

IMPACT OF SEDIMENT RESUSPENSION AND PHOTOCHEMISTRY ON
DISSOLVED ORGANIC CARBON AND COPPER SPECIATION

Michelle Leigh Smith

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Approved by

Advisory Committee

Dr. Robert J. Kieber

Dr. Stephen A. Skrabal

Co-Chair

Co-Chair

Dr. Robert F. Whitehead

Co-Chair

Accepted by

Dean, Graduate School

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ABSTRACT

Changes in dissolved organic carbon (DOC) and Cu speciation caused by sediment resuspension and photochemistry in the highly turbid, organic rich waters of the Cape Fear River Estuary (CFRE) have been investigated. The concentration of DOC in filtered estuarine samples exposed to simulated sunlight decreased 4 -27 μM compared with dark controls which also decreased but to a lesser extent. This indicated that organic carbon was being converted to inorganic carbon in light exposed samples and consumed in dark controls. Unfiltered irradiated samples containing ambient river particles experienced an increase in DOC relative to samples with no particles, indicating particles are capable of producing DOC upon exposure to light. When suspended sediments (2 g wet sediment per L) were present, 3-145 μM DOC was released in light exposed samples relative to dark controls. The DOC released was directly related to the percent organic carbon in the sediment. When resuspended sediment samples were exposed to photosynthetically available radiation (PAR) rather than full spectrum light, there was significantly less DOC produced suggesting UVA/UVB light is the most effective at engendering changes in DOC.

A series of photolysis experiments were also conducted to determine the effects of irradiation and resuspended sediments on total dissolved copper (TDCu) concentrations. In relatively uncontaminated environments, there was little or no effect of sediments or irradiation on TDCu levels in the estuary. In more contaminated environments, such as seen in San Diego Bay and the Port of Wilmington in the CFRE, there was a significant increase in TDCu production after irradiation in 0.2 μM filtered water containing sediments. These results suggest that the impact of sediment resuspension on TDCu

concentration depends to a large extent on how much Cu is present in the irradiated sediments.

In addition to TDCu, the impact of light exposure and sediments on Cu(I) was also investigated. Copper(I) concentrations in filtered CFRE water increased in light exposed samples suggesting production of reduced Cu from other dissolved Cu species. Little impact of ambient particles or sediments on Cu(I) concentrations were observed. The effect of full spectrum and PAR on the photodegradation of strong Cu binding ligands was also studied in filtered water with no added sediments. When exposed to full spectrum light, ligand concentrations decreased from 55 nM to 10 nM, whereas samples exposed only to PAR decreased from 50 nM to 19 nM, indicating that PAR is very effective at the degradation of Cu ligands in the water column.

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INTRODUCTION

The goal of this project was to study the impacts of sediment resuspension events (wind and wave mixing, shipping and dredging activities), and photochemistry on the biogeochemical cycling of dissolved organic carbon and copper (Cu) in the organic rich Cape Fear River estuary. This research provided an improved understanding of the in situ physical and chemical processes that affect the distribution of dissolved organic carbon (DOC) and speciation of dissolved Cu in estuarine waters. This thesis consists of two parts. The first discusses the role of sediment resuspension and photochemistry on DOC and the second examines the role of these processes on Cu speciation.

Cu Biogeochemistry In Natural Waters

Cu is a trace metal and, in natural waters may exist in various forms such as free hydrated ions (i.e., $\text{Cu}^{2+}(\text{aq})$) or complexed with organic and inorganic ligands (Donat and Bruland, 1995; Stumm and Morgan, 1996). In most natural waters Cu is strongly complexed by organic ligands, which are a small fraction ($\sim < 0.1\%$) of the total dissolved organic matter (DOM) pool. This complexation of Cu by organic ligands controls the activity of the free hydrated Cu^{2+} ion and thus Cu bioavailability (Sunda and Guillard, 1976; Brand et al., 1983; Brand et al., 1986; Sunda et al., 1987, 1990). In surface oceanic and estuarine waters, dissolved Cu appears to be complexed by at least two classes of organic ligands: a very strong class (commonly termed L_1) which generally exists at concentrations ranging from 1-40 nM, with conditional stability constants (with respect to free Cu^{2+} ion, K^{cond}) of 10^{12} to 10^{14} , and weaker classes (i.e., L_2 , L_3), which exist at higher concentrations (6-150 nM), but with lower values of K^{cond} (10^8 - 10^{10}) (van den Berg, 1984; Buckley and van den Berg, 1986; van den Berg et al., 1987; Hering et al., 1987;

Moffett and Zika, 1987a; Sunda and Hanson, 1987; Coale and Bruland, 1988, 1990; Apte et al., 1990; Moffett et al., 1990; Sunda and Huntsman, 1991; Donat and van den Berg, 1992; van den Berg and Donat, 1992; Donat et al., 1994; Moffett, 1995). Copper has a strong affinity for organic matter (Landing and Feely, 1981; Fischer et al., 1986; Kerner and Geisler, 1995), and is typically associated with (Morel and Hudson, 1985) or adsorbed onto particles (Davis, 1984; Tessier et al., 1996). Therefore, Cu is cycled with particulate organic matter (POM) in oceanic and coastal waters (Davis, 1984; Tessier et al., 1996).

The Role of Sediments and Photochemistry on Cu

The distribution, speciation, and behavior of Cu in overlying waters can be affected by processes which occur in the water column itself and by interactions with bottom sediments. In disturbed sediments, exchanges can occur during resuspension, which commonly occurs in harbors and estuaries as a result of wind, wave, and tidal stirring, shipping and berthing activities (e.g., propeller wash), and dredging.

Resuspension can engender a number of direct and indirect effects on the speciation, concentration, and potential bioavailability of Cu in overlying waters. Direct changes can occur by the dispersion of sediment pore waters, which are typically enriched in total metals, metal-complexing organic and inorganic (e.g., sulfide) ligands relative to bottom waters, leading to increases in concentrations of these constituents in overlying waters (Skrabal et al., 2000). Indirect changes can occur in several ways, including: 1) the release of Cu from oxidizing sulfide phases present in anoxic or hypoxic sediments; 2) scavenging of dissolved Cu in overlying waters by resuspended Fe and Mn oxyhydroxides and POM; 3) indirect or direct transformation of photoactive sedimentary

components (including POM and Fe and Mn phases) in surface waters with the accompanying release of associated Cu.

Of all the potential effects on metal cycling and speciation that may occur as a result of sediment resuspension, the role of photochemical transformations in estuaries is the least studied. However, several studies have indicated the role that such transformations may play in significantly altering the speciation of Cu. For example, photochemical degradation has been cited as the mechanism by which Cu(II)-organic ligand complexes in the ocean are dissociated to Cu(I) and oxidized ligand, with subsequent reoxidation of the Cu(I) to form inorganic Cu(II). Evidence for this mechanism is partly provided by Moffett and Zika (1988), who consistently observed significant concentrations of Cu(I) and H₂O₂ (which is photochemically produced from light-absorbing organic matter; Cooper et al., 1988) in oceanic surface waters during daylight hours. Decreasing concentrations of Cu(I) with depth during daylight hours and little or no Cu(I) and H₂O₂ production in the absence of sunlight suggested a photochemical origin of these species. Photochemical reactivity may also affect the cycling of the strongest Cu-complexing ligand class (L₁). Both Coale and Bruland (1988) and Moffett et al. (1990) found lower L₁ concentrations in surface waters relative to deeper waters within the photic zone, suggesting relatively high lability possibly induced by photochemical reactivity.

Another photochemical mechanism which may affect Cu mobility is the potential release of this metal by photoreduction of common carrier phases, including Fe(III) and Mn(IV) oxides and POM (Waite, 1990; Stumm and Morgan, 1996). Photoreduction of Mn oxides has been observed in surface oceanic waters (Sunda et al., 1983; Sunda and

Huntsman, 1988; Waite et al., 1988; Waite and Szymczak, 1993). Similar reactions may occur for Fe(III) oxides in natural waters, including surface and atmospheric waters (Behra and Sigg, 1990; Faust, 1994). Typically these photoreactions occur in the presence of dissolved or colloidal organic matter with which Cu may be associated, including fulvic and humic acids (Waite et al., 1988) and organic acids such as oxalate (Zuo and Hoigne, 1992). These types of reactions might be expected to be potentially important following resuspension of estuarine bottom sediments into illuminated surface waters. Oxic bottom sediments are generally quite rich in Fe(III) and Mn(IV) oxides which are effective scavengers of dissolved trace metals such as Cu (e.g., Murray, 1975; Tessier et al., 1996). Upon exposure to light, photoreduction may occur leading to the release of dissolved Cu to overlying waters. A similar process might occur for Cu bound to POM in resuspended bottom sediments (e.g., Davis, 1984) when they are exposed to light in surface waters.

An additional consideration of the interaction of light with metals is the role of photochemically produced reactive species, principally H_2O_2 , which may interact with the cycle of Cu and also affect its speciation and fate in estuarine waters. The formation of H_2O_2 is considered to occur as a result of the action of sunlight (at wavelengths < 400 nm) on colored DOC. The H_2O_2 thus produced may act both reductant and oxidant for metals. Oxidation of reduced metals such as Fe(II) and Cu(I) by H_2O_2 in seawater has been reported by Moffett and Zika (1987b). Photoreduction of Fe(III) and Mn(IV) in the presence of organic matter is probably also mediated by H_2O_2 (Sunda et al., 1983; Hong and Kester, 1986; McKnight et al., 1988; Waite et al., 1988; Sulzberger et al., 1989; Bertino and Zepp, 1991). Reactions of H_2O_2 with organically complexed metals such as

Cu(II)-ligand complexes can result in the production of reduced metal complexes and oxidized ligands (Balzani and Moggi, 1990; Blough and Zepp, 1995). This mechanism has been proposed for the cycling of strong Cu(II) organic complexes in the ocean (Moffett and Zika, 1988) as discussed previously.

Clearly, the action of light on dissolved organic matter, with the accompanying release of reactive intermediates such as H₂O₂, plays a potentially important role in the cycling and speciation of trace metals such as Cu. Photochemically initiated reactions should be particularly important in estuarine environments such as the Cape Fear which are relatively rich in DOC of varying terrestrial and oceanic sources.

The Role of Sediments and Photochemistry on Dissolved Organic Carbon

DOC is known to be photoreactive, and can be photochemically degraded into dissolved inorganic carbon (DIC) a part of which is CO₂ and CO (Miller and Zepp, 1995; Zepp 2002; Gao and Zepp 1998). Irradiation of DOC creates DIC compounds that absorb more weakly in UV regions than do initial DOC compounds (Gao and Zepp, 1998). Sediments also play a role in altering DOC concentrations in natural waters. The amount of releasable organic carbon from sediment resuspension is related to the amount of organic carbon in the sediments (Komada et al., 2002). Komada and Reimers (2001) found that sediment resuspension alters the partitioning of organic carbon between the particulate and dissolved phase due to the release of organic carbon loosely bound to the mineral surfaces of the particles. Experiments indicated a net conversion of POC to DOC in dark resuspension experiments, although the DOC release was relatively small (Komada and Reimers, 2001). Koelmans and Prevo (2003) also found that DOC was produced from particulate organic matter. They also observed that in aquatic sediment

resuspensions DOC can also be degraded by photolysis, adsorption onto particles, or by biological uptake.

METHODS

Study Area and Sampling

The Cape Fear River drains the largest river basin in the state of North Carolina. In the estuarine portion of the river, near Wilmington, NC, two coastal plain rivers, the Black and Northeast Cape Fear rivers, contribute organic-rich freshwater to the mainstem river. Seawater sources include the Atlantic Ocean and the Atlantic Intracoastal Waterway at the seaward end of the estuary. In general, the estuary is well mixed vertically because of the relatively short water residence time and rapid flow. Water depths in the estuary range from 1-2 m near the margins to ~10-15 m in the main channel.

Sediment and water sampling were conducted primarily at two sites, both of which are subject to shipping and berthing activities. Each site was located in different salinity and water chemistry regimes (low salinity waters with a significant blackwater component *vs.* high salinity waters with a significant seawater component) (Figure 1). The lower estuary site (station 2) is located approximately at mile marker (M) 23 near Southport. The upper estuary site (station 1) is located in between M35 and M42. Both study sites show preliminary evidence of contamination with metals, including Cu (Röhl, 1980; Mallin et al., 1998) although detailed, systematic studies to address this issue have not been performed.

Bottom sediments and overlying water were collected at each site for use in photochemical resuspension experiments. The sampling took place three times per year

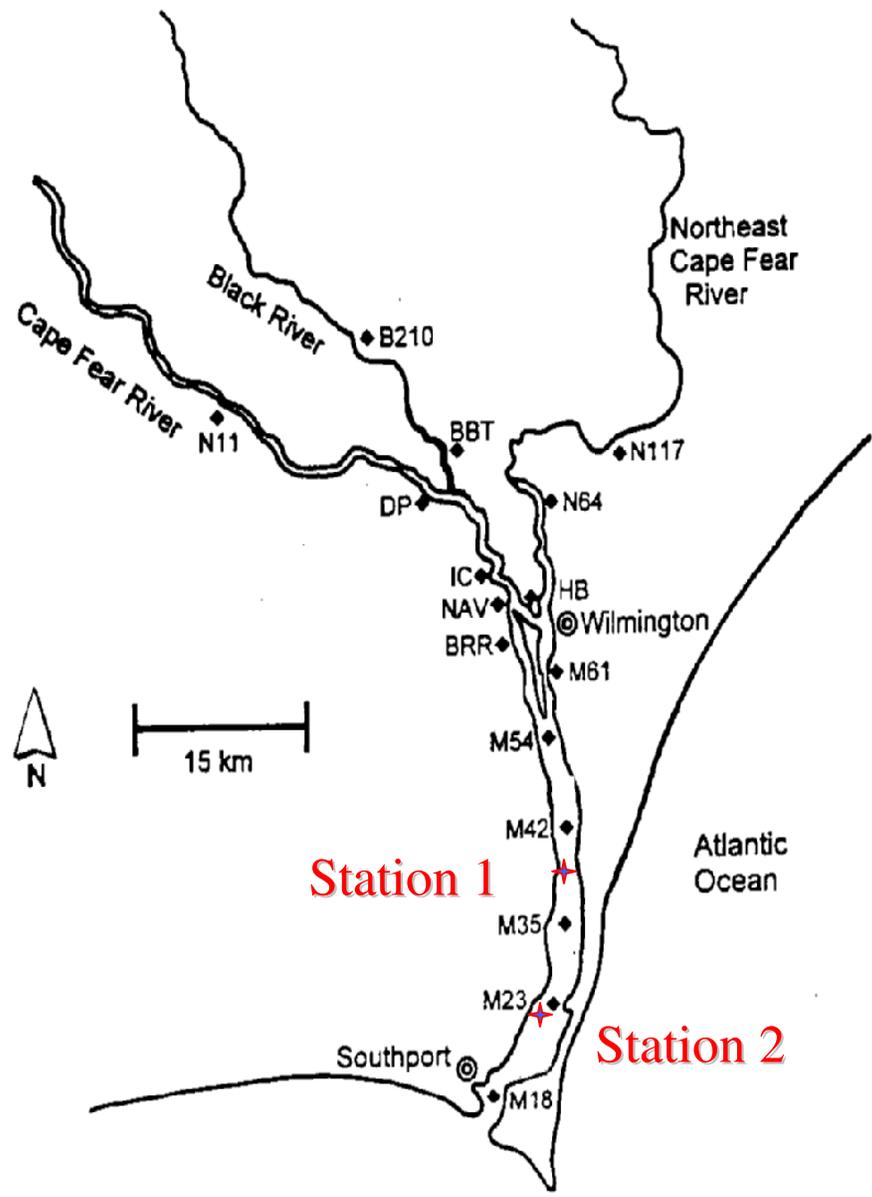


Figure 1. Lower Cape Fear River sampling stations M18 to M61.

at each site. Seasonal sampling encompassed periods of intense sunlight coupled with active production of organic matter (summer) and periods of lower sunlight intensity and reduced organic production (winter). For one experiment sediment samples and overlying water were collected in early spring (2003) from stations M18, 23, 35, 42, 54, and 61 to study various processes over the salinity gradient of the estuary. Sediment samples were also collected from San Diego Bay in April of 2003 for selected experiments. All sediment samples were analyzed for percent organic carbon content and leachable Cu.

Photochemical Resuspension Experiments

Using bottom sediments and overlying water at each site, sediment suspensions were prepared at concentrations relevant to disturbed environments ($1-2 \text{ g L}^{-1}$; Schubel, 1975). Three high density polyethylene cups were filled with surface sediment (2-3 cm depth) from the box core taken at each site and homogenized into one sample for each respective site to use for experiments. Controlled photolysis experiments were performed with $0.2 \text{ }\mu\text{m}$ filtered water, unfiltered water and $0.2 \text{ }\mu\text{m}$ filtered water plus added sediment using procedures described in Kaczynski and Kieber (1993). Sub-samples were apportioned into six 500 mL quartz flasks, whereas two aliquots were stored for analysis of initial concentrations of TDCu, Cu-complexing ligands, Cu(I), and DOC. Three quartz flasks were enclosed in black polyethylene bags to serve as dark controls. The three light flasks were placed in a constant temperature water bath (set at ambient estuarine temperature) and irradiated in sunlight for 9 hours using a Spectral EnergyTM solar simulator (1 kW Xe arc light source) with AM1 filter to remove wavelengths not found in the solar spectrum. At the end of the experimental period the 3 dark and 3 irradiated light flasks were filtered separately through Meissner Stylux $0.2 \text{ }\mu\text{m}$ polyethersulfone acid-

washed capsule filters at the end of the experiment and individually analyzed for TDCu, Cu-complexing ligands, Cu(I), and DOC to determine photochemically-induced changes in these analytes for triplicate samples.

Core Resuspension Experiments

A stainless steel box corer measuring approximately 0.25m² was used to collect undisturbed sediments aboard the ship. Unfiltered overlying water was collected with an air operated double-diaphragm plastic pump and Kynar tubing. The bottom water samples were stored in 50 L polyethylene carboys in the dark at *in situ* temperatures. Trace metal clean acrylic cores (14 cm diameter, 50-60 cm in length) were placed down in the sediments to extract sediment. The bottoms of the cores were internally sealed with polyethylene caps and externally sealed with a manually tightened rubber gasket to prevent water leakage. The cores were placed in a plastic box for transport to UNCW. Two cores were taken at each site and placed in an environmental chamber at ambient temperature. The cores were covered with a plastic lid equipped with a sampling port and bubbled gently with filtered air. Initial concentrations (T0) were taken from each core for DOC and TDCu. One core from each site was left undisturbed for 4 days. The other core from each site was intentionally mixed using a plastic plunger (13 cm diameter) once a day for 4 days. A final filtered sample on day 4 was taken from all cores for DOC and TDCu.

Analytical Techniques

Contamination control

To avoid contamination of samples, all apparatus used for trace metal analyses, including core tubes, bottles, filters, and sampling and analytical implements, were

rigorously acid-washed. All sample manipulations and analyses were performed under class 100 laminar flow hoods within a positive pressure clean room.

Metal speciation

To determine the speciation of dissolved Cu, electroanalytical methods were utilized. Electroanalytical methods provide estimations of the concentration of metal-complexing ligands, the conditional stability constants of the metal-ligand complexes, and the speciation of the metal; i.e., expressing the concentrations of organic complexes, inorganic complexes, and free hydrated ion (Ruzic, 1982; van den Berg, 1984; Donat et al., 1994).

The speciation of dissolved Cu was determined using competitive ligand equilibration-cathodic stripping voltammetry. This technique utilized a Bioanalytical Systems model CV50W potentiostat connected to a model CGME mercury drop electrode. The CSV-CLE method involved the establishment of a competitive equilibrium between Cu, the Cu-complexing ligands naturally present in the sample, and a competing organic ligand, 8-hydroxyquinoline (8HQ), added to the sample. The relatively strong competition provided by ligand, 8-hydroxyquinoline allows detection of Cu-complexing ligands strengths of K^{cond} ranging from $\sim 10^{12}$ to 10^{15} (Donat et al., 1994). This detection window was held as constant as possible during all Cu speciation determinations so that the concentrations and strengths of Cu-complexing ligands could be compared throughout the study (Shank, 2003). Sample aliquots (5 mL) were buffered with 1 M N-[2-hydroxyethyl]piperazine-N'-[2-ethane-sulfonic acid] (HEPES) at their ambient pH, then were spiked with incrementally increasing concentrations of Cu and allowed to establish a new equilibrium overnight. The Cu-8HQ complexes were

deposited at a hanging mercury drop electrode on the CGME, and then a negative-going potential scan was applied. The reduction current from the Cu bound to the added competing ligand 8HQ under the newly established equilibrium conditions was then measured (using square wave voltammetry) as a function of potential. Using Ruzic – van den Berg linearization procedures (e.g., van den Berg, 1982; Ruzic, 1982), the concentration and conditional stability constant of the Cu-complexing ligands was calculated.

Total dissolved Cu

Samples were UV irradiated with a 1.2 kW high pressure Hg-vapor lamp (Ace Glass) for 6 hours in Teflon beakers covered with inverted quartz beakers. Total dissolved copper in small sample volumes from the photolysis experiments were determined on acidified (1 μ L ultrapure HCl (Fisher Optima) per mL) sample aliquots (7 mL) using a CSV method (van den Berg 1986). Samples were buffered at their ambient pH with 5 M ultrapure QNH₄OH (Fisher Optima), 70 μ L 1 M HEPES, and 70 μ L of ~1003 μ M 8HQ. Samples were quantified by standard addition, using spikes of a ~20 nM Cu standard.

Cu(I)

Dissolved Cu(I) concentrations in estuarine samples exposed to photochemical/resuspension experiments were determined using the solvent extraction technique of Moffett and Zika (1988). This solvent extraction procedure utilized the Cu(I)-specific chelator 2,9-dimethyl-1,10-phenanthroline (dmp) in concert with the strong Cu(II) chelator ethylenediamine, which prevents artifactual formation of Cu(I)

during the extraction procedure. Cu(I)-dmp complexes were extracted into methylene chloride and back-extracted into a small volume of 5% HNO₃.

For each photochemical experiment, three 250-ml aliquots were filtered within 15 minutes of collection from irradiated samples and dark controls, through 0.2 μm and placed into fluorinated high-density polyethylene (FHDPE) bottles. The extraction procedure was identical to that described by Moffett and Zika, (1988) except that 250 mL aliquots were used and extracted into ~2 mL final volumes, resulting in preconcentration factors of ~125. Concentrations of Cu in the extracted samples were determined using graphite furnace atomic absorption spectrophotometry with a Perkin Elmer 5100 PC instrument equipped with a 5100 ZL Zeeman Furnace module and AS 70 autosampler and programmed with recommended conditions. Concentrations were calculated using standard additions (Kieber et al., 2003). Percent recovery of Cu(I) was not reported due to uncertain recovery during experiments. Copper (I) results are reported instead as Δ[Cu(I)], which assumes that the recovery is similar in all samples extracted.

Dissolved organic carbon

Dissolved organic carbon was determined on acidified water samples with a Shimadzu TOC 5000 carbon analyzer equipped with a ASI 5000 auto-sampler. This instrument was previously used in conjunction with an Equatorial Pacific Ocean DOC methods inter-comparison study and found to generate very low instrumental blanks (Sharp et al., 1993; Sharp et al., 1995). The collection and analysis of DOC samples employed the cleaning protocol used during the Joint Global Ocean Flux Study (JGOFS) Equatorial Pacific Ocean DOC methods comparison study (Sharp et al., 1993; Sharp et

al., 1995). Sample storage vials are cleaned prior to use by thoroughly rinsing with Milli-Q water and muffle at 550°C for two hours or more to remove organic material.

Percent organic and water loss

Sediments used for solar simulator experiments were analyzed for organic carbon and water loss. Drying dishes were muffled at 550°C, then kept in a desiccator to prevent water absorption. Triplicate samples were prepared with approximately 3 g of wet sediment per dish. The samples were put in an oven at 60°C overnight for water loss measurement. The samples were then muffled at 550°C to determine percentage mass loss, which is taken to represent the organic content of the sediment. These values were divided by the conversion factor of 1.7 to give %OC (ISO 10694 and BS7755, 1995).

Cu in sediments

Sediments were also measured for leachable Cu concentrations. Two aliquots of 1 g wet sediment from each seasonal collection were placed in 50 mL plastic centrifuge tubes, with 20 mL of 1 M ultrapure HCl (Fisher Optima) added and samples were gently shaken over night. The tubes were then centrifuged for 10 minutes, and 15 mL of the supernatant was withdrawn and placed in Teflon containers for analysis by graphite furnace AAS as described previously.

RESULTS AND DISCUSSION

Dissolved Organic Carbon (DOC)

Interactions between DOC, estuarine water, sediments and light

A series of controlled photolysis experiments were conducted in the Cape Fear River Estuary (CFRE) with and without added sediments in order to understand the role sediment resuspension plays in DOC cycling within the estuary. In 0.2 µm filtered CFRE

samples with no added sediment, the concentration of DOC decreased in all cases when samples were irradiated in the solar simulator for 9 hours (Figure 2). This decrease represents photochemical conversion of organic to dissolved inorganic carbon (equation 1).



This process has been observed in earlier studies reviewed by Mopper and Kieber (2002), who discussed the photooxidation of DOC and its conversion into CO₂ and CO. They concluded that the photodegradation of DOM is important to carbon cycling in the ocean. This degradation can occur by the production of volatile carbon species through a light mediated process, or by photochemical or biological oxidation of DOC to CO₂ (Mopper and Kieber, 2002). UV irradiation has been shown to mineralize DOC to DIC (Zepp 2002), and Mopper and Kieber (2002) showed that in the photic zone, photochemical production of CO₂ and CO is an important cycle for remineralisation of carbon. In filtered water samples with no added sediments that were placed in the dark, DOC concentrations were variable but not statistically different from initial concentrations in most cases.

When the same water samples as shown in Figure 2 were irradiated without prior filtration there was an increase in DOC during light exposure relative to the filtered samples with no ambient particles (Figure 3). In cases where there was a DOC loss upon irradiation in the presence of particles, it was always less than when no particles were present. This suggests ambient particles in the CFRE water are capable of releasing DOC upon exposure to sunlight and that DOC is being both destroyed via equation 1 and produced via equation 2.

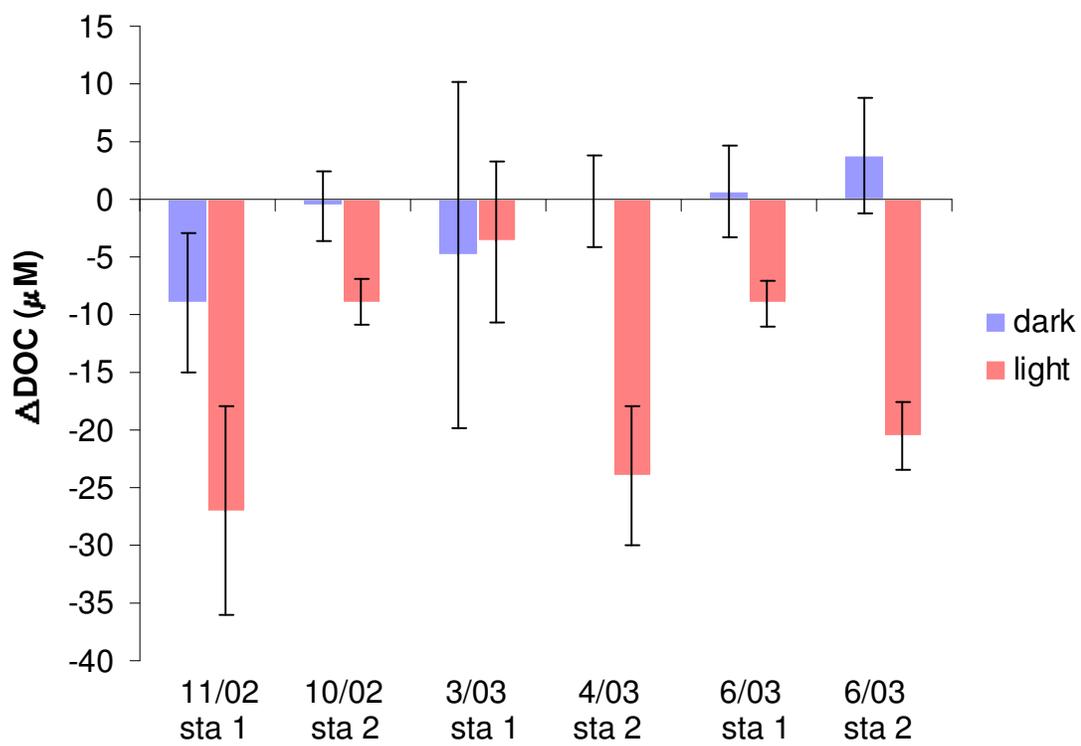


Figure 2. Change (Δ) in DOC concentrations (μM) for filtered ($0.2 \mu\text{m}$) triplicate CFRE water samples exposed to dark and simulated sunlight for 9 hours, relative to initial values for two sites.

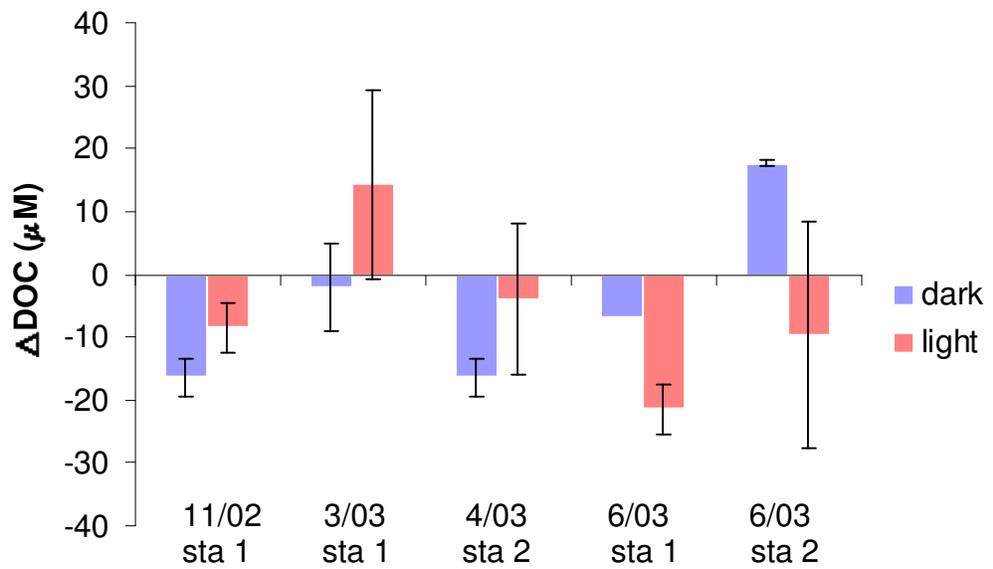
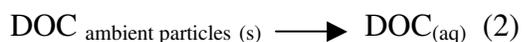


Figure 3. Change (Δ) in DOC concentrations (μM) for unfiltered triplicate CFRE water samples exposed to dark and simulated sunlight for 9 hours, relative to initial values for two sampling sites.



Koelmans et al. (2002) stated that DOC is capable of being produced by incomplete mineralisation of particulate organic matter, while at the same time being utilized by bacteria or photochemically degraded. Water samples that were unfiltered and left in the dark also had a decrease in DOC. Compared to filtered samples with no ambient particles (or bacteria), dark samples had a greater decrease in DOC when particles were present. The particles may be readsorbing the DOC (Koelmans et al., 2002) or the DOC may be being utilized by microbes. Avery et al. (2003) found that approximately 9% of DOC in the CFRE was degraded over a one week period, suggesting that the loss was attributable to a bioavailable fraction. Dissolved organic carbon decreases in this study were measured only over the 9-hour treatment. The amount of bioavailable DOC lost over this period was found to be approximately 1.4%, in agreement with previous studies which found bioavailable DOC to be between 1-30% in various rivers (Aminot et al., 1990; Coffin et al., 1993; Munster, 1993; Kroer, 1993; Sondergaard and Middelboe, 1995; Moran et al., 1999, 2000; Fukushima et al., 2001; Raymond and Bauer, 2001; Ogawa et al., 2001).

The impact of resuspended sediments on DOC release was evaluated by comparison of irradiated samples with sediment to the same filtered and unfiltered samples discussed above. Filtered water samples with added sediment showed significant increases in DOC release in the light exposed samples in all cases (Figure 4). Zepp (2002) stated that UV irradiation influences the decomposition of particulate organic carbon. The decomposition of particulate organic carbon and production of DOC occurs by a light mediated process (equation 3).

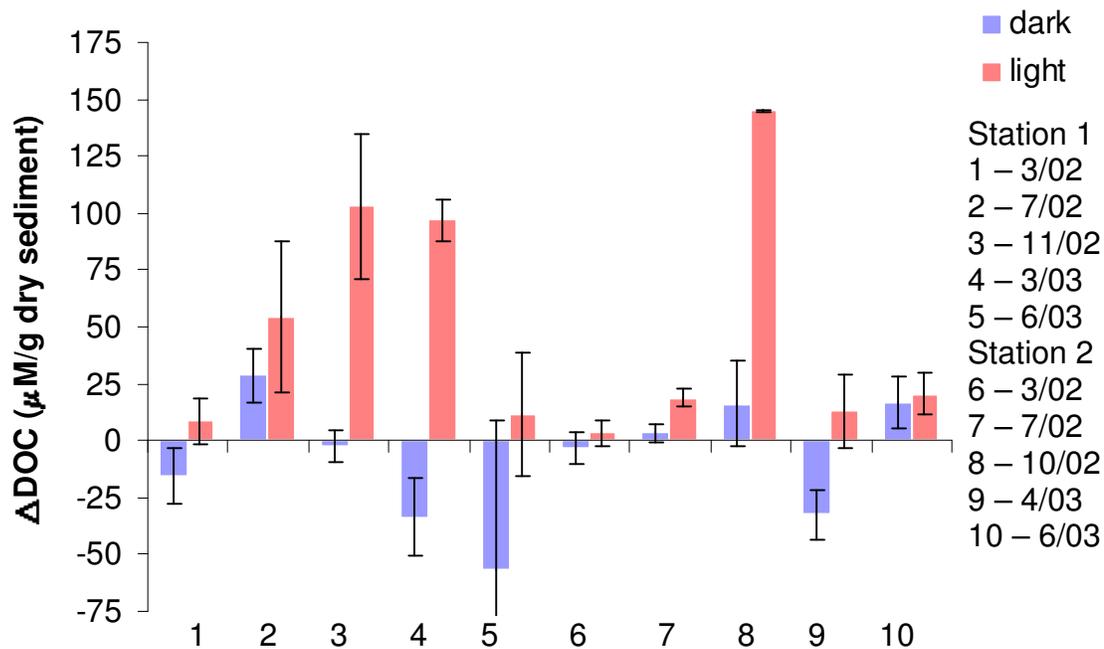


Figure 4. Change (Δ) in DOC concentrations ($\mu\text{M/g}$ dry sediment) for filtered ($0.2 \mu\text{m}$) triplicate CFRE water samples with added sediment (2 g wet sediment per L) exposed to dark and simulated sunlight for 9 hours from two sampling sites.



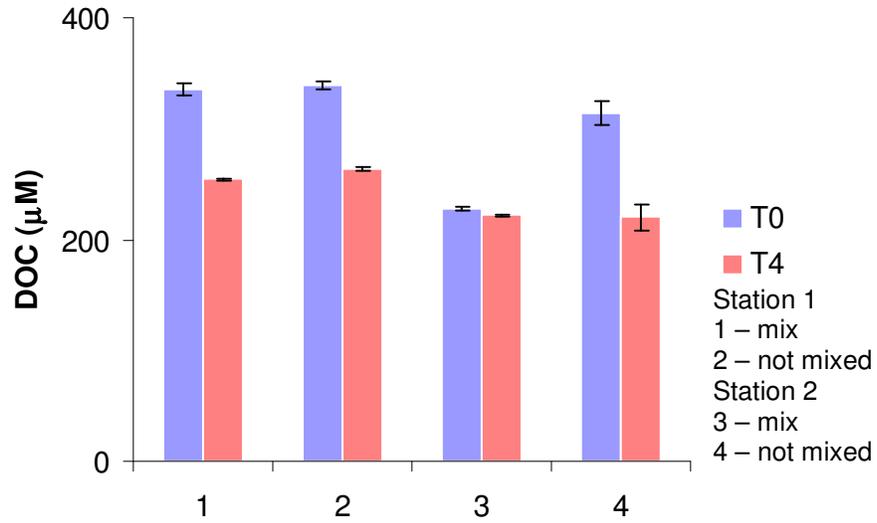
Dark controls were somewhat variable with loss of DOC in some cases and increases in others. Increases in the dark may result from some non-photochemical release of DOC from sediments, however it was always a much smaller change than in light exposed flasks. Koelmans and Prevo (2002) suggested that the disturbance of sediments plays an important role in DOC formation by particulate carbon bound to sediments being mobilized and desorbed. Koelmans and Prevo (2002) resuspended sediments at various ratios to a constant water volume from Lake Nieuwkoopse plassen and the Rhine River in the Netherlands. He removed benthic organisms from the soil before the experiments. He found the initial amount of particulate organic matter in the samples and noted the decrease in this concentration during resuspension while it was being converted to DOC. Koelmans and Prevo (2002) stated sediment resuspension could be faster than mineralisation in generating the decrease in POC, hence causing an increase in DOC. Komada and Reimers (2001) performed similar experiments using water and sediments from the Hudson River, Raritan-Lower New York Bay complex, and the Inner New York Bight. Komada and Reimers (2001) found that during a resuspension, organic carbon that was loosely bound to mineral surfaces was released. Their results showed that resuspension changed the organic carbon content in the mineral sorbed fraction of the sediment compared to the aqueous phase. Komada and Reimers (2001) stipulated that the more the particles are diluted in the water column, the greater the release of DOC could be, if POC is converted to DOC by desorption.

To further study DOC concentrations in dark controls, a series of core resuspension experiments were conducted to determine the effects of sediment

resuspensions on bottom waters. The control core contained undisturbed sediment and unfiltered overlying water. In the second core, the sediment was disturbed once per day for 4 days. Compared to initial concentrations, the majority of the cores that were disturbed had decreases in DOC concentrations after 4 days (figure 5a, b). The cores left undisturbed had DOC concentrations that remained close to initial concentrations. This is consistent with the data collected from the dark controls in the experiments with unfiltered water, and filtered water with sediment. In dark controls with unfiltered water, there was a decrease in DOC concentration after 9 hours, and in filtered water with sediment, the concentrations were variable with some DOC concentrations decreasing, while others showed a small increase.

Sediments from five sites along the CFRE were collected from stations M21 to M61, in order to test the significance of organic carbon gradients on DOC production from sediments (Table 1). In filtered water samples with added sediments exposed to light, there was an increase in DOC release compared to dark samples (Figure 6). The increase in DOC release became greater as the percent organic carbon in the sediments increased (Figure 7). A similar relationship was observed by Koelmans and Prevo (2002), whom found that the mass of organic carbon in the sediment determined the amount of organic carbon released by desorption. Koelmans and Prevo (2002) hypothesized that it was the sediment to water ratio that determined the organic carbon release, but he found this relationship to be non-linear. There was 60 times more organic carbon in the sediments in Lake Nieuwkoopse Plassen in the Netherlands than in the Rhine River, and when using equal sediment mass, there was a larger production of organic carbon (Koelmans and Prevo, 2002). Komada and Reimers (2001) found that the amount of

a. DOC for March 2003 core resuspension experiment



b. DOC for June 2003 core resuspension experiment

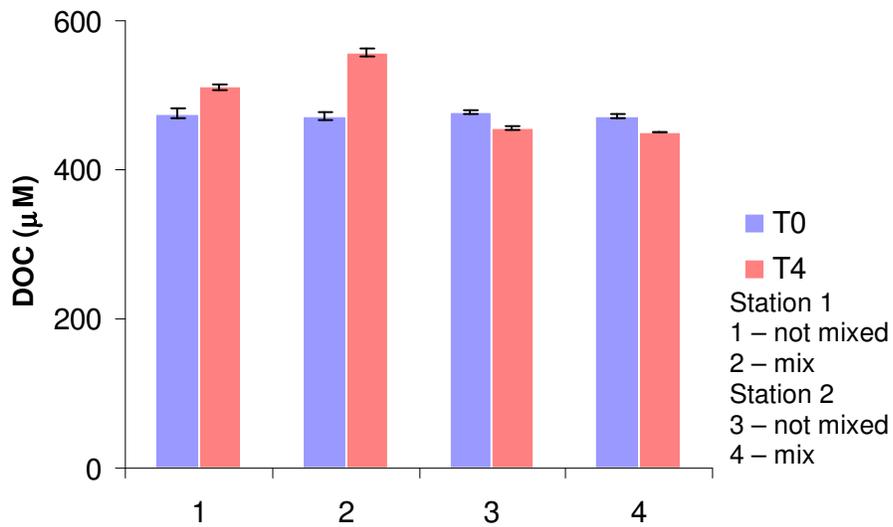


Figure 5. a. DOC concentration (μM) for unfiltered CFRE water in core experiment from March 2003 with disturbed and undisturbed sediments for initial values (T0), and values after 4 days (T4). b. DOC concentration (μM) for unfiltered CFRE water in core experiment from June 2003 with disturbed and undisturbed sediments for initial values (T0), and values after 4 days (T4).

Table 1. Results of resuspension experiments in the presence of sediments, and in the presence or absence of simulated solar radiation in triplicate samples from the CFRE. T0, D, L indicates average dissolved organic carbon (DOC) concentrations initially, in the dark control, and after irradiation for 9 hours, respectively. Change (Δ) in D and L are changes in dark and light concentrations, respectively, compared to T0 samples. Also shown are percent organic carbon in the sediment, and labile Cu concentrations (1 M HCl-leachable).

	DOC (μ M)			DOC (μ M/g dry sediment)		% Organic Carbon	nmol Cu/g dry sediment
	T0	D	L	Δ D	Δ L		
M21	388	397	432	10 \pm 9	45 \pm 11	1.3	2.7 \pm 0.04
M32	393	374	420	-35 \pm 36	51 \pm 9	3.5	13.1 \pm 1
M42	381	373	430	-14 \pm 4	83 \pm 7	2.8	14.9 \pm 1
M54	384	375	441	-18 \pm 6	111 \pm 52	3.8	15.8 \pm 3
M61	390	395	473	14 \pm 12	241 \pm 59	5.5	49.9 \pm 0

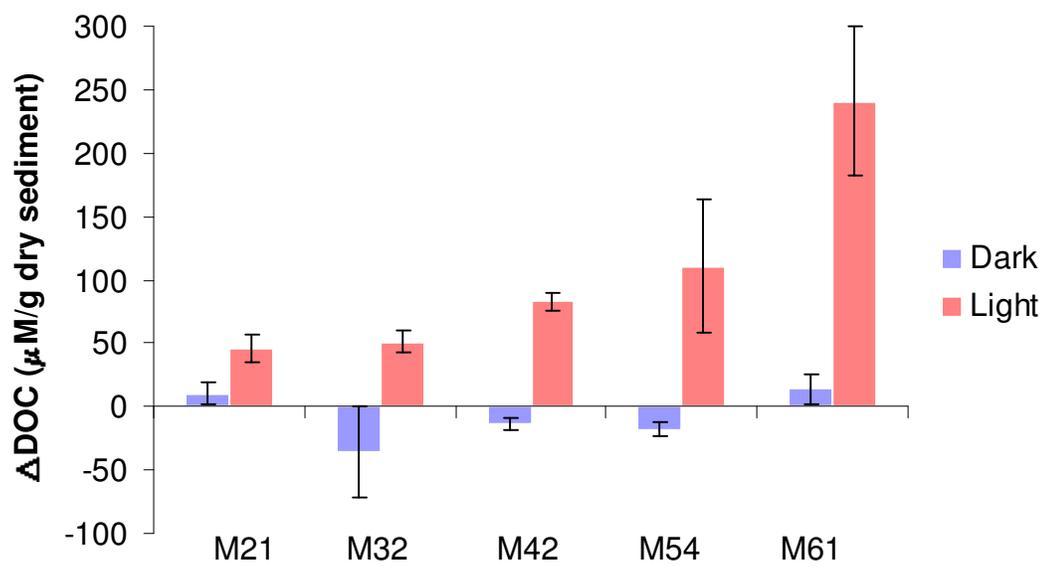


Figure 6. Change (Δ) in DOC concentrations ($\mu\text{M/g}$ dry sediment) for filtered ($0.2 \mu\text{m}$) triplicate CFRE water samples with added sediment (2 g wet sediment per L) in dark controls and irradiated samples after 9 hours with respect to initial values for various sites along the estuarine salinity gradient.

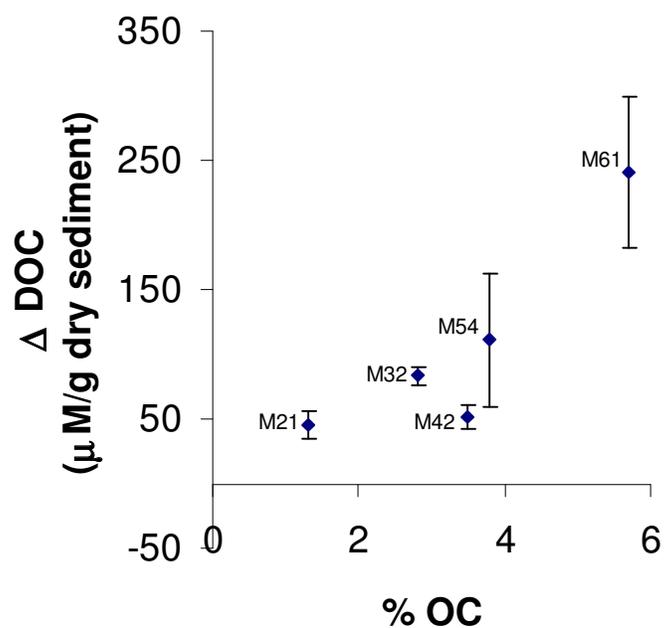


Figure 7. Change (Δ) in DOC concentrations ($\mu\text{M/g}$ dry sediment) after irradiation for 9 hours compared to initial concentrations in filtered ($0.2 \mu\text{m}$) triplicate CFRE water samples with added sediment (2 g wet sediment per L) versus percent (%) organic carbon (OC) content at various sampling sites.

DOC released was equal to the amount that was bound to minerals in the sediment.

Particulate organic carbon found in the high density fraction phase of the sediment was the best predictor of OC release (Komada and Reimers, 2001). Bulk POC and low density fractions were not good predictors, or showed no relationship (Komada and Reimers, 2001).

Role of PAR on release and uptake of DOC

To determine if the effects of full spectrum light varied from PAR, filtered water samples with added sediments were exposed to PAR only (Figure 8). On average, in the CFRE, PAR penetrates to 1.3 meters at M61 to 2.4 meters at M18 (Mallin et al., 2002). In contrast, penetration of UV light ($\lambda < 400$ nm) is less than 30 cm in the CFRE (Whitehead, unpublished data). Dissolved organic carbon concentrations still increased when exposed to PAR, although to a lesser extent than when exposed to full spectrum. Since PAR reaches a substantial depth in the estuary, resuspension events may cause significant increases of DOC in the water column.

Effects of photolysis on DOC

A photodegradation experiment was also conducted to compare concentrations of DOC in filtered water exposed to full spectrum and PAR. In samples exposed to full spectrum, there was a consistent decrease in DOC concentration throughout the experiment (Figure 9), as was seen in the 9 hour photolysis experiment with filtered water. When using PAR, samples showed a small decrease in concentration, but not to the extent observed with full spectrum light. Both PAR and full spectrum samples showed a decrease in DOC compared to samples left in the dark for the same time period.

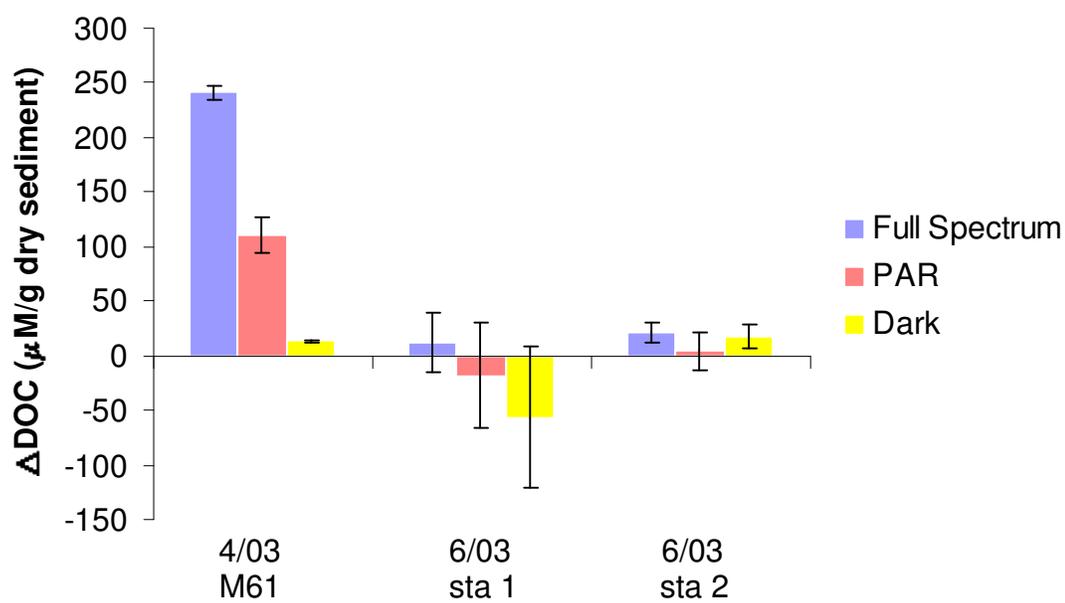


Figure 8. Change (Δ) in DOC concentrations (μM per gram dry sediment) from initial values to after irradiation for 9 hours with full spectrum light, PAR, and dark controls in filtered ($0.2 \mu\text{m}$) triplicate CFRE water samples with added sediments (2 g wet sediment per L) from three sites.

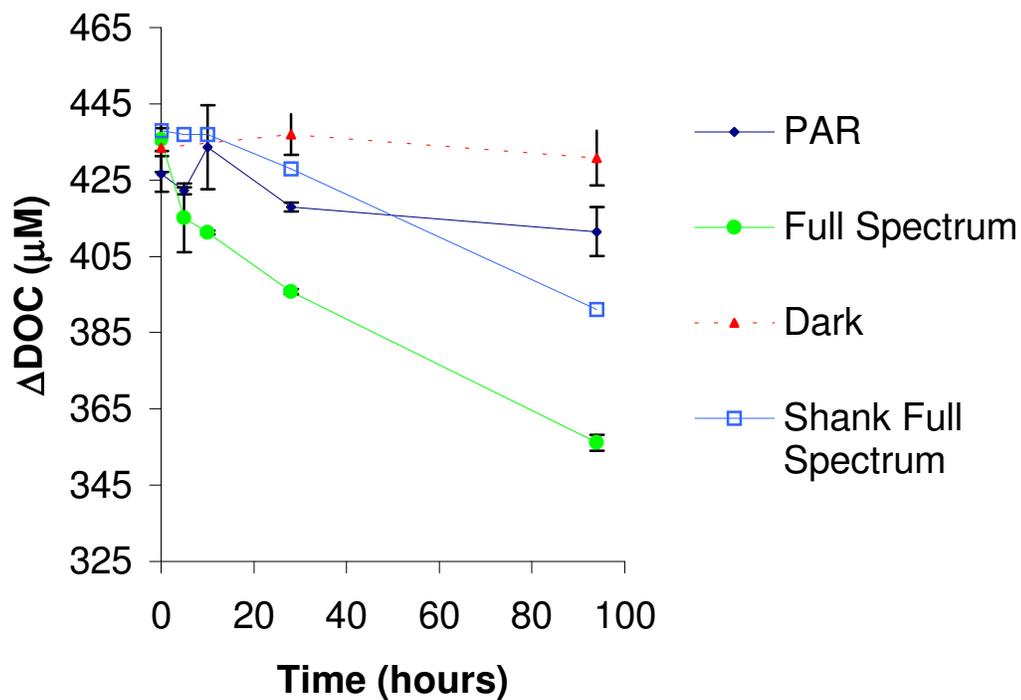


Figure 9. Photodegradation of DOC (μM) in hours for filtered ($0.2 \mu\text{m}$) triplicate CFRE water samples. Results are shown for PAR, full spectrum light, average dark controls from all experiments, and full spectrum light degradation experiment conducted by Shank (2003).

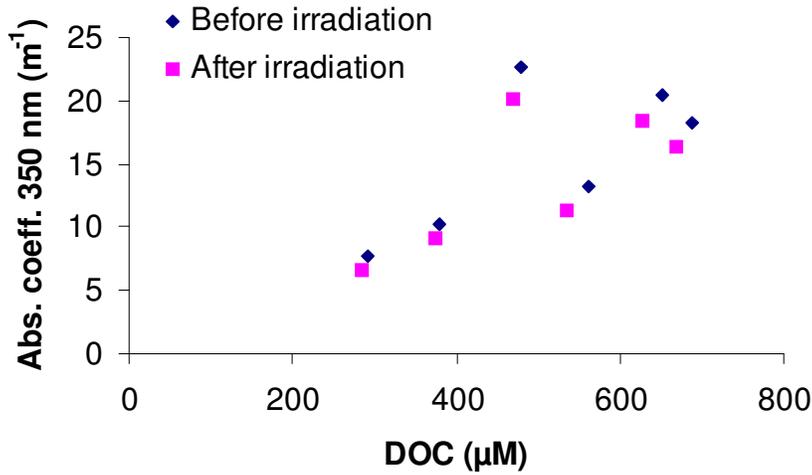
A strong relationship was found between the absorbance coefficient at 350 nm and DOC concentration (Figure 10a). Since any photochemical reaction must be initiated by the absorbance of a photon, the relationship between the loss of absorbance (photobleaching) and the consumption of DOC was investigated. The data presented in this research are scattered, but fit well with data presented by Whitehead (2000) for estuarine water samples with similar DOC concentrations and salinities from the St. Lawrence Estuary (Figure 10b). The combined data show that only ~35% of the loss of absorbance is due to complete degradation of DOC. In other words, more than half of all photodegradation may result in the production of non-absorbing DOC moieties rather than inorganic carbon. Alternatively, the same data may be interpreted to mean that only about one-third of the DOC (i.e. the chromophoric fraction) pool is photochemically active. Interestingly, a plot of the fractional loss of Cu ligands versus the fractional absorbance loss from Shank' s (2003) data yields a slope close to unity. This would suggest that all of the Cu ligands are both chromophoric and photochemically active.

Interactions Between Cu, Estuarine Water, Sediments, and Light

Total dissolved Cu uptake and release

A series of controlled photolysis experiments were conducted to examine possible uptake and release of dissolved Cu in filtered and unfiltered CFRE water and in filtered CFRE water with sediments. These experiments were conducted seasonally at two stations in the CFRE having different sediment types (station 1- sandy mud; station 2- muddy sand) and salinity regimes. There was no clear trend in increase or decrease of total dissolved Cu in either station 1 or 2 among the three types of treatments. Most changes in both light exposed and dark flasks were relatively small and variable with

a. Absorbance versus DOC



b. Fractional loss of DOC versus fractional loss of a_{CDOM}

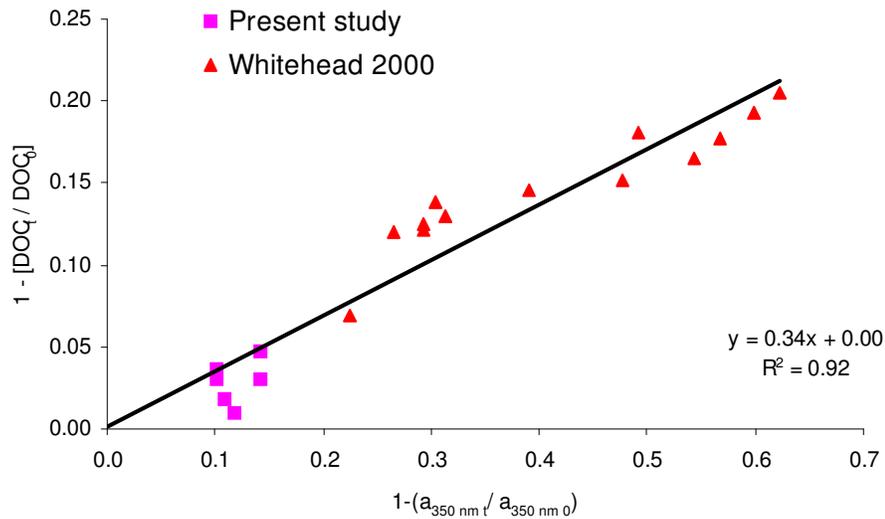


Figure 10. a. Absorbance coefficient (350 nm) versus DOC (μM) for filtered ($0.2\ \mu\text{m}$) triplicate CFRE water samples before and after irradiation for 9 hours. b. Fractional loss DOC versus the fractional loss of a_{CDOM} at 350 nm. Represents filtered ($0.2\ \mu\text{m}$) averaged triplicate CFRE water samples from station 1 and 2 exposed to simulated sunlight for 9 hours from the present study, and St. Lawrence River water samples exposed to simulated sunlight for longer exposure times. Results were corrected for initial values and dark controls.

respect to loss and gain of Cu (Table 2). There also did not appear to be any seasonal variability in the data. The small effect of solar irradiation in all treatments in CFRE was observed even in sediments containing widely varying concentrations of leachable Cu (3-20 nmol Cu/g dry sediment) and organic carbon (0.4-16.5%) (Table 3). Slightly more consistent releases of dissolved Cu upon photolysis occurred in the set of experiments using unfiltered waters (Table 4). In six of eight of these trials a small release of Cu was observed, suggesting that Cu associated with suspended material in the CFRE is potentially more reactive. This Cu is likely to be associated with organic matter (Davis, 1984; Herzl et al., 2003) and thus may be more easily released when a fraction of the organic matter is photolyzed. Alternatively, the Cu may be associated with Fe-Mn oxyhydroxides which may be reduced upon photolysis, leading to the release of Cu.

In addition to the relatively low-Cu containing sediments used in the photolysis experiments reported in Table 3, a second set of relatively more contaminated sediments from San Diego Bay (2300 nmol Cu/g dry sediment) were also photolyzed. Filtered (0.2 μm) water samples with sediments (2 g wet sediment per 1 L) added were resuspended; three aliquots were exposed to light and three were left in the dark. The light exposed sediment showed a very large increase in total Cu concentration relative to the dark control (Table 3). Similar photolysis experiments employing filtered CFRE water and sediments collected along the salinity gradient of the CFRE were conducted to include a greater range of sediment types than those presented in Table 3. In these experiments, the only significant release of Cu after photolysis occurred with sediments in the upstream estuarine station M61; the remaining stations gave small losses or gains similar to those discussed previously (Figure 11). Sediments at M61 contain a higher leachable Cu

Table 2. Results of resuspension experiments in the absence and presence of simulated solar radiation in samples from the CFRE. Triplicate water samples are filtered (0.2 μm) with no added sediments. T0, D, L indicate average total dissolved Cu concentrations, initially, in the dark control, and after irradiation for 9 hours, respectively. Change (Δ) in D and L are changes in dark and light concentrations, respectively, compared to T0 samples. Not applicable (N/A) indicates results not obtained.

Total Dissolved Cu (nM) Filtered No Sediment					
	T0	D	L	ΔD	ΔL
Station 1					
March-02	N/A				
July-02	N/A				
November-02	12.5	11.1	11.6	-1 ± 2	-0.9 ± 0.6
March-03	8.2	9.3	8.5	1 ± 0.9	0.3 ± 0.8
June-03	10.1	8.9	9.5	-1 ± 1	-0.5 ± 0.08
Station 2					
March-02	N/A				
July-02	N/A				
October-02	N/A				
April-03	27.2	13.7	11.4	-13 ± 3	-16 ± 0.6
June-03	8.3	10.3	8.9	2 ± 0.04	0.6 ± 0.8

Table 3. Results of resuspension experiments in the absence and presence of simulated solar radiation in samples from the CFRE and San Diego Bay. Triplicate water samples were filtered (0.2 μm) with added sediment (2 g wet sediment per L). T0, D, L indicate average total dissolved Cu concentrations initially, in dark controls, and after irradiation for 9 hours, respectively. Change (Δ) in dark and light concentrations, respectively, are compared to T0 samples. Also shown are labile Cu concentrations (1 M HCl-leachable) and percent organic carbon in sediments. Not applicable (N/A) refers to results not obtained.

Total Dissolved Cu (nM/g dry sediment)							
Filtered + Sediment							
	T0	D	L	ΔD	ΔL	nmol Cu/g dry sed	%OC
Station 1							
March-02	6.7	6.4	7.0	-0.4 ± 1	0.5 ± 2	N/A	1.5
July-02	7.7	8.5	8.6	1 ± 2	2 ± 4	N/A	3.5
November-02	19	10.9	13.4	-20 ± 1	-13 ± 6	20 ± 2	5.7
March-03	8.3	6.6	6.1	-6 ± 2	-1 ± 1	8 ± 0.4	4.9
June-03	6.3	8.2	7.3	5 ± 4	1 ± 0.4	10 ± 4	6.9
Station 2							
March-02	4.1	5.1	5.5	1 ± 1	2 ± 0.4	N/A	2.6
July-02	6.5	7.4	5.8	1 ± 5	-1 ± 2	N/A	0.43
October-02	5.0	5.2	11.6	0.4 ± 9	11 ± 4	3 ± 0.4	3.9
April-03	10.0	6.9	9.3	-3 ± 4	-4 ± 3	7 ± 1	4.5
June-03	9.0	7.8	10.6	-7 ± 4	2 ± 3	5 ± 0.1	16.6
San Diego Bay							
April-03	20.8	31.8	46.6	22 ± 5	47 ± 6	2271 ± 353	5.2

Table 4. Results of resuspension experiments in the absence and presence of simulated solar radiation in samples in the CFRE. Triplicate water samples were unfiltered with no added sediments. T0, D, L indicates average total dissolved concentrations initially, in the dark controls, and after irradiation for 9 hours, respectively. Change (Δ) in D and L are changes in dark and light concentrations, respectively, compared to T0 samples. Not applicable (N/A) refers to results that were not obtained.

Total Dissolved Cu (nM) Unfiltered No Sediment					
	T0	D	L	ΔD	ΔL
Station 1					
March-02	N/A				
July-02	7.4	6.5	8.1	-0.9 \pm 0	0.7 \pm 2
November-02	0.92	1.5	2.5	1 \pm 2	-0.5 \pm 2
March-03	12.6	7.9	9.9	-5 \pm 1	-3 \pm 1
June-03	6.1	9.2	10.0	3 \pm .02	4 \pm 0.9
Station 2					
March-02	N/A				
July-02	3.4	4.4	6.3	1 \pm 0	3 \pm 1
October-02	5.7	6.6	11.6	-0.4 \pm . 1	3 \pm 0.9
April-03	10.8	10.5	12.0	-0.3 \pm 0.7	1 \pm 0.09
June-03	8.7	10.3	10.1	2 \pm 0.3	1 \pm 0.3

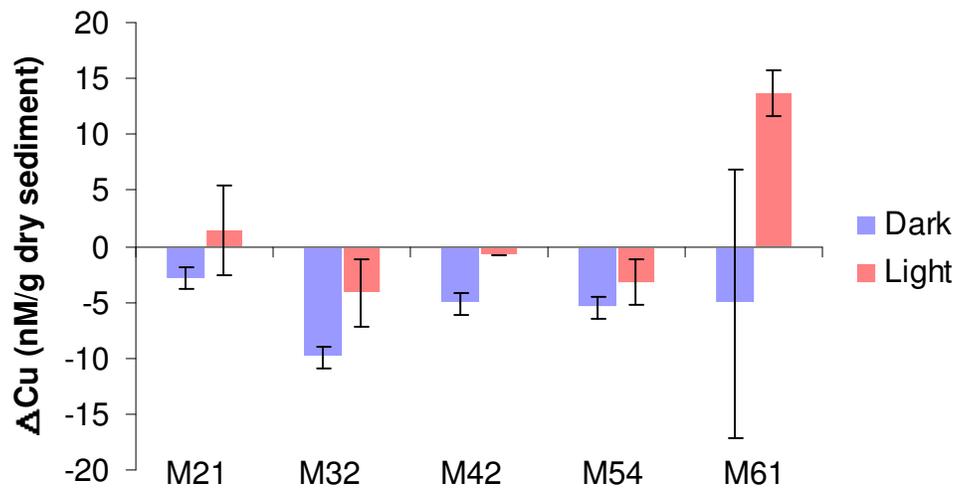


Figure 11. Change (Δ) from initial values to after 9 hours of Cu (nM per g dry sediment) for triplicate light exposed and dark controls of 0.2 μm filtered CFRE water with added sediment (2 g wet sediment/L) at stations in the CFRE along the estuarine salinity gradient.

concentration (50 nmol/g dry sediment) relative to station 1 and station 2 sediments (Table 5). Results of the photolysis experiments using the San Diego Bay and M61 sediments clearly indicate that photolytic release of Cu is only significant in sediments with relatively high Cu concentrations. The San Diego Bay sediments are known to be highly contaminated with Cu (Flegal and Sanudo-Wilhelmy, 1993) and the M61 site is adjacent to the Port of Wilmington and therefore subject to impacts from shipping activities.

In the CFRE transect, percent organic carbon was highly correlated to the amount of Cu in the sediments (Figure 12). This relationship is similar to that found by Turner et al. (2002), who also found acid-leachable Cu to be positively correlated to particulate organic carbon in sediments from the Mersey estuary, UK. Previous studies have also found that the amount of Cu found in riverine, estuarine and coastal sediments is associated with organic material (Gerringa, 1990; Shaw et al., 1990; Shulkin and Bogdanova, 2003). Although the total Cu concentration at M61 increased significantly after photolysis of resuspended sediments (Figure 11), other sediments with relatively low Cu concentrations showed little or no change upon exposure to light even though their percent organic carbon consistently increased towards M61. Dark controls all decreased suggesting a net uptake of Cu by these sediments along this gradient. Herzl et al. (2001) found similar results in the Tamar estuary in the U.K. for dark sediment resuspensions. In that work, after five hours of resuspension, total dissolved Cu concentrations decreased by 50% due to adsorption of Cu onto particles (Herzl et al., 2001). The present study found that after 9 hours, total Cu concentrations decreased by an average of 41%. The release at M61 should be viewed therefore as a minimum

Table 5. Results of resuspension experiments in the absence and presence of simulated solar radiation in samples from stations in the CFRE. Triplicate water samples were filtered (0.2 μm) with added sediments (2 g wet sediment per L). T0, D, L indicate average total dissolved Cu concentrations initially, in the dark control, and after irradiation for 9 hours, respectively. Change (Δ) in D and L are changes in dark and light concentrations, respectively, compared to T0 samples. Also shown are percent organic carbon in the sediments and labile Cu concentrations (1 M HCl-leachable).

	Total dissolved Cu (nM/g dry sediment) Filtered + Sediment					% Organic Carbon	nmol Cu/g dry sediment
	T0	D	L	ΔD	ΔL		
M21	6.6	4.1	8.0	-3 ± 1	1 ± 4	1.3	2.7 ± 0.04
M32	7.8	2.5	5.6	-10 ± 1	-4 ± 3	3.5	13.1 ± 1
M42	6.8	3.7	6.3	-5 ± 1	-0.8 ± 0	2.8	14.9 ± 1
M54	7.9	5.0	6.3	-5 ± 1	-3 ± 2	3.8	15.8 ± 3
M61	9.2	7.6	13.9	-5 ± 12	14 ± 2	5.5	49.9 ± 0

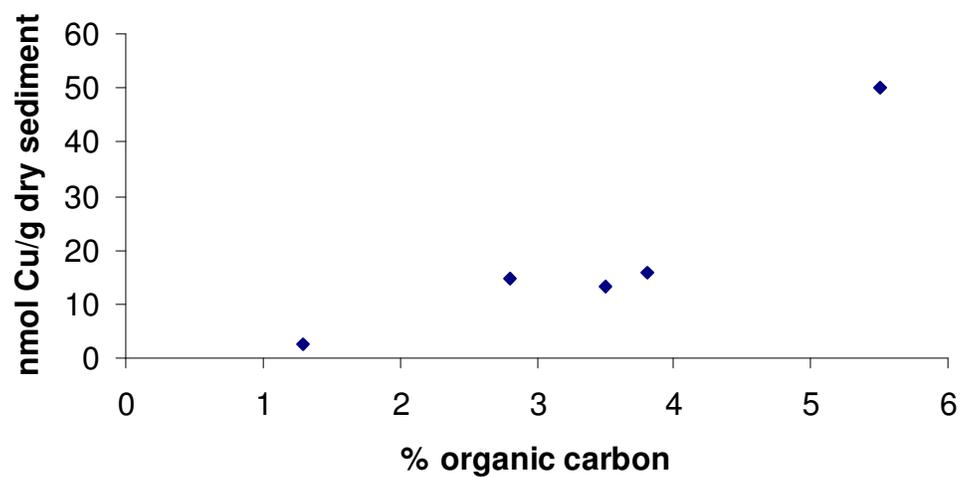


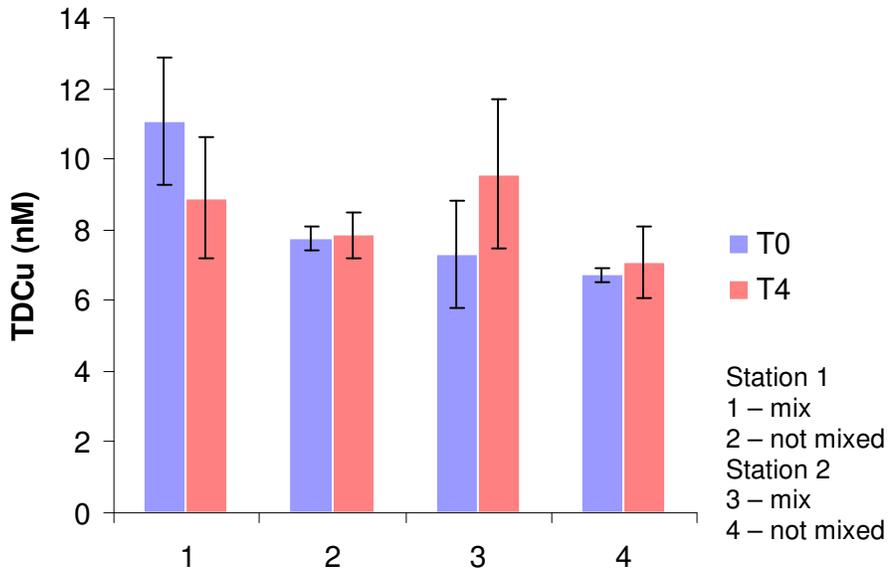
Figure 12. Percent organic carbon from triplicate dry sediment samples vs. Cu (nmol per gram dry sediment) for sampling sites M23, M35, M42, M54 & M61, respectively, in the CFRE in April 2003.

production value as some Cu may also have been taken up by the sediment. In contrast, Shulkin and Bogdanova (2003) found that riverine sediments that contained elevated amounts of Cu and organic matter resulted in greater release of dissolved Cu in resuspension experiments. To further support this conclusion, a series of core resuspension experiments were conducted to determine the effects of sediment resuspension on bottom waters. One core was left undisturbed, while a second core was disturbed everyday for 4 days. Total Cu concentrations again varied among the experiments with no clear trends (Figure 13a, b). These results suggest that in the relatively uncontaminated sediments of station 1 and 2, there is little effect of sediment resuspension either in the dark or light on total copper. The results presented in Table 3 and Table 5 suggest that high Cu containing sediments at anthropogenically impacted locations will release Cu when they are resuspended and irradiated whereas relatively uncontaminated sediments will either remove Cu from the water column or have no effect.

Role of PAR on total dissolved Cu release and uptake

To study the relative effects of full spectrum sunlight and PAR on Cu release and uptake in the estuary, a set of experiments were conducted with water and resuspended sediments (Figure 14). In the CFRE, PAR penetrates from 1.3 meters at M61 to 2.4 meters at M18 (Mallin et al., 2002). In two out of the three experiments, PAR photolysis caused Cu concentration increases that were the same or less than full spectrum photolysis, while the dark decreased in both. Although full spectrum sunlight is effective at releasing Cu from sediments and suspended particles in estuaries, UV penetrates to only a relatively shallow depth (<30 nm) (Whitehead, unpublished data). Releases by

a. TDCu for March 2003 core resuspension experiment



b. TDCu for June 2003 core resuspension experiment

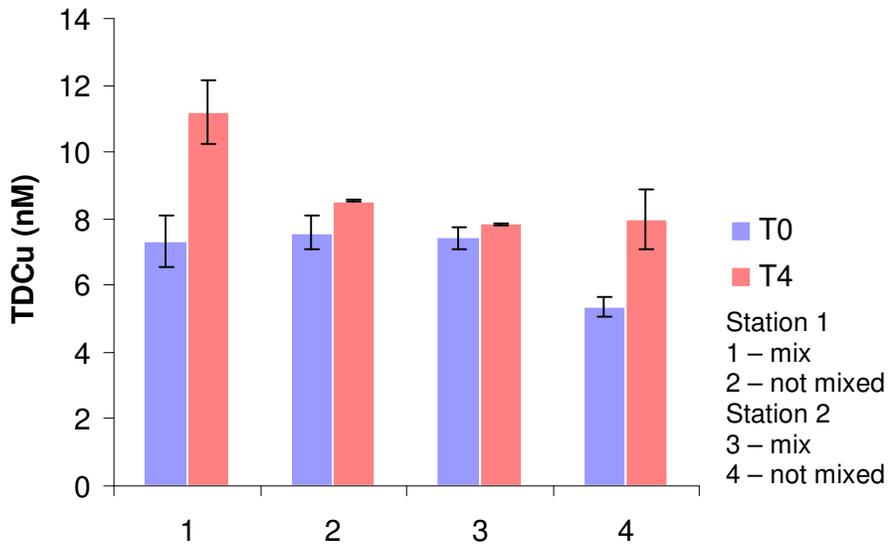


Figure 13. a. TDCu concentration (nM) for unfiltered CFRE water in core experiment from March 2003 with disturbed and undisturbed sediments for initial values (T0), and values after 4 days (T4). b. TDCu concentration (nM) for unfiltered CFRE water in core experiment from June 2003 with disturbed and undisturbed sediments for initial values (T0), and values after 4 days (T4).

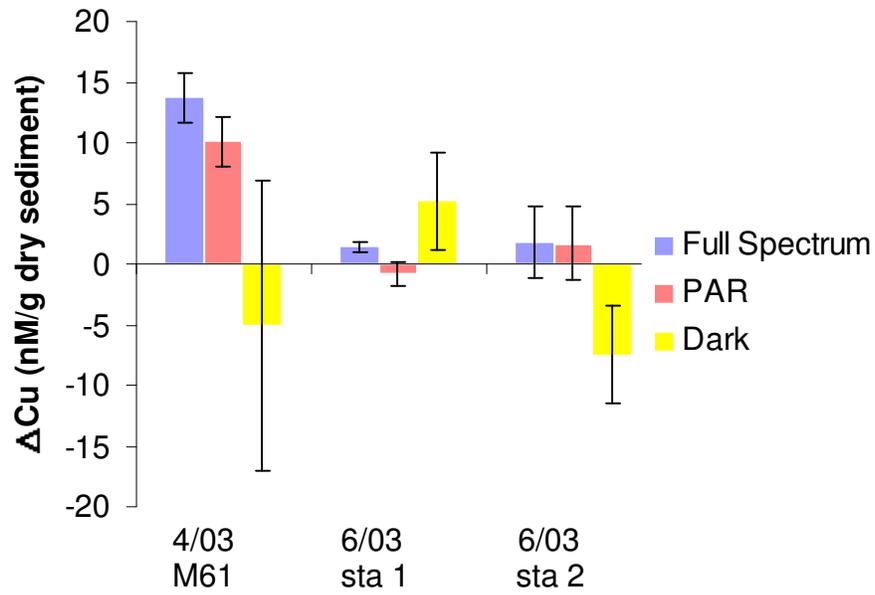


Figure 14. Change (Δ) in total Cu concentrations (nM per gram dry sediment) from initial values of triplicate samples of filtered (0.2 μ m) CFRE water with added sediments from three sites exposed for 9 hours to full spectrum, PAR, and dark controls.

PAR, however, may occur up to 2 m deep in the water column, even in darkly colored waters such as those of the CFRE.

Cu redox behavior

Copper (I) extractions were completed on samples collected for the three types of photochemical experiments to determine the effect of sediment resuspension and photolysis on Cu redox speciation. Samples that were 0.2 μm filtered with no sediment added had large increases in Cu(I) concentrations in all cases when exposed to simulated sunlight (Figure 15). Dark samples increased as well in most cases although to a lesser extent than irradiated samples. This suggests that Cu(I) is produced photochemically in CFRE water (equation 3). Earlier studies have suggested that Cu(I) can be reduced from



Cu(II) photochemically or biologically (Moffett and Zika, 1988). Copper (II) may also be reduced in redox reactive complexes by photochemical means (Moffett and Zika, 1988). Microbially-mediated reduction of Cu(II) could explain the increase in dark samples. Various compounds such as thiols are also known to reduce Cu(II) to Cu(I) (Leal and van den Berg, 1998). Thiols have been detected in sediment porewaters (Shea and MacCrehan, 1998) and estuarine waters (Tang et al., 2000), and may explain how Cu(I) may be formed non-photochemically.

Unfiltered samples with no sediments were also irradiated in order to determine the impact of ambient particles on Cu(I) photoproduction. Light exposed samples had an increase in Cu(I) compared to initial values (Figure 16). Dark samples also showed an increase but never as great as in the light. The magnitude of the increase in light exposed samples was always equal to or less than in filtered samples. In some cases (11/02) there

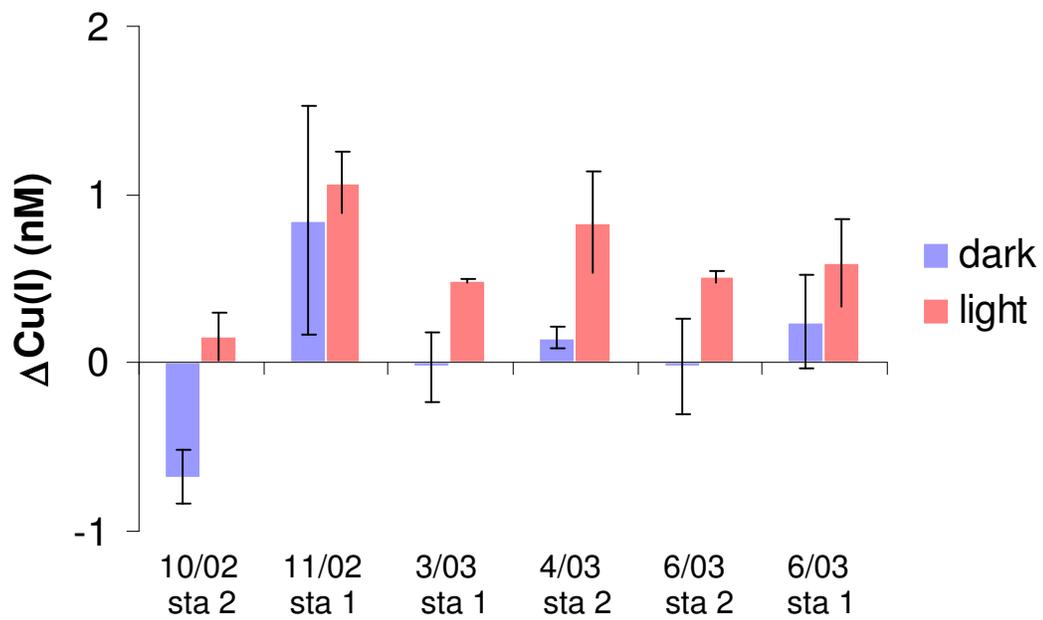


Figure 15. Change (Δ) in Cu(I) concentration (nM) for dark controls and irradiated samples after 9 hours compared to initial values, for filtered (0.2 μm) CFRE water triplicate samples from two sites.

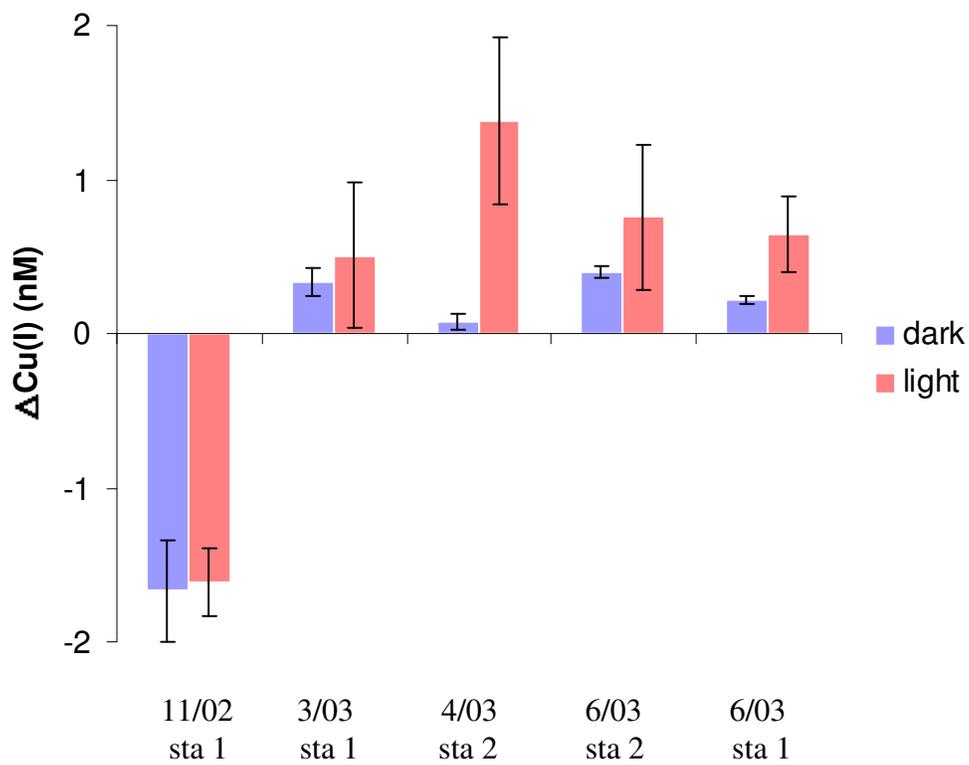


Figure 16. Change (Δ) in Cu(I) concentration (nM) for dark controls and irradiated samples after 9 hours compared to initial values, for unfiltered CFRE water triplicate samples from two sites.

was a significant decrease in Cu(I) compared to filtered samples. These results suggest that ambient particles either have no impact on Cu(I) production or cause a net uptake/oxidation of Cu(I). Kieber et al. (1992) performed a similar photolysis study on chromium, using filtered and unfiltered water exposed to dark and sunlight for one hour. In samples that were filtered, there was no apparent change in chromium concentration comparing before and after photolysis. In samples that were left unfiltered, chromium was reduced during photolysis indicating that particles play a role in chromium speciation during light exposure (Kieber et al., 1992). These results indicate that different transition metals are controlled by unique redox speciation, and there must be another component that effects Cu(I) concentrations in the CFRE.

Filtered water samples with 2 g wet sediment per L were also irradiated in order to evaluate the role of sediments in the redox speciation of Cu (Figure 17). Samples with added sediments showed increases in light exposed samples. As was the case with unfiltered samples, increases in the light were equal to or smaller than in filtered water suggesting that sediments were not a significant source of Cu(I). In five of the seven dark samples there were significant decreases in Cu(I). This indicated that sediments, as was suggested for ambient particles, may be a net sink of Cu(I) in estuarine waters either through absorption or increased oxidation.

Effects of photolysis on strong Cu-complexing ligands

Strong Cu binding ligands in the CFRE have been found to be extremely photoreactive. Shank (2003) conducted various degradation experiments using natural sunlight and simulated sunlight and noted significant degradation of strong (L1-type) Cu-complexing ligands in all cases. Two degradation experiments were conducted with

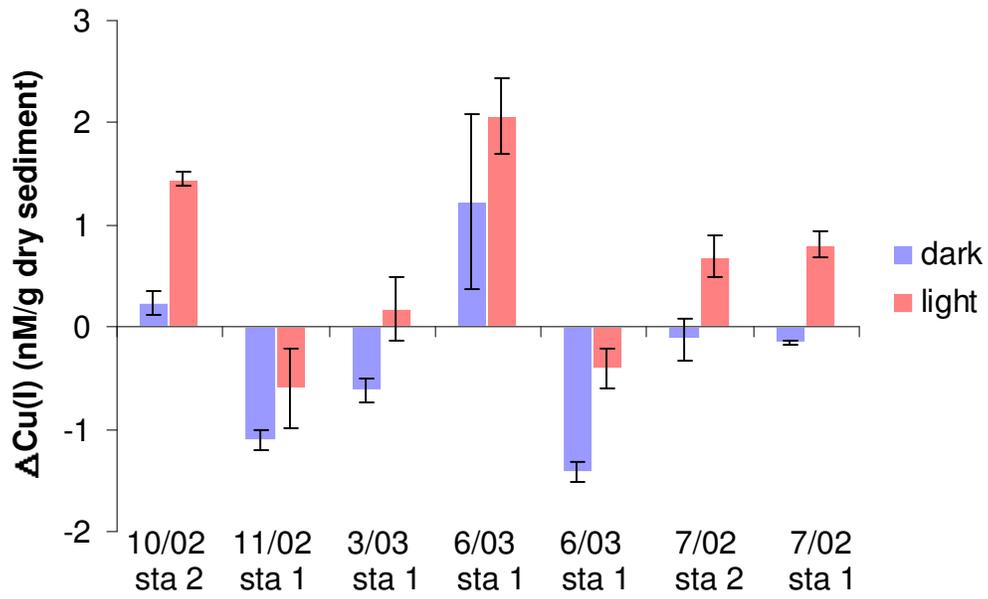


Figure 17. Change (Δ) in Cu(I) concentration (nM/g dry sediment) for dark controls and irradiated samples after 9 hours compared to initial values, for filtered (0.2 μm) CFRE water triplicate samples with added sediments (2 g wet sediment per L) from two sites.

0.2 μm filtered water (salinity ~ 20) exposed to simulated sunlight for four days (Figure 18). One experiment was conducted under full spectrum light equivalent to the procedure in Shank (2003) whereas the second was conducted using PAR only. The experiment using full spectrum showed a decrease of Cu ligand from 55 nM to 10 nM in samples exposed to light throughout the four days. Dark controls also showed degradation but not to the extent of those exposed to light. Shank (2003) found ligand concentrations decreasing from 106 nM to 5 nM over the 4 days of his experiment. Samples exposed to PAR also showed ligand degradation from 50 nM to 19 nM. These results demonstrate that PAR alone is almost as effective as full spectrum light in degrading Cu-complexing ligands. This is particularly important in highly absorbing coastal waters where UV penetration is limited to very shallow depths.

SUMMARY AND CONCLUSIONS

DOC concentrations decreased upon irradiation in filtered water with no added sediment, indicating that organic carbon is being converted to inorganic carbon by a light mediated process. Dark control concentrations decreased as well although losses were probably not statistically significant. Estuarine samples containing ambient particles showed an increase in DOC concentrations after irradiation relative to filtered samples with no ambient particles. This reveals that suspended particles in the water column are capable of producing DOC upon exposure to simulated sunlight. Filtered estuarine samples resuspended with sediment usually showed a significant DOC release after irradiation compared to dark controls. The DOC release from samples containing sediments was directly related to the percent organic carbon found in the sediment. When comparing DOC degradation releases from PAR and UVA/UVB irradiation of filtered

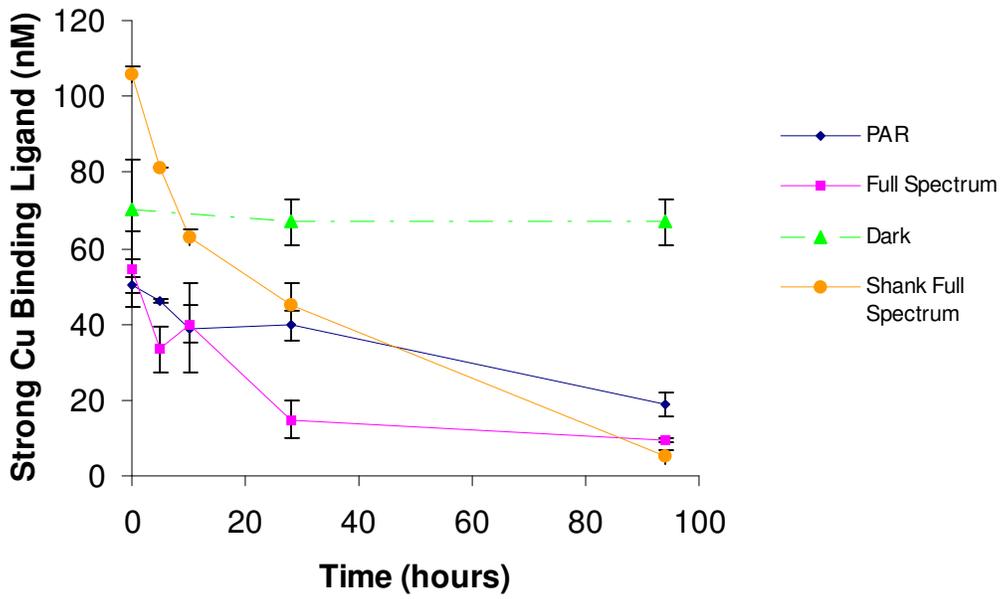


Figure 18. Photodegradation of strong Cu binding ligands (nM) in hours. Filtered (0.2 μm) CFRE water was used. Photodegradation measured for PAR, full spectrum light, average dark controls from all experiments, and full spectrum light degradation experiment conducted by Shank (2003).

estuarine water with no sediment, it was found that DOC concentration decreases from PAR were less than those from full spectrum irradiation, therefore UVA/UVB light is the most effective for DOC degradation. In organic rich sediment suspensions from the CFRE, PAR was a little less than half as effective as full spectrum sunlight in producing DOC from particles. However, since PAR penetrates much more deeply into the water column than does UVA/UVB light, PAR photolysis may be a significant mechanism for DOC production even in darkly colored coastal and estuarine waters. Photolytic production and destruction of DOC in such waters may be an important part of the global carbon cycle because DOC can be degraded to dissolved inorganic carbon, a fraction of which is CO₂.

In relatively uncontaminated environments (with respect to Cu) there was little or no effect of irradiation or resuspended sediments on TDCu. In sediments with elevated Cu concentrations, however, there was a significant increase in TDCu after irradiation with added sediments. Therefore, the impact of sediment resuspensions on TDCu is dependent on the amount of Cu in the sediments. If the contaminated sediments in impacted harbors and estuaries are distributed into the water column, Cu concentrations can increase as a result of sediment-light interactions. Copper(I) concentrations increased in filtered irradiated samples. There was little impact of ambient particles or sediment on Cu(I) concentrations, which suggested the production of reduced Cu from other dissolved Cu species. The effects of full spectrum and PAR irradiation were also determined for strong Cu binding ligands. In full spectrum irradiation, ligand concentrations decreased by a factor of 5.5 over a 4 day period in filtered estuarine samples, whereas after PAR irradiation, ligand concentrations decreased by a factor of 5 over the same period. These

results indicated that PAR is almost as effective as full spectrum sunlight in the degradation of Cu ligands. This is important considering UVA/UVB reaches up to 2.4 cm in the CFRE whereas PAR can reach up to ~2 m. In the open oceans PAR can reach a few hundred meters, suggesting that PAR photolysis is important in the cycling of strong Cu complexing ligands in open ocean waters.

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