than irradiation of the water samples with ambient sunlight.

Photochemical transformations of DOM via photolysis of Fe(III)-DOM complexes

In iron-rich surface waters, an important pathway of photochemical DOM transformation is photolysis of Fe(III)-DOM complexes (Anesio and Granéli, 2004; Brinkmann et al., 2003a; Brinkmann et al., 2003b; Gao and Zepp, 1998; Kaiser and Sulzberger, 2004; Meunier et al., 2005; Molot et al., 2005; White et al., 2003; Xie et al., 2004). Photolysis of Fe(III)-DOM complexes is likely to occur in a similar way as photolysis of Fe(III)-oxalate or -citrate complexes (Fig. 3) (Balmer and Sulzberger, 1999; Borer et al., 2007; Faust and Zepp, 1993; Waite and Morel, 1984; Zuo and Holgné, 1992), i.e., to involve carboxyl groups contained in DOM as Fe(III) ligands (Meunier et al., 2005; Sulzberger and Laubscher, 1995; Voelker et al., 1997). Photolysis of such complexes can be described by the following reaction sequence: Ligand-to-metal charge-transfer transition creating a charge-transfer state,



which is, in part, thermally deactivated,



and, in part, forms Fe(II) and the radical $\text{RCOO}\cdot$:



It is likely that the radical RCOO^\bullet undergoes decarboxylation like simple carboxylic acids such as oxalate or citrate, particularly with DOM compounds that exhibit hydroxyl groups in α -position to carboxylic acid groups (Abrahamson et al., 1994; Borer et al., 2007):



Carbon-centered radicals R^\bullet may react with each other to form non-radical products. If the radical R^\bullet is an alkyl radical, then formation of organic peroxy radicals by addition of O_2 is likely to take place (Blough and Zepp, 1995 and refs. cited therein). Peroxy radicals can further react by different pathways (Blough and Zepp, 1995 and refs. cited therein): (i) termination reactions to form non-radical and non-peroxidic products, e.g., polymerization products, (ii) abstraction of HO_2^\bullet , and (iii) H-atom abstraction to generate organic peroxides and secondary radicals. The study by Voelker and coworkers (1997) with heterogeneous iron systems and Suwannee River Fulvic Acid (SRFA) suggests that photolysis of Fe(III)-SRFA complexes and subsequent reactions are not dominant sources of HO_2^\bullet .

Several studies suggest that LMW compounds are more reactive towards UV-induced Fe(II) formation than HMW compounds, both in sea- and freshwater

samples (Meunier et al., 2005; Powell and Wilson-Finelli, 2003; Song et al., 2005). This higher reactivity of LMW materials in UV-induced reduction of Fe(III) may be rationalized by more efficient photolysis of Fe(III) complexes with LMW ligands, as compared to HMW ligands, possibly due to a higher content of carboxyl functional groups contained in aquatic LMW DOM (Reemtsma and These, 2005). Indeed, (poly)-carboxylic acids with a limited number of hydroxy groups have been identified as the major compound class in fulvic acid isolates (Reemtsma et al., 2006). Based on a combination of experimental studies and mathematical kinetic modeling, Meunier and coworkers (2005) hypothesized that in irradiated LMW DOM fractions from a lake, Fe(II) was formed through photolysis of Fe(III)-DOM complexes. Kinetic modeling further suggested that Fe(II) was stabilized by a ligand that likely was formed during irradiation (Fig. 4, Table 1).

In iron-rich, sunlit aquatic systems, the three pathways of DOM phototransformations discussed in this section may take place simultaneously, and the iron-catalyzed pathways are coupled. Furthermore, photooxidation of DOM also may take place at the surface of Fe(III)-(hydr)oxides (Voelker et al., 1997; Waite and Morel, 1984; Wells et al., 1991). It is not trivial to distinguish between the various types of iron-catalyzed phototransformations of DOM. One ap-

Table 1. Reactions and kinetic parameters used in the kinetic model (modified from Meunier et al., 2005).

No.	Equation	Kinetic parameters for the LMW DOM sample from Lake Murten	References
1 ^a	$\text{Fe(III)} + h\nu \rightarrow \text{Fe(II)} + \text{products}$	$k = 0.001 \text{ s}^{-1}$	Miller et al. (1995) ^b
2 ^c	$\text{CDOM} \xrightarrow{\text{O}_2, h\nu} \text{CDOM}^{+\bullet} + \text{O}_2^{\bullet-}$	$r = 9.9 \times 10^{-8} \text{ M s}^{-1} \text{ (fp1)}$	
3	$\text{Fe(III)} + \text{O}_2^{\bullet-} \rightarrow \text{Fe(II)} + \text{O}_2$	$k = <10^3 \text{ M}^{-1} \text{ s}^{-1} \text{ (fp2)}$	
4	$\text{Fe(II)} + \text{O}_2 \rightarrow \text{Fe(III)} + \text{O}_2^{\bullet-}$	$k = 20.78 \text{ M}^{-1} \text{ s}^{-1}$	King (1998) ^d
5	$\text{Fe}^{\text{II}}\text{L} + \text{O}_2 \rightarrow \text{Fe}^{\text{III}}\text{L} + \text{O}_2^{\bullet-}$	$k = 0.21 \text{ M}^{-1} \text{ s}^{-1} \text{ (fp3)}$	
6	$\text{Fe(II)} + \text{O}_2^{\bullet-} + 2 \text{H}^+ \rightarrow \text{Fe(III)} + \text{H}_2\text{O}_2$	$k = 1.00 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	Rush and Bielski (1985) ^e
7	$\text{Fe}^{\text{II}}\text{L} + \text{O}_2^{\bullet-} + 2 \text{H}^+ \rightarrow \text{Fe}^{\text{III}}\text{L} + \text{H}_2\text{O}_2$	$k = 5.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1} \text{ (fp4)}$	
8	$\text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} + \cdot\text{OH} + \text{OH}^-$	$k = 7.86 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	King and Farlow (2000) ^f
9	$\text{Fe}^{\text{II}}\text{L} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{\text{III}}\text{L} + \cdot\text{OH} + \text{OH}^-$	$k = <10^2 \text{ M}^{-1} \text{ s}^{-1} \text{ (fp5)}$	
10	$\text{Fe}^{\text{III}}\text{L} \rightarrow \text{Fe(III)} + \text{L}$	$k = 1.00 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$	
11	$\text{O}_2^{\bullet-} + \text{O}_2^{\bullet-} + 2 \text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$k = 3.98 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$	Zafiriou (1990) ^g
12	$\text{O}_2^{\bullet-} + \text{sinks} \rightarrow \text{products}$	$k = 4.63 \text{ s}^{-1}$	Estimated from Voelker et al. (2000), and Goldstone and Voelker (2000) ^h
13	$\text{Fe}^{2+} + \text{L} \leftrightarrow \text{Fe}^{\text{II}}\text{L}$	$K = >10^{10} \text{ M}^{-1} \text{ (fp6)}$	

fp = fitting parameter.

^a Fe(III) stands for total dissolved Fe(III) in the LMW DOM sample, whose initial concentration was 6.8 nM.

^b We assumed rate constants of photolysis of Fe(III) complexes in the range of that suggested by Miller et al. (1995).

^c $[\text{CDOM}] = 52 \mu\text{M}$ in the LMW DOM sample based on measured DOC concentration and assuming that ~65% of DOC is colored. The rate, r , of superoxide formation includes the CDOM concentration, $r = k \times [\text{CDOM}]$.

^d Rate constant given by King (1998) for $I = 0$, corrected for $I = 7 \text{ mM}$ using Debye Hückel; alkalinity = 3.4 mM, pH = 8.2.

^e For inorganic, dissolved Fe(II) at pH > 6.

^f Rate constant given by King and Farlow (2000) for $I = 0$, corrected for $I = 7 \text{ mM}$ using Debye Hückel; alkalinity = 3.4 mM, pH = 8.2.

^g This rate constant was calculated according to Zafiriou (1990) as follows: $\log k = 12.7 - 1.0(\text{pH})$, with pH = 8.2.

^h This rate constant for reaction of superoxide with additional sinks is a rough estimate based on Table 1 in Voelker et al. (2000) and Figure 2 in Goldstone and Voelker (2000).

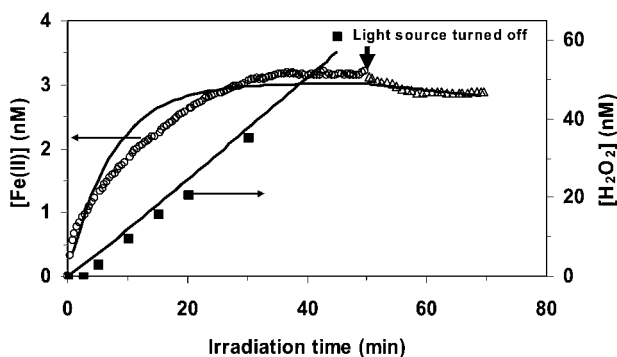


Figure 4. Experimental data (symbols) and modeling results (solid lines) of the concentrations of Fe(II) and H_2O_2 during and after irradiation with simulated sunlight ($I_0 \sim 1.0 \text{ kW m}^{-2}$) of LMW DOM (pH = 8.2) from Lake Murten (Switzerland) (from Meunier et al., 2005; copyright Eawag, Dübendorf, 2005; reproduced with permission from Eawag).

proach that allows this distinction is the combination of laboratory experiments with mathematical kinetic modeling (Meunier et al., 2005; Voelker et al., 1997) (Fig. 5). Another approach is the comparison of the loss of carboxyl groups and formation of CO_2 (Xie et al., 2004).

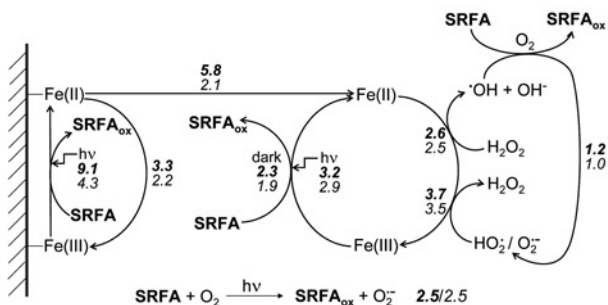


Figure 5. Pathways of light-induced transformations of Suwannee River Fulvic Acid (SRFA) in irradiated, aerated systems, containing initially $40 \mu\text{M}$ Fe in the form of lepidocrocite ($\gamma\text{-FeOOH}$) and 10 mg L^{-1} SRFA. The numbers in italics indicate the amount of iron (in μM) oxidized or reduced by each of the depicted process after 300 min of irradiation at pH 3 (top numbers) and at pH 5 (bottom numbers). These numbers were assessed with the help of a mathematical kinetic model using information gained from separate experiments in simpler systems. The rate of light-induced oxidation of SRFA at the surface of $\gamma\text{-FeOOH}$ was highest in this system, followed by photolysis of Fe(III)-SRFA complexes in solution, followed by photolysis of SRFA itself, followed by thermal oxidation of SRFA by Fe(III), and finally by the oxidation of SRFA via $\cdot\text{OH}$ attack, where the hydroxyl radicals were formed in the Fenton reaction (modified from Voelker et al., 1997).

UV-induced changes of the absorption properties of CDOM

As stated in the Introduction, photochemical transformations of CDOM often result in the loss of color in terms of a decrease in the absorption coefficient $a(\lambda)$ (referred to as photobleaching of CDOM).

Hence photobleaching is the result of CDOM photo-degradation and is often accompanied by a decrease in the molecular weight of CDOM (Brinkmann et al., 2003a; Frimmel, 1998; Stabenau et al., 2004; Stabenau and Zika, 2004; Tremblay et al., 2007). The rate of CDOM photobleaching has been shown to depend on various factors including (i) intensity and wavelength of solar radiation (Del Vecchio and Blough, 2002; Gao and Zepp, 1998; Molot and Dillon, 1997b), (ii) salinity and the presence of iron (Gao and Zepp, 1998; Hefner et al., 2006; Minor et al., 2006; Molot and Dillon, 1997b), (iv) water residence time (Chen et al., 2007; Larson et al., 2007), (v) the extent of stratification (Chen et al., 2007; Del Vecchio and Blough, 2002; Del Vecchio and Blough, 2004a; Vodacek et al., 1997), and (vi) pH (Brinkmann et al., 2003a; Molot and Dillon, 1997b; Molot et al., 2005). As a consequence of CDOM photobleaching, the penetration of UV radiation into water bodies increases and enhances the exposure of aquatic organisms, e.g., phytoplankton, to the damaging UV-B radiation.

Photobleaching of CDOM can occur through the various pathways described above, including reaction of CDOM with $\cdot\text{OH}$ that is formed in photo-Fenton reactions (Brinkmann et al., 2003a; Molot et al., 2005; White et al., 2003; Xie et al., 2004). Upon photobleaching, the spectral slope S (see Eq. 12 below) of CDOM spectra often increases but also may decrease, depending on the pathway of photobleaching. In the following subsections we discuss in more detail

- Absorption properties of CDOM
- Changes of the spectral slope upon photobleaching of CDOM
- Dependence of CDOM photobleaching on salinity, pH, the presence of iron, and wavelengths
- Penetration depth of solar radiation into water bodies

Absorption properties of CDOM

CDOM exhibits broad, featureless absorption spectra, decreasing approximately exponentially throughout the ultraviolet and visible wavelength regimes. CDOM spectra have typically been fitted to the expression (Blough and Green, 1995; Davies-Colley and Vant, 1987; Ma and Green, 2004; Stedmon et al., 2000; Twardowski et al., 2004),

$$a(\lambda) = a(\lambda_0)e^{-S(\lambda-\lambda_0)} \quad (12)$$

where $a(\lambda)$ and $a(\lambda_0)$ are the absorption coefficients at wavelength λ and reference wavelength λ_0 , respectively (typically in m^{-1}), and S is the spectral slope, which is a parameter that characterizes how rapidly

the absorption decreases with increasing wavelength. A refined model for CDOM absorption spectra has been used in several studies (Murphy et al., 2008; Stedmon et al., 2000; Twardowski et al., 2004). The absorption coefficient $a(\lambda)$ is,

$$a(\lambda) = 2.303 \times A(\lambda) \times r^{-1} \quad (13)$$

where $A(\lambda)$ is the absorbance at wavelength λ and r is the path-length (typically in m). Studies of marine waters in the eastern Caribbean (Blough et al., 1993) and off the coast of south Florida (Blough and Green, 1995) have found that S is generally larger for oligotrophic "blue" waters (0.02 nm^{-1}) than for coastal "brown" waters ($0.013\text{--}0.018 \text{ nm}^{-1}$). Values of S for terrestrial sources of CDOM range from $0.01\text{--}0.02 \text{ nm}^{-1}$ (Davies-Colley and Vant, 1987; Zepp and Schlotzhauer, 1981). Similarly, more recent studies have found large increases in S in transects from end members dominated by input of terrigenous organic matter, e.g., wetlands and fjords, to marine end members dominated by algal-derived compounds (Helms et al., 2008; Stedmon et al., 2000). Values of $a(300)$ range from $<0.1 \text{ m}^{-1}$ for "blue" seawaters to $>50 \text{ m}^{-1}$ for some coastal waters and freshwaters (Blough et al., 1993; Green and Blough, 1994; Haag and Hoigné, 1986; Morel et al., 2007).

In many aquatic systems, particularly in freshwater systems, $a(\lambda)$ values are correlated with DOC concentration (Del Vecchio and Blough, 2004a; Molot and Dillon, 1997a; Morris et al., 1995; Pace and Cole, 2002). However, $a(\lambda)/\text{DOC}$ ratios may vary to a great extent. For example, Del Vecchio and Blough (2004a) reported that the $a(400)/\text{DOC}$ ratio decreased by over an order of magnitude with increasing salinity in the Middle Atlantic Bight, due to (i) different DOC and CDOM content in the freshwater and oceanic end members, and (ii) photobleaching of CDOM in the surface waters of the shelf.

Changes of the spectral slope upon photobleaching of CDOM

The loss of absorption (i.e., smaller absorption coefficients, $a(\lambda)$) upon CDOM photodegradation is usually greater at longer wavelengths, leading to an increase in the spectral slope S (Blough et al., 1993; Del Vecchio and Blough, 2002; Del Vecchio and Blough, 2004a; Hefner et al., 2006; Helms et al., 2008; Ma and Green, 2004; Minor et al., 2007; Moran et al., 2000; Twardowski and Donaghay, 2002; Vodacek et al., 1995; Vodacek et al., 1997; Xie et al., 2004). However, also decreases in S upon CDOM photobleaching have been observed (Brinkmann et al., 2003a; Gao and Zepp, 1998; Morris and Hargreaves, 1997; White et al., 2003).

An interesting phenomenon is that decreases in S are generally observed when photo-Fenton reactions are likely to be involved in CDOM photobleaching (Brinkmann et al., 2003a; Morris and Hargreaves, 1997; White et al., 2003). White and coworkers (2003) compared $\cdot\text{OH}$ production rates (normalized to the absorption coefficient at 350 nm) to changes in the spectral slope upon irradiation (with a solar simulator) of water samples from the Satilla River, New Jersey Pine Barrens, Mississippi River Plume, and Florida Keys. Except for the Mississippi River Plume sample (where photolysis of nitrate or nitrite was the likely source of $\cdot\text{OH}$), they observed a general trend that samples with larger $\cdot\text{OH}$ production rates experienced larger decreases in S , whereas S values for samples with small $\cdot\text{OH}$ production rates, such as the Florida Keys sample, increased upon irradiation. The phenomenon of a decrease in S in photo-Fenton systems may tentatively be interpreted in terms of a shift in the type of chromophores involved, i.e. from ligand-to-metal charge-transfer transitions to coupled intramolecular charge-transfer transitions between hydroxy-aromatic donors and quinoid acceptors.

Dependence of CDOM photobleaching on salinity, pH, the presence of iron, and wavelengths

The environmental factors (salinity, pH, the presence of iron, wavelength of solar radiation) that affect CDOM photobleaching kinetics are interdependent. The extent of CDOM photobleaching generally increases with decreasing salinity (Minor et al., 2006) and pH (Brinkmann et al., 2003a; Molot et al., 2005), possibly reflecting the higher photochemical reactivity of terrestrial-derived CDOM and the importance of photo-Fenton reactions. For example, Brinkmann and coworkers (2003a) found an enhancement of CDOM photobleaching around pH 5 upon addition of iron to water samples from a humic-rich bog lake.

Regarding both the pH- and wavelength-dependence of CDOM photobleaching, Molot and Dillon (1997b) found that irradiation wavelengths $>320 \text{ nm}$ dominated photobleaching between pH 5–7, whereas below pH 5, the role of UV-B increased. They rationalized these findings in terms of photobleaching via photo-Fenton reactions occurring most efficiently in acidic waters and under the influence of UV-B radiation. Indeed, the apparent quantum yield of Fe(II) formation has been shown to decrease with increasing wavelength between 300–450 nm in irradiated lake water samples (pH 7.6) (Emmenegger et al., 2001). Furthermore, formation of $\cdot\text{OH}$ (as measured by degradation of atrazine via attack by $\cdot\text{OH}$) in homogeneous photo-Fenton systems was found to occur with highest rates between pH 4–5 (in the range $3 < \text{pH} < 8$) (Balmer and Sulzberger, 1999), which was

mainly due to different photolysis efficiencies of the pH-dependent Fe(III) species. From the above discussion, it seems thus reasonable to assume that UV-B radiation is particularly effective in CDOM photobleaching in acidic, iron-rich aquatic systems.

Penetration depth of solar radiation into water bodies

The penetration depth of solar radiation into water bodies can be calculated on the basis of measured diffuse attenuation coefficients, K_d , and considering Beer-Lambert's law,

$$\log \frac{W(\lambda)}{W_z(\lambda)} = K_d(\lambda) \times z \quad (14)$$

where z is the depth of a water body (in m), $W(\lambda)$ and $W_z(\lambda)$ are the photon flux at the surface and at depth z , respectively (usually in $\text{einstein m}^{-2} \text{s}^{-1} \text{nm}^{-1}$), and $K_d(\lambda)$ is the diffuse attenuation coefficient at wavelength λ (in m^{-1}). The depth at which only 1% of the incident photon flux at wavelength λ is transmitted is then,

$$z_{1\%}(\lambda) = 4.606 \times K_d(\lambda)^{-1} \quad (15)$$

Diffuse attenuation coefficients are determined from the slope of the linear regression of the natural logarithm of downwelling solar irradiance vs. depth z . In lakes, attenuation depths ($z_{1\%}$) for UV-B (e.g., at 305 nm) range from several centimeters to ~10 m (Morris et al., 1995), whereas in clear open ocean waters, $z_{1\%}$ (310 nm) values >60 m have been measured (Morel et al., 2007).

Photobleaching of CDOM affects the penetration depth of solar radiation. Reche and coworkers (1999) found a significant positive relationship between photobleaching rate coefficients, k_b , and $z_{1\%}$ for photosynthetic active radiation (400–700 nm) in their studied lakes. Photobleaching rate coefficients, k_b were determined from the slope of ln-linear regressions according to a first-order kinetics expression,

$$a(\lambda)_t = a(\lambda)_0 e^{-k_b(\lambda)D_c} \quad (16)$$

where $a(\lambda)_t$ and $a(\lambda)_0$ are the absorption coefficient at a given wavelength at time t and time 0, respectively (in m^{-1}), $k_b(\lambda)$ is the photobleaching rate coefficient at a given wavelength (in $\text{m}^2 \text{einstein}^{-1}$), and D_c is the cumulative sunlight dose, $D_c = \int_{\lambda} W(\lambda) d\lambda \times t$ (in einstein m^{-2}). Since the kinetics of CDOM photobleaching depends on the intensity of solar radiation, $K_d(\lambda)$ and $z_{1\%}(\lambda)$ are expected to vary seasonally. Morris and Hargreaves (1997) observed highest K_d values (lowest transparency) at 320 nm in early spring and again in late fall in three Pocono Plateau lakes.

The half-life of light absorption by CDOM at a given wavelength can be expressed as

$$t_{1/2} = \frac{\ln 2}{k_b(\lambda)D} \quad (17)$$

where D is the sunlight dose, $D = \int_{\lambda} W(\lambda) d\lambda$ (in $\text{einstein m}^{-2} \text{s}^{-1}$). Reche and coworkers (2000) assessed half-lives of light absorption by CDOM (i.e., the time to reduce light absorption at 320 and 440 nm by 50%) in two model lakes, one situated in the northern hemisphere (NH, Institute of Ecosystem Studies, Millbrook, USA) and the other in the southern hemisphere (SH, Ushuaia, Argentina). For the NH site, the half-life at 440 nm was 6.6 and 342 d for DOC = 0.3 and 30 mg L^{-1} , respectively, while that for the SH site ranged from 1.2–103 d for similar DOC concentrations. The half-life at 320 nm was 5–8 times smaller in the SH than in the NH site, depending on DOC concentration. These findings were interpreted in terms of CDOM photobleaching being strongly dependent on the intensity and wavelength of solar radiation (see previous subsection).

Effects of UV radiation on the bioavailability and mineralization of DOM

The bioavailability of DOM largely depends on its origin, thus chemical composition, and diagenetic alteration. UV-induced transformations of DOM can increase or decrease the bioavailability of DOM, depending on the initial bioavailability and subsequent transformation pathways. UV-induced changes of DOM bioavailability might heavily affect microbial DOM mineralization. Furthermore, mineralization of DOM also occurs as an abiotic, UV-induced process. These items are discussed in the following subsections.

Origin, chemical composition and bioavailability of DOM

The bioavailability (or bioreactivity) of DOM depends on its chemical composition and thus its origin. Algal-derived DOM has been reported to be biologically more labile than terrigenous DOM (Bertilsson and Jones, 2003; Biddanda and Cotner, 2003; Boyd and Osburn, 2004; Chen et al., 2004; Davis and Benner, 2007; Kaiser et al., 2004; Karlsson et al., 2007; McCallister et al., 2006; Obernosterer and Benner, 2004; Perez and Sommaruga, 2006; Tranvik and Bertilsson, 2001; Vähätalo and Wetzel, 2004). Likely reasons for this phenomenon are the following: (i) autochthonous DOM is enriched in carbohydrates, and (ii) the C/N ratio of plankton and bacteria is much smaller than that of vascular plant tissues (Aluwihare

et al., 2002; Benner et al., 1992; Ertel et al., 1986; Hedges et al., 1986; Hedges et al., 1994; Hedges et al., 2000; Hopkinson et al., 1998; Kaiser et al., 2004; McCallister et al., 2006; McKnight et al., 1991) (see subsection "Bulk characterization of DOM").

The bioavailability of DOM also depends on its polydispersity. Amon and Benner (1994; 1996a) reported that HMW DOM was utilized to a greater extent by bacterioplankton than LMW DOM, both in freshwater and seawater samples. These authors (1996a) proposed a conceptual model whereby the bioreactivity of DOM decreases along a continuum of size (from large to small). A number of studies have directly or indirectly corroborated this size-continuum model (Benner et al., 1997; Hernes and Benner, 2006; Kim et al., 2006; McCallister et al., 2006; Repeta and Aluwihare, 2006; Scully et al., 2004; Seitzinger et al., 2005).

Kaiser and Sulzberger (2004) found, on the other hand, that LMW and hydrophilic compounds collected from the Tagliamento River (a semi-natural, oligotrophic alpine river in northeast Italy) exhibited a higher bioreactivity than HMW and hydrophobic DOM compounds from this river. In this riverine system, HMW and hydrophobic components are derived from the leaching of soils that contain highly altered plant material and bacterial biomass, whereas highly bioavailable LMW and hydrophilic components are likely derived from the decomposition of diagenetically young fine particulate organic matter (FPOM) and autochthonous microalgae biomass. An interesting phenomenon reported by Kaiser and Sulzberger (2004), which points to Amon and Benner's (1996a) continuum size model was the following: Size exclusion chromatograms of LMW and HMW DOM fractions from the Tagliamento River before and after incubation with riverine bacterioplankton revealed that the riverine bacteria utilized and released compounds at the high and low end, respectively, of the apparent molecular weight distribution of these fractions.

According to Amon and Benner's (1996a) continuum model, the bioavailability of DOM also decreases along a continuum of diagenetic state (from fresh to old). Heterotrophic bacteria preferentially utilize carbohydrate- and protein-carbon from fragments of plants and microbial tissues (Baldock et al., 2004), carbohydrate-, protein-, and lignin-carbon from partially decomposed residues (Baldock et al., 2004; Ertel et al., 1986; Frazier et al., 2005; Hernes and Benner, 2006), resulting in the formation of biorecalcitrant chemical structures that are dominated by alkyl C (Baldock et al., 2004; Smittenberg et al., 2006). Hence microbial transformations and release of organic compounds as well as bacterial remnants can

contribute significantly to the pool of highly processed, biorecalcitrant DOM in marine systems (Baldock et al., 2004; Ogawa et al., 2001).

UV-induced changes of the bioavailability of DOM

Several studies have shown that direct or indirect (¹O₂-mediated) phototransformations of DOM enhance its bioavailability (Bertilsson and Tranvik, 1998; Bertilsson et al., 1999; Brinkmann et al., 2003b; Goldstone et al., 2002; Herndl et al., 1997; Jørgensen et al., 1998; Kieber et al., 1989; Lindell et al., 1995; Mopper et al., 1991; Moran et al., 2000; Pullin et al., 2004; Reche et al., 1998; Scully et al., 2003; Vähätalo et al., 2003; Vähätalo and Wetzel, 2008; Wetzel et al., 1995). This UV-mediated increase in DOM bioavailability can be due to the following combined effects: (i) UV-induced formation of oxygen-rich compounds (Kim et al., 2006; Kujawinski et al., 2004; Kulovaara et al., 1996), (ii) UV-induced increase in the concentration of amino acids and carbohydrates (Jørgensen et al., 1998; Nieto-Cid et al., 2006), which are dominant energy sources to bacteria (Baldock et al., 2004; Benner, 2003; Jørgensen et al., 1998; Nieto-Cid et al., 2006; Repeta and Aluwihare, 2006; Simon and Rosenstock, 2007), and (iii) UV-induced formation of LMW compounds, e.g., carbonyl compounds and carboxylic acids including formic, acetic, pyruvic, oxalic, malonic, and succinic acids (Bertilsson and Tranvik, 1998; Bertilsson et al., 1999; Brinkmann et al., 2003b; Corin et al., 1996; Frimmel, 1998; Goldstone et al., 2002; Kieber et al., 1989; Kieber et al., 1990; Kujawinski et al., 2004; Moran and Zepp, 1997; Obernosterer et al., 1999a; Pullin et al., 2004; Wetzel et al., 1995).

The observation that UV-induced break-down of DOM into LMW compounds increases DOM bioavailability seems to be in contradiction with the continuum-size model by Amon and Benner (1996a) (see above). Obviously, whether UV-induced formation of LMW compounds results in an increase or decrease in DOM bioavailability largely depends on the bioavailability of the initial compounds and on the transformation pathways. LMW compounds that are highly processed both by biotic and abiotic reactions, may be extremely recalcitrant (Amon and Benner, 1994; Baldock et al., 2004; Kawasaki and Benner, 2006; Ogawa et al., 2001). For example, Pullin and coworkers (2004) reported that LMW compounds could not account for most of the observed sunlight and ¹O₂-induced increases in DOM bioavailability.

There are an increasing number of studies showing contrasting effects of UV-induced transformations on DOM bioavailability, transforming bioavailable into biorecalcitrant compounds and vice-versa (Benner and Biddanda, 1998; Biddanda and Cotner, 2003;

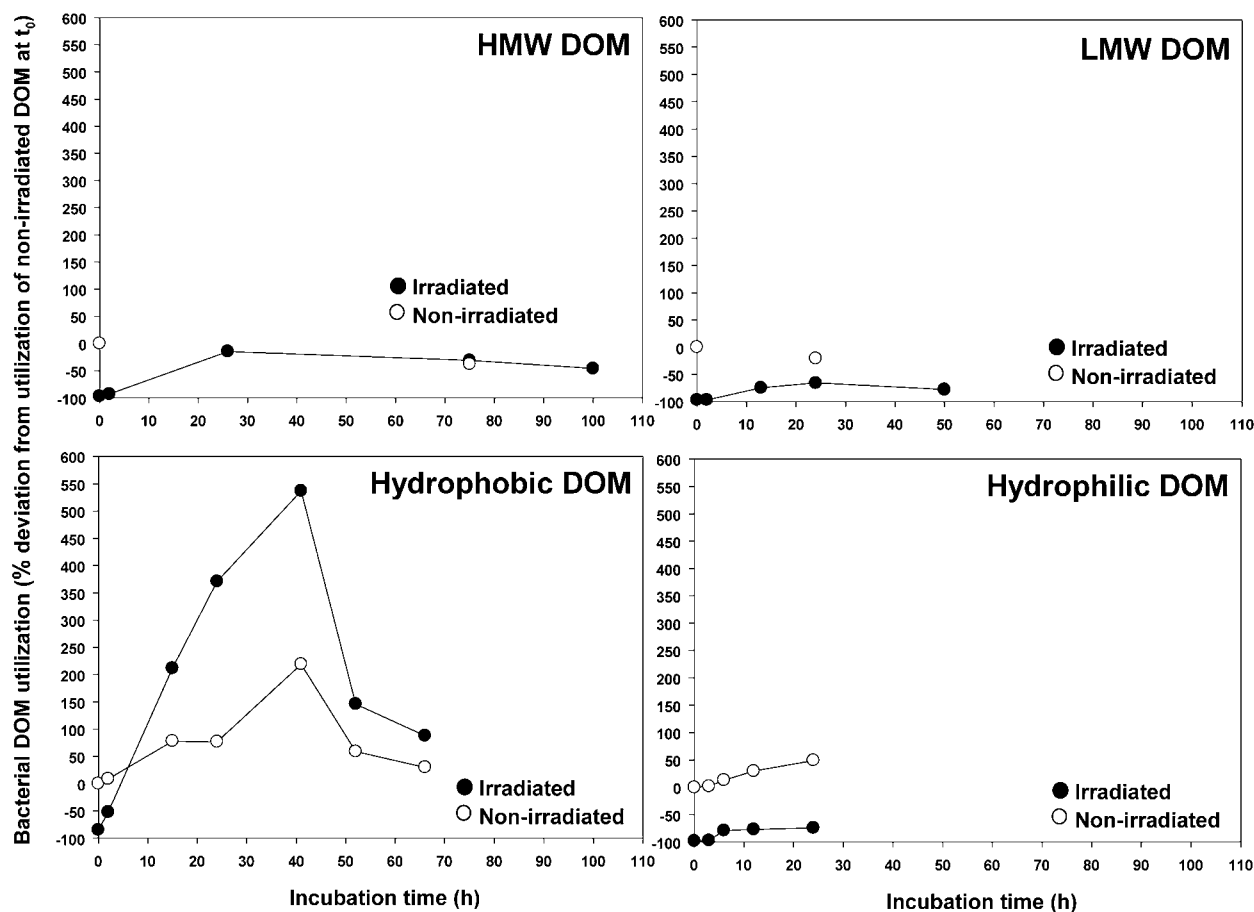


Figure 6. Long-term bioassay experiments on irradiated (filled circles) and non-irradiated (open circles) DOM fractions sampled during April 2000 in the Tagliamento River (Italy): (A) HMW, (B) LMW, (C) hydrophobic, and (D) hydrophilic DOM. Bacterial DOM utilization is based on measurements of bacterial biomass production ($\text{fg C cell}^{-1} \text{d}^{-1}$). Changes in bacterial DOM utilization were calculated as % deviation of utilization of non-irradiated DOM before long-term incubation (modified from Kaiser and Sulzberger, 2004).

Judd et al., 2007; Kaiser and Sulzberger, 2004; Obernosterer et al., 1999b; Obernosterer and Benner, 2004; Tranvik and Bertilsson, 2001). Kaiser and Sulzberger (2004) found that photochemical transformations decreased the bioavailability of initially bioreactive LMW and hydrophilic compounds from the Tagliamento River, whereas the bioavailability of initially biorecalcitrant hydrophobic compounds increased upon irradiation, while that of HMW compounds did not change (Fig. 6).

UV-induced transformations often have a positive effect on the bioavailability of terrigenous DOM, while the bioavailability of autochthonous DOM is less positively affected or even decreases (Biddanda and Cotner, 2003; Judd et al., 2007; Kaiser and Sulzberger, 2004; Obernosterer and Benner, 2004; Reche et al., 1998; Tranvik and Bertilsson, 2001). The former may be rationalized by allochthonous DOM becoming more like autochthonous DOM upon UV-induced transformations (in terms of chemical composition) (Dittmar et al., 2007; Minor et al., 2007; Tremblay et al., 2007). UV-induced transformations

have been shown to be particularly efficient in increasing the bioavailability of terrigenous DOM if it is diagenetically highly altered and vice versa (Benner and Biddanda, 1998; Biddanda and Cotner, 2003; Kaiser and Sulzberger, 2004; Obernosterer et al., 1999b). These findings are in agreement with the model by Amon and Benner (1996a) according to which the bioreactivity of DOM decreases along a continuum of diagenetic state. In marine and lacustrine systems, the concentration of diagenetically old DOM, i.e., of biorefractory DOM compounds, increases with depth, and UV-induced transformations of surface and deep water DOM have been shown to decrease and increase DOM bioavailability, respectively (Benner and Biddanda, 1998; Biddanda and Cotner, 2003; Obernosterer et al., 1999b).

Mineralization of DOM

In both photomineralization and microbial respiration of DOM (oxidation of DOM to CO_2 , H_2O , and major and minor nutrients), molecular oxygen (O_2) is consumed and CO_2 is produced. The ratio of DOC loss

to O₂ consumed or CO₂ produced in DOM photomineralization has been reported to be around one in various aquatic systems (Amon and Benner, 1996b; Kortzinger et al., 2001; Xie et al., 2004). The rate of DOM photomineralization increases with decreasing pH (Anesio and Granéli, 2004) and also depends on the precipitation regime (Clark et al., 2004; Rodriguez-Zuniga et al., 2008). In marine systems, it also depends upon sea ice cover (Bélanger et al., 2006). These authors predict that ongoing reduction in the extent of sea ice cover will greatly accelerate photomineralization of terrigenous DOM in Arctic surface waters. Furthermore, UV-induced mineralization of above-ground litter may result in a substantial fraction of carbon fixed in plant biomass being lost directly to the atmosphere (Austin and Vivanco, 2006).

The question about the fate of terrigenous DOM in the oceans has puzzled and still puzzles biogeochemists. Terrigenous DOM comprises only a small fraction (0.7–2.4%) of the total DOM in the ocean (Opsahl and Benner, 1997). A large fraction of terrigenous DOM introduced into open ocean waters must be mineralized in estuarine and coastal waters, where photomineralization plays a prominent role (Amon and Benner, 1996b; Bélanger et al., 2006; Del Vecchio and Blough, 2004a; Hansell et al., 2004; Hedges et al., 1997; Hernes and Benner, 2003; Kowalczyk et al., 2005; Minor et al., 2007; Opsahl and Benner, 1998; Rodriguez-Zuniga et al., 2008; Stabenau and Zika, 2004; Vähätalo and Wetzel, 2004). Studies on the half-life of terrigenous compounds within the bulk DOM pool show that their mineralization is relatively fast, being within the range of 7 years (Hansell et al., 2004), and ocean residence times fall between 20 to 130 years (Opsahl and Benner, 1997). Hence, photomineralization processes, especially in the coastal ocean, may be important next to microbial consumption and may even become of increasing importance due to climate-driven loss of sea-ice cover in arctic regions.

Conclusions

The molecular-level elucidation of the chemical composition of DOM has greatly helped to elucidate UV-effects on the chemical composition and thus optical properties and bioavailability of DOM. It also has enabled the prediction of how the photo- and bioreactivity depend on DOM origin. Such information is needed to model the global carbon cycle, particularly with respect to consequences of climate change. We believe that further sophistication of analytical tools and intelligent combinations of methods will continue to improve our understanding of the chemical composition, structure, conformation, opti-

cal, and redox properties of DOM and how they control DOM photo- and bioreactivity (Fan et al., 2000; Fimmen et al., 2007; Hertkorn et al., 2006; Paul et al., 2006; Schmitt-Kopplin et al., 1998a; Schulten and Schnitzer, 1997; Simjouw et al., 2005). For example, the study by Hertkorn et al. (2006), involving a combination of NMR, capillary electrophoresis (Schmitt-Kopplin et al., 1998b), and FT-ICR-MS, is one of the promising analytical approaches to decipher what is referred to as molecularly uncharacterized carbon (Hatcher, 2004; Hedges et al., 2000). Furthermore, for the elucidation of light-induced processes on a molecular basis, time-resolved spectroscopic methods are needed, which so far have been applied in only a few environmental-photochemical studies (Brucoleri et al., 1993; Del Vecchio and Blough, 2004b; Wang et al., 2007b).

In assessing UV-induced changes of the chemical composition of DOM and thus of carbon cycling, the role of climate change also has to be taken into account (Zepp et al., 2007) (Fig. 7). Climate change includes warming and, as a consequence, reduction in sea ice cover and stratification of aquatic systems (Behrenfeld et al., 2006; Zepp et al., 2007 and refs. cited therein), ocean acidification (Caldeira and Wickett, 2003; Doney, 2006), and changes in continental hydrology (Zepp et al., 2007 and refs. cited therein). Increasing temperatures and changes in the frequency and intensity of precipitations can enhance the discharge of DOM from terrestrial into aquatic systems (Freeman et al., 2001; Mack et al., 2004; Peterson et al., 2002). As discussed above, terrigenous DOM exhibits a greater photoreactivity than autochthonous DOM, and UV-induced transformations of terrigenous DOM generally increase its bioavailability and, in turn, microbial respiration (Bertilsson and Tranvik, 1998; Obernosterer and Benner, 2004; Pullin et al., 2004). Furthermore, terrigenous DOM also is subject to photomineralization (Bélanger et al., 2006). Hence, the result of UV radiation and changes in continental hydrology could be a net loss of organic carbon from terrestrial ecosystems and a UV-mediated positive feedback to CO₂ accumulation in the atmosphere (Zepp et al., 2007 and refs. cited therein) (Fig. 7). Boreal wetlands in the Arctic, where increased UV radiation and reduction in sea ice cover are more pronounced, are particularly sensitive to such UV-induced feedback mechanisms (Bélanger et al., 2006; Zepp et al., 2007 and refs. cited therein).

Increased stratification of lakes and oceans enhance UV-induced CDOM bleaching (Chen et al., 2007; Del Vecchio and Blough, 2002; Del Vecchio and Blough, 2004a; Vodacek et al., 1997). Stratification also reduces the transport of UV-absorbing compounds from deeper water into the euphotic zone, thus

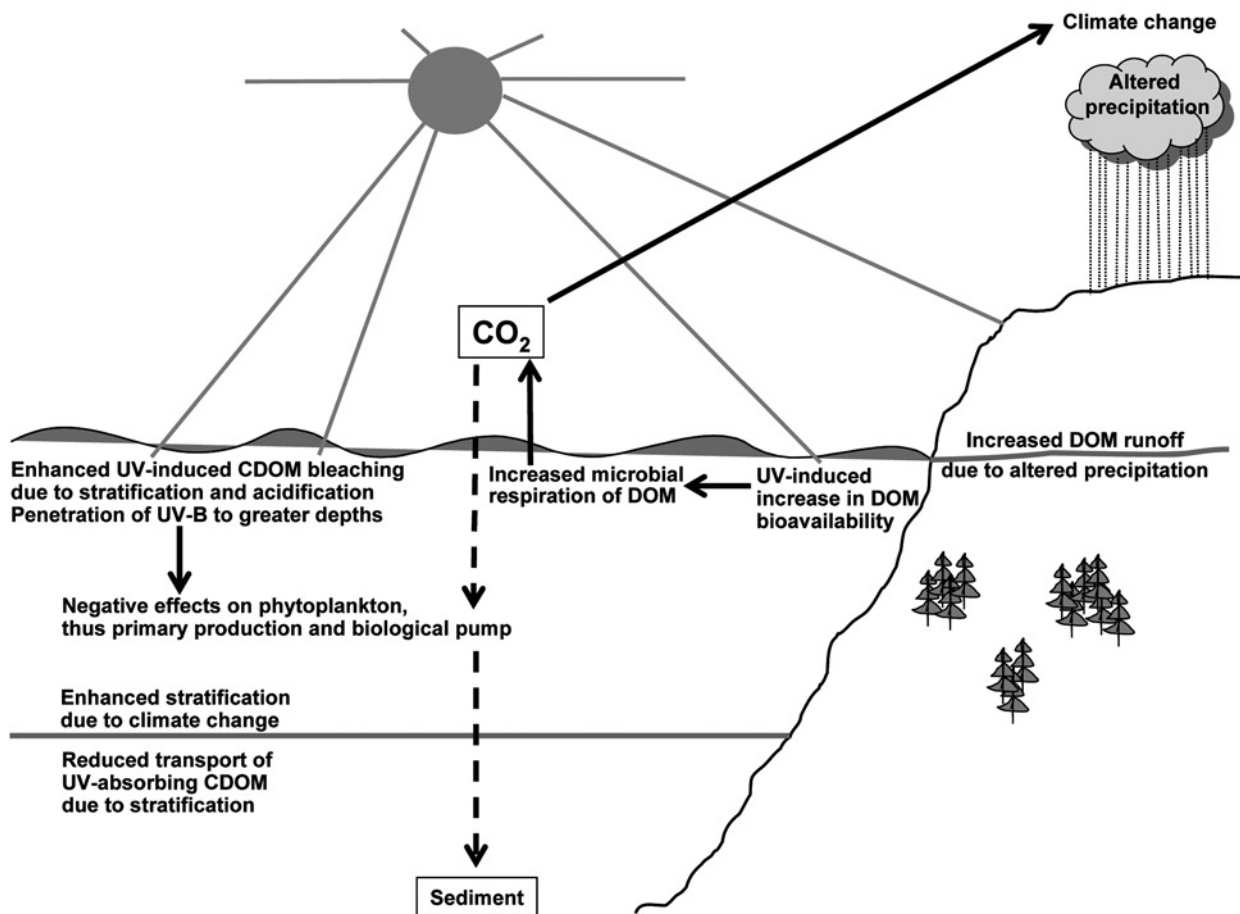


Figure 7. Potential combined effects of UV radiation and climate change on aquatic source (solid arrows) and sink (dashed arrows) terms of atmospheric CO₂. In this simplified scheme, only microbial respiration of DOM and the biological pump are considered as an aquatic source and sink, respectively, of atmospheric CO₂.

worsening the effects of CDOM photobleaching on UV-B penetration (Zepp et al., 2007 and refs. cited therein). Also, decreasing pH values of oceans and freshwater systems due to increased atmospheric CO₂ concentrations (Caldeira and Wickett, 2003; Doney, 2006) may enhance UV-induced bleaching of CDOM (see subsection “Dependence of CDOM photobleaching on pH and wavelength”) and hence increase UV penetration into water bodies. UV-B-induced damages of the phytoplankton in the oceans is critical since the global ocean plays a major role in carbon sequestration (Behrenfeld et al., 2006; Mikaloff Fletcher et al., 2006), where the biological pump (photosynthesis by phytoplankton and subsequent sedimentation of a fraction of phytoplankton residues) plays a key role (Buesseler et al., 2007). UV-B-induced damages to phytoplankton could render the biological pump less effective and hence CO₂-related ocean acidification could represent another UV-mediated positive feedback mechanism of CO₂ accumulation in the atmosphere (Fig. 7).

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