

Photochemistry of Cu complexed with chromophoric dissolved organic matter: implications for Cu speciation in rainwater

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Abstract Significant quenching of fluorescence by Cu in rainwater samples from southeastern North Carolina demonstrates that chromophoric dissolved organic matter (CDOM) is an effective ligand for Cu in rainwater. A strong inverse correlation between the decrease in fluorescence upon Cu addition and CDOM abundance suggests the presence of excess binding sites for Cu in high CDOM samples. Electroanalytical studies indicate that CDOM extracted from C₁₈ cartridges formed Cu complexes with concentrations and conditional stability constants similar to ligands found in ambient rainwater. When authentic rainwater samples were photolyzed with simulated sunlight both photoproduction and photodestruction of ligands were observed, suggesting the photochemical response of Cu-complexing ligands in rainwater is the result of two competing reactions. The rate of CDOM photobleaching was directly related to changes in strong ligands ($K_{CuL} \sim 10^{15}$) whereas weaker ligands ($K_{CuL} < 10^{13}$) were not correlated, suggesting the photolabile CDOM resides in the strong ligand class. A photolysis study comparing filtered and unfiltered rainwater samples indicated that Cu-complexing ligands adsorbed onto or otherwise associated with particles are photodegraded much more rapidly than dissolved ligands. Photolysis with UV radiation appears to be most effective at engendering changes in Cu ligands, however a significant photochemical response was also observed when samples were exposed to photosynthetically active radiation with wavelengths greater than 400 nm. Results from this study demonstrate that complexation of Cu by CDOM has important ramifications for controlling both the speciation of the metal and the reactivity of CDOM in rainwater.

Keywords Atmosphere · Chromophoric dissolved organic matter · Copper · Metals · Photochemistry · Precipitation · Speciation

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1 Introduction

Copper is present in rainwater at concentrations of 10^{-8} – 10^{-9} M (Arimoto et al. 1985; Church et al. 1984; Kieber et al. 2004) and has been implicated in a number of important atmospheric reactions including the oxidation of SO_2 , and cycling of OH, H_2O_2 and O_2^- (Graedel et al. 1986; Matthijssen et al. 1995; Sedlak and Hoigne 1993; Weschler et al. 1986). Copper also plays an important role in the speciation of other trace metals in the troposphere including iron and chromium (Graedel et al. 1985; Losno 1999; Matthijssen et al. 1995). Chemical modelling suggests the redox chemistry of copper will differ in urban, remote and marine rains, and that copper may influence the pH of the atmosphere via its reduction by HO_2 (Herrmann et al. 2000). The few studies which have described the chemical speciation of Cu in terrestrial and marine rainwater indicate that a variable fraction of dissolved Cu is complexed with strong organic ligands possessing conditional stability constants of 10^9 – 10^{14} (Nimmo and Fones 1997; Spokes et al. 1996; Witt and Jickells 2005; Witt et al. 2007). In each of these studies, when ligand concentrations exceeded those of total dissolved Cu (TDCu), very low levels (10^{-11} – 10^{-13} M) of free hydrated Cu^{2+} could be maintained. However, in samples having Cu concentrations that exceeded ligand levels, some portion of Cu must have existed in weaker complexes with proportionally larger free ion concentrations. The fraction of free hydrated Cu ion is particularly significant because this fraction is the most bioavailable form of Cu in surface waters (Sunda and Guillard 1976) and is likely to have the greatest catalytic abilities in atmospheric reactions (Weschler et al. 1986).

The nature and composition of Cu-complexing ligands in rainwater remain poorly understood, reflecting the relatively uncharacterized nature of the larger pool of dissolved organic carbon (DOC) in rainwater (Likens et al. 1983; Seitzinger et al. 2003; Willey et al. 2000). Spokes et al. (1996) suggest that Cu-complexing ligands determined in rainwater over a semi-urban site in the United Kingdom originated primarily from soil organic matter. Recent results from our laboratory have demonstrated that rainwater from a coastal site in southeastern North Carolina (USA) showed consistently higher levels of both Cu and strong Cu-complexing ligands in events originating from continental trajectories compared to marine or mixed pathways, suggesting a terrestrial and/or anthropogenic sources of the ligands (Witt et al. 2007). Decayed biological material, smoke and soot may also be potential terrestrial sources of Cu complexing ligands (Mukai and Ambe 1986) as they contain a variety of functional groups and moieties known to be effective for binding metals, including free and bound phenolic OH groups, quinine structures, amino acids, amino sugars, peptides and aliphatic compounds (Stevenson 1982). Humic-like material has also been identified in the atmosphere in aerosol, rain and fog water samples (Krivacsy et al. 2000; Likens et al. 1983; Mukai and Ambe 1986). Humic acids are capable of forming strong complexes with Cu of a similar strength to those seen in rain water and have been proposed as a potential ligand source (Astrom and Corin 2000; Wang et al. 1999; Witt and Jickells 2005). Recent work in our laboratory has demonstrated the presence of chromophoric dissolved organic matter (CDOM) in rain which is fluorescent and displays humic-like properties. Based on results from this and earlier studies, the first goal of the present manuscript is to explore the possibility that CDOM is an effective Cu-complexing ligand in rainwater.

Kieber et al. (2004) demonstrated that ~25% of the total dissolved Cu in coastal rainwater from southeastern North Carolina consists of Cu(I) and that conversions between Cu(II) and Cu(I) can be driven by photochemical processes. Since the electrochemical techniques used to determine Cu speciation cannot distinguish between complexation of Cu (I) and Cu(II) (Leal and Van den Berg 1998), it is likely some portion of Cu(I) is also organically complexed. Processes that affect ligand concentrations can have critical effects

on Cu speciation with resulting impacts on atmospheric reactions involving Cu(I) and Cu(II). For example, photoproduction of Cu(I) from Cu(II)/dicarboxylate complexes in model solutions has been observed by Wu et al. (2000) who have proposed that this is an important source of Cu(I) in surface seawater. Previous studies in surface waters have demonstrated that photochemical processes have significant impacts on Cu speciation, including degradation of Cu-complexing ligands (Croot et al. 1999; Laglera and Van den Berg 2006; Shank et al. 2006). Conversely, the extent of complexation of Cu can alter photochemically-induced processes such as photobleaching of CDOM (Brinkmann et al. 2003) and consumption reactions of photoproduced radicals such as O_2^- (Voelker et al. 2000). Therefore, the second goal of this study is to explore the role of photochemical processes in altering the ligands which strongly complex Cu.

2 Methods

2.1 Sample collection and storage

Rain samples were collected on an event basis at the University of North Carolina Wilmington (UNCW) between July 2003 and August 2005. The UNCW rain collection site (34°13.9'N, 77°52.7'W) is located ~8.5 km from the Atlantic Ocean and situated in a large open area of ~1 ha within a turkey oak, long leaf pine, and wire grass community typical of inland coastal areas in southeastern North Carolina. The collection site is located close to the laboratory enabling analyses to be carried out within minutes of sample collection.

Samples were collected using Aerochem Metrics model 301 automatic sensing wet/dry precipitation collectors. The collectors were equipped with a polyethylene funnel connected by FEP-Teflon-lined Tygon tubing to a 2 l FEP-Teflon bottle extensively cleaned using trace metal clean procedures (Kieber et al. 2001; Tramontano et al. 1987). Measurements of pH were made immediately after collection. Samples for TDCu and speciation analyses were filtered using an acid washed Millipore filtration system with 0.2 μm membrane filters (Supor®) in a laminar flow clean hood and stored refrigerated in fluorinated high-density polyethylene (FLPE) bottles.

Samples were divided according to season and storm origin for data analysis. Storm origin was determined by air mass back trajectory for the rain event calculated using the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model accessed via NOAA Air Resources Laboratory READY (Real-time Environmental Applications and Display System) website (Draxler and Rolph 2003). Paths of air masses were calculated at 10, 500 and 1,000 m above ground level starting at Wilmington and were modelled for 5 days prior to the storm event. These heights were chosen to represent the surface level and as approximations of the upper limits of the marine boundary layer by night and day respectively (Wayne 1999). Rain events were assigned based on this air mass back trajectories as terrestrial, marine, or mixed.

2.2 Electrochemical studies of Cu complexation

Copper speciation was measured using adsorptive cathodic stripping voltammetry (ACSV) using a Bioanalytical Systems model CV50W potentiostat connected to a model CGME controlled growth mercury electrode stand operated in the hanging mercury drop electrode (HMDE) mode and equipped with a Ag/AgCl reference electrode and a Pt counter electrode. The ACSV measurements were carried out with salicylaldoxime (SA) as the

competing ligand (Campos and Van den Berg 1994). This method allows determination of the concentration of Cu-complexing ligands and the conditional equilibrium constant for the Cu-ligand complex (K'_{CuL}). From these quantities, concentrations of inorganically complexed and free hydrated Cu^{2+} ion can be estimated. Sample volume requirements for these titrations are large (~60 ml per titration) relative to amounts collected in most rainstorms, limiting the number of samples and replicates that could be analysed. Copper speciation measured in rain samples did not appear to be influenced by the amount of time between collection and analysis. Results of titrations carried out immediately after samples were collected and those carried out after several weeks of storage did not show differences which were larger than the uncertainty in the measurements.

A solution of 1.0 M HEPES (N-(2-hydroxyethyl) piperazine-N'-2-ethane-sulphonic acid; Calbiochem, Ultrol grade) in 0.5 M high-purity ammonium (BDH Aristar) was used for the pH ~7.8 buffer. This pH was chosen because the voltammetric sensitivity for $\text{Cu}(\text{SA})_2$ is greatest at this value (Campos and Van den Berg 1994). Previous studies have found that the complexation of copper in rainwater is unaffected by pH between about 3.8 and 7.8, suggesting titrations carried out at pH 7.8 are still relevant to rain conditions (Witt and Jickells 2005). Stock solutions of 0.01 M SA (Acros Organics) in ultrapure 0.1 M HCl (Fisher Optima) were prepared every 8 weeks and stored in a refrigerator. Buffer solution was added to rain in a HDPE bottle to yield a final buffer concentration of 0.01 M HEPES. An appropriate concentration of SA was added in different titrations to investigate a range of detection windows or competition levels, expressed as values of $\log \alpha_{\text{Cu}(\text{SA})_2}$ (where $\alpha_{\text{Cu}(\text{SA})_2} = [\text{Cu}(\text{SA})_2] / [\text{Cu}^{2+}]$). The side reaction of the SA with other species in the rain was determined by calculating $\log K_{\text{CuSA}}$ and $\log \beta_{\text{Cu}(\text{SA})_2}$ using equations of Campos and van den Berg (1994) for a salinity of 0.005 M [$\log K_{\text{CuSA}} = 10.12 - 0.37 \times \log(\text{salinity})$]; $\log \beta_{\text{Cu}(\text{SA})_2} = 15.78 - 0.53 \times \log(\text{salinity})$]. Incrementally increasing volumes of Cu were added to aliquots of buffered sample and allowed to equilibrate overnight (>12 h) in closed FEP Teflon bottles. All titration series were prepared in duplicate. Solutions of Cu were prepared from a commercial 1,000 mg L^{-1} reference standard ($\text{Cu}(\text{NO}_3)_2$; Fisher or EMD). All reagents were prepared and all analyses carried out within a laminar flow clean hood located in a clean room. High-purity water used for preparation of all analytical solutions was supplied by a Milli-Q (MQ) deionized water system (>18 $\text{M}\Omega \text{ cm}^{-1}$; Millipore Corp.)

The contents of each bottle were transferred to a Teflon electrochemical cell for analysis following equilibration. Samples were stirred and deoxygenated with humidified ultrapure N_2 for 3 min prior to the initial analysis to reduce background oxygen levels. Deposition of the Cu-SA complex onto a size 13 Hg drop (approximate surface area 0.03 cm^2) was performed while stirring at -0.15 V for 30 s. Stirring was then stopped for an equilibration period of 10 s at the initial scan potential of -0.15 V . The scan was then carried out from -0.15 to -0.5 V using a square waveform at a frequency of 25 Hz, a scan increment of 2 mV and a pulse height of 20 mV. The current peak height for the $\text{Cu}(\text{SA})_2$ complex was then recorded. Data for each titration were linearised with a Scatchard transformation to yield the ligand concentration and conditional stability constant (Bruland et al. 2000; Scatchard 1949).

2.3 Total dissolved Cu

Filtered rain was UV oxidized for 6 h using a 1.2 kW mercury arc lamp to destroy organic matter (Spokes et al. 1996; Yokoi et al. 1995) prior to TDCu determinations. A 5 ml aliquot of sample was then placed in a Teflon electrochemical cell and buffered to pH 7.8 with HEPES and SA to a final concentration of 80 μM . This sample was analysed by ASCV as above, except a deposition potential of -1.1 V was used to ensure full dissociation of any

remaining Cu-natural ligand complexes. The concentration of Cu in the sample was determined by standard additions. Concentrations of Cu in field blanks were of a similar magnitude to the uncertainty in the Cu measurement itself and it was thus not necessary to correct subsequent measurements.

2.4 Hydrophobic DOM extraction

Hydrophobic dissolved organic matter was extracted using C₁₈ Sep-Pak cartridges (Waters) by the method described by Kieber et al. (2006). Cartridges were preconditioned by washing with 10 ml acetonitrile (HPLC grade) followed by 10 ml MQ water. Rain samples (500 ml) were then loaded onto the column followed by a 10 ml MQ wash to remove residual salts before bound constituents were eluted with 5 ml acetonitrile. Samples were eluted into a preweighed 25 ml muffled round-bottom flask and concentrated to dryness under reduced pressure. The flask was reweighed, ~25 ml of UV-irradiated rain was added, and the mixture was sonicated for 1 h. An aliquot of this solution was added to UV-irradiated rain to a final concentration of 1 ± 0.1 mg of extracted material l⁻¹. The efficiency of extraction was assessed by comparing retention of fluorescence and absorbance levels and indicated that 80% of these optical properties were retained following extraction.

Changes in Cu concentration following extraction on C₁₈ columns were also determined. After precleaning columns as described above, 5 ml of rain were passed through the column and discarded. This was followed by an additional 25 ml of sample slowly injected onto the column and collected as it eluted into an acid-cleaned FEP-Teflon container. A second 25 ml portion was placed directly into a Teflon container and the Cu pre-concentrated to 5 ml by gently heating on a hot plate within a laminar flow clean hood. Concentrated rain samples were then analysed by graphite furnace absorption spectroscopy with quantification by the method of standard additions to determine the Cu concentrations before and after exposure to the separation procedure. To investigate the blanks involved, this method was carried out with Milli-Q in place of a rain sample. The concentration of copper did not change significantly following passage through the column and this data was thus not blank corrected.

2.5 Excitation emission matrix spectroscopy

Major fluorescence regions that are present in rainwater excitation-emission matrices (EEMs) have been designated by letters to describe their likely origins (Coble 1996; Kieber et al. 2006). Advances have been made in linking CDOM fluorescence with source and seasonal patterns of samples through use of principal component analysis (Boehme et al. 2004; Stedmon and Markager 2005), although the exact chemical compositions remain unknown. Four peaks will be used to describe CDOM based on integration regions described for rainwater elsewhere (Kieber et al. 2006). Peak A is common to most aquatic environments containing dissolved humic-like substances and is believed to denote CDOM that is relatively less aromatic in nature (Coble 1996). The C peak is characteristic of terrestrially derived humic-like substances possessing relatively more aromaticity whereas the M peak is characteristic of marine derived humic material and the T peak has been used to indicate the presence of protein-like substances (Coble 1996).

Samples for optical analysis were filtered under low vacuum through 0.2 μm, acid-washed Gelman Supor® polysulfonone filters enclosed in a glass filtration apparatus. Samples were stored in acid-washed, pre-combusted amber glass vials with Teflon coated lids at 4°C in the dark. Samples were brought to room temperature before analysis and were compared to filtered (0.2 μm) MQ water. Highly absorbing samples were diluted with MQ

water to the point where the absorbance reading at 300 nm (A_{300} , 1 cm pathlength) was ≤ 0.02 to minimize inner filtering effects. Excitation-emission matrix (EEM) fluorescence properties were determined on a Jobin Yvon SPEX Fluoromax-3 scanning fluorometer equipped with a 150 W Xe arc lamp and a R928P detector. Although higher resolution is possible, EEMs were generally constructed by concatenating emission spectra measured every 4 nm from 250 to 550 nm using excitation wavelengths from 250 to 500 nm at 4 nm intervals (Del Castillo et al. 1999). The instrument is configured to collect the signal in ratio mode with dark offset using 5 nm bandpasses on both the excitation and emission monochromators. Scans are corrected for instrument configuration using factory supplied correction factors (Coble et al. 1993). Post-processing of scans is performed using FLToolbox 1.91 (Wade Sheldon, University of Georgia) developed for MATLAB®. The software eliminates Rayleigh and Raman scattering peaks by excising portions (± 10 – 15 nm FW) of each scan centred on the respective scatter peak. The excised data is replaced using three-dimensional interpolation of the remaining data according to the Delaunay triangulation method and constraining the interpolation so that all nonexcised data are retained. Following removal of scatter peaks, data were normalized to a daily-determined water Raman intensity (275 nm excitation, 303 nm emission, 5 nm bandpasses) and converted to Raman-normalized quinine sulfate equivalents (QSE) in ppb (Coble et al. 1998). Replicate scans generally agreed within 5% in terms of intensity and within bandpass resolution in terms of peak location.

2.6 Photolysis experiments

Photolysis experiments were performed in acid-washed 250 ml FEP-Teflon bottles. FEP generally transmits a high portion of natural sunlight. A 1 mm film transmits over 90% up to about an angle of incidence of about 45° and over 92% at normal incidence is transmitted though 8 mm FEP film (DuPont 1996). A Spectral Energy Corp. solar simulator (LH 153 lamp housing, 1 kW Xe arc lamp, LPS 256 SM power supply) equipped with an AM1 filter to remove wavelengths not found in the solar spectrum was used as a light source. The spectral quality and intensity of the solar simulator is very similar to that of midsummer, noon-time solar irradiance for 34°N latitude (Kieber et al. 2006). It is likely the light received by the rain samples in the bottles is less than it would receive in the atmosphere as there may be some light attenuation through the depth of the bottle and a lack of reflectance off the inside of water droplets which would increase light inside the droplet. However this technique offers the best approximation of radiation possible with minimum contamination of samples. A constant flow temperature bath surrounded light-exposed cells in order to maintain constant temperature during irradiation. Photochemical experiments were run at the approximate temperature of rain at the time of collection, (20 – 25°C). Dark controls were kept at the same temperature as irradiated samples. Light measurements were made with an Ocean Optics SD2000 spectrometer connected to a fibre optic cable terminated with a CC-UV cosine collector. The system was calibrated with a NIST-traceable tungsten lamp and data was collected with OOIrrad software. Selected experiments were conducted with only photosynthetically active radiation (PAR) where a filter was used to cut off wavelengths below 400 nm.

2.7 Cu addition studies

Samples of rainwater were spiked to a final concentration of 50 nM Cu(II) by addition of 250 μl of a secondary Cu(II) stock (20 μM ; pH=3) to 100 ml of a 0.2 μm filtered,

unbuffered rainwater sample. There was no measurable change in pH of samples after Cu addition indicating any changes observed were not due to differences in hydrogen ion concentrations. Samples were allowed to equilibrate for 1 h after the Cu spike. The fluorescence of Cu spiked samples was then compared to analogous unspiked samples in order to determine the impact of Cu(II) on rainwater fluorescence. Agreement between replicate EEM's measurements was within 5% or better in terms of intensity and within bandpass resolution in terms of peak location (Kieber et al. 2006).

2.8 Supporting data

Measurements of pH were made using a Ross electrode with low ionic strength buffers. Dissolved organic carbon (DOC) was analysed using a Shimadzu 5000 TOC analyser as described in previous rain studies in our laboratory (Willey et al. 2000).

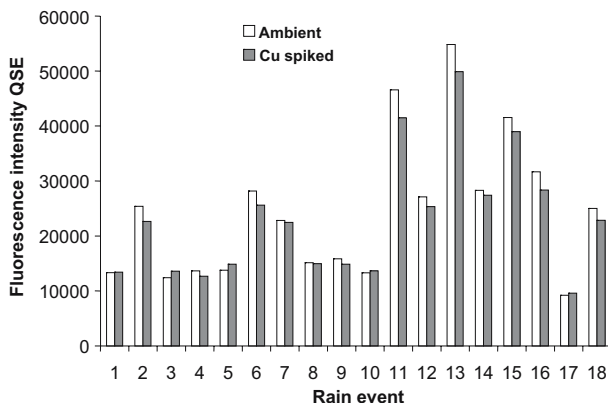
3 Results and discussion

3.1 Cu complexation with CDOM

One of the most important uncertainties regarding Cu speciation in atmospheric waters is the nature and chemical characteristics of the Cu-complexing ligands. Earlier studies have suggested that CDOM in rainwater is an effective metal ligand, especially for trace metals such as Fe (Kieber et al. 2005). CDOM has also been linked to Cu complexation in previous studies of fresh and seawater through studies of fluorescence (Berger et al. 1984; Ryan and Weber 1982) One of the primary goals of the present research was to determine if CDOM could also be an effective chelator of Cu in rainwater. The abundance of CDOM in this study was quantified by integration of the four major fluorescence peaks in the EEMs of CDOM in rainwater (Kieber et al. 2006). Comparison of the integrated fluorescence before and after addition of Cu allows for a determination of the complexing capacity of CDOM for Cu in precipitation. It should be noted that in addition to copper binding to CDOM there may be additional complexation with other non fluorescing organic material in the rain.

The total integrated fluorescence of 18 rainwater samples was measured before and after addition of 50 nM Cu(II) (Fig. 1). Fluorescence offers a greater sensitivity for the low DOC concentrations in rain water than would be achieved with absorbance. The presence of Cu

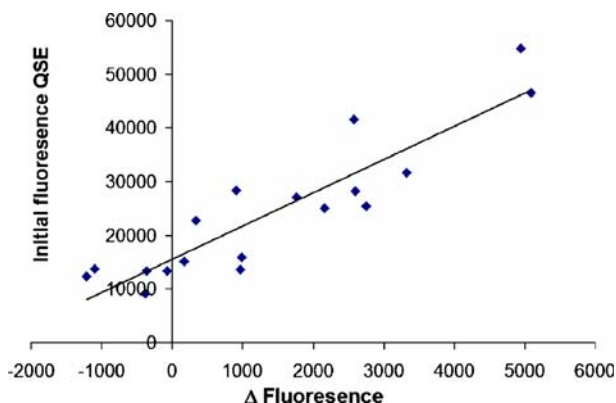
Fig. 1 Total integrated fluorescence intensity of rainwater before and after addition of a 50 nM Cu(II) spike in 18 different rain events. EEMS were constructed by concatenating emission spectra measured every 4 nm from 250 to 550 nm using excitation wavelengths from 250 to 500 nm (4 nm intervals) (Del Castillo et al. 1999)



(II) decreased or quenched fluorescence relative to rainwater with no added Cu in the majority of samples. The quenching of fluorescence indicates that the added inorganic Cu (II) is capable of complexing with excess CDOM ligand sites in rainwater. This quenching is similar to results observed for addition of Cu(II) to river water in southeastern North Carolina (Willey 1984). Fluorescence quenching of organic matter by added Cu(II) is a well known phenomenon in surface waters. The quenching technique was used by Ventry et al. (1991) in the determination of equilibrium parameters for Cu(II) complexation by fulvic materials extracted from soils and streams and by Boussemart et al. (1989) to examine Cu complexation in porewaters of marine sediments. Midorikawa and Tanoue (1998) used fluorescence quenching of Cu(II) to demonstrate that two ligand classes with different stability constants occurred in oceanic water. In a more recent study Plaza et al. (2005) also found addition of Cu(II) to highly chromophoric samples of humic acids extracted from soils decreased their fluorescence intensities. The similarity in quenching of fluorescence by added Cu(II) observed in atmospheric and surface waters suggests that complexation of Cu with CDOM may occur by analogous mechanisms.

Closer inspection of the data presented in Fig. 1 reveals that the degree to which fluorescence is quenched depends to some extent on the initial abundance of CDOM in the sample. Ambient Cu present in rainwater (volume weighted average concentration ca. 5 nM) may have already occupied all CDOM binding sites in low fluorescence samples prior to Cu addition resulting in no available binding sites for the added Cu. The change in fluorescence upon addition of Cu was examined as a function of initial fluorescence in order to explore this possibility further (Fig. 2). There was a strong correlation (Pearson Product Moment Correlation: $p=0.000002$, $n=19$, $r=-0.861$) between the decrease in fluorescence upon Cu addition and initial fluorescence of samples. This indicates that complexation of Cu(II) with CDOM is related to the abundance of CDOM present in the sample. This is most likely because of increasing binding sites available for Cu in high CDOM samples, although the presence of other metals will also exert an influence as these compete for the metal binding sites of CDOM and this should also be considered when interpreting these results. When the abundance of CDOM is significantly smaller, most binding sites may already be occupied therefore added Cu does not quench CDOM fluorescence. The increase in fluorescence in the lowest initial fluorescence samples in Figs. 1 and 2 upon Cu addition may result if Cu (II) was displacing a more effective fluorescence quenching species present in CDOM. The Cu(II) in this instance would act as a fluorescence quenching metal but if it were less effective relative to the species it replaced

Fig. 2 Change in total integrated fluorescence of CDOM upon addition of a 50 nM Cu(II) spike as a function of initial total integrated CDOM fluorescence



this would be seen as an enhancement of fluorescence upon Cu addition. A similar scenario was used to explain the fluorescence enhancement of seawater magnesium during estuarine mixing where replacement of a fluorescence quenching species in natural organic matter by magnesium resulted in fluorescence enhancement as the quenching effect of the other species was removed (Willey 1984). The data presented in Figs. 1 and 2 suggests that CDOM is an effective ligand for dissolved Cu in rainwater. This conclusion is consistent with the results of Shank et al. (2004) who also demonstrated that CDOM (in the form of C_{18} -extractable substances) was a very effective, and in some cases dominates the strong ligand class in estuarine waters in southeastern North Carolina.

Additional experiments were performed with CDOM extracted from rainwater to determine the binding capabilities of CDOM relative to ligands determined experimentally in ambient rainwater. CDOM was extracted from two rain samples by C_{18} solid phase cartridges (Kieber et al. 2006). Extracted material was then mixed with a UV-irradiated rain sample (final concentration $\sim 1 \text{ mg l}^{-1}$) and an electroanalytical titration carried out at $\log \alpha_{\text{Cu}(\text{SA})_2} = 6.0(2.5 \mu\text{M SA})$. Prior to extraction, Scatchard plots suggested the presence of two strong ligand classes in both rains from which CDOM originated (Table 1). These are likely part of a continuum of copper ligands of various binding strengths present in the rain. Also, the uncertainties of the conditional stability constants are large enough so that there may not be a significant difference between the pairs of ligand strengths detected. Conditional stability constants of the ligands observed at the detection window chosen were between 10^{13} and 10^{15} . In rain samples, extracted material formed strong organic complexes with Cu of a similar binding strength to those observed in the original rain sample. The detection of strong ligand complexes between C_{18} -extractable CDOM and Cu in combination with the data presented in Figs. 1 and 2 provides strong evidence that CDOM is an effective Cu ligand in rainwater.

A small volume of rain (30 ml) was passed through an additional C_{18} cartridge and the TDCu concentration measured before and after exposure to the column (Table 1). The changes observed in the Cu concentration were small in comparison to the uncertainties,

Table 1 Titrations of organic material extracted with C_{18} Sep-Pak columns and corresponding rain events

	[Cu]	[L] ₁	Log K_{CuL_1}	[L] ₂	Log K_{CuL_2}	CDOM A peak	CDOM total
E589	29±1.3	38.2±8.4	14.5±0.6	16.2±12.7	13.5±0.3	4,970	28,096
E589 after passage through Sep-Pak	25.5					10,773	60,609
Extracted E589 in irradiated E578 (1 mg extracted material l^{-1})	4.4±1.8 ^a	14.3±1.8	14.5±0.04	39.4±3.5	13.1±0.06	569	2,702
e581	9.2±1.2	17.7±1.8	≥15	31.6±3.1	14.0±0.11	6,070	43,096
E581 after passage through Sep-Pak	9.0					4,334	109,950
Extract of E581 in irradiated E580 (1 mg extracted material l^{-1})	3.4±0.1 ^a	Not detected	Not detected	12.1±6.7	14.5±0.3	965	11,537

^a [Cu] in sample to which extract is added.

The uncertainty in the values of K'_{CuL} and [L] show the standard deviation from the mean based on replicate measurements. Copper and ligand concentrations in nanomolar units. CDOM fluorescence is given in quinine sulphate equivalents (Coble et al. 1998).

especially for sample e581 which had a lower initial [Cu]. It does appear that the concentration of Cu decreased by a small amount following passage through the column suggesting a fraction of the complexed Cu in rainwater was associated with very hydrophobic material. Not all Cu was retained by the column, implying that some fraction of the dissolved Cu in rainwater is associated with relatively more polar organic complexes, is only weakly complexed, or exists as free hydrated ion. This is similar to the conclusion drawn by Witt and Jickells (2005) who previously explored Cu speciation in UK rainwater.

3.2 Effect of irradiation on Cu-complexing ligands

One of the most important consequences of complexation of Cu with CDOM is the potential for changes in speciation caused by photochemical reactions. CDOM is the dominant chromophore and fluorophore in rainwater and as such plays a central role in a wide variety of photochemical reactions (Kieber et al. 2006). A series of rainwater samples were irradiated under a solar simulator for 6.5 h, approximately equivalent to one full day of sunlight at sea level at the sampling location, in order to examine changes in Cu-complexing ligands caused by photolysis. It is difficult to establish accurately the amount of radiation received by water droplets. From radiative transfer modelling (eg Madronich's TUV model; Madronich 1987), the actinic flux at 7.5 km exceeds ground level actinic flux by up to 3 fold (particularly in the UV wavelengths) under cloud free conditions. However, under cloudy conditions the comparison becomes more difficult. Above or within the upper part of optically thick clouds, irradiance can be twice as high as the corresponding cloud free atmosphere. On the other hand, in the lower part and beneath optically thick clouds irradiance is reduced several fold. Within and beneath optically thin clouds, the irradiance is usually higher than clear sky conditions. Given these modelling results, it seems likely that the magnitude of irradiation experienced by water droplets in clouds will be equal to 6 fold greater than that at the surface. Therefore the results presented here for the impact of photochemistry on Cu ligands should be viewed as minimum estimates. Samples were drawn out at a number of time points and analyzed in duplicate for Cu speciation using ACSV with SA as the competing ligand. Titrations to determine Cu speciation were carried out using a competition level of $\log \alpha_{\text{Cu}(\text{SA})_2} = 7.6(20 \mu\text{M SA})$. This level allowed detection of one very strong class of Cu-complexing ligands, possessing conditional stability constants $\leq 10^{15}$. Van Leeuwen and Town (2005) suggest that by using an overnight equilibrium time the maximum stability constant that can be measured is 10^{14} as there is not sufficient time for stronger complexes to achieve equilibrium. The titrations carried out in this study suggest there are strong copper ligands, of a binding strength of at least 10^{14} in many rain samples, but given the equilibrium time these are listed as minimum conditional stability constants where appropriate. Chemical characteristics of rain samples prior to and following irradiation are listed in Tables 2 and 3.

Initial concentrations of TDCu and strong ligands ranged from 2.1 to 80 nM and 3.8 to 82 nM respectively. Volume weighted copper and ligand concentrations were highest in samples of terrestrial origin (48 ± 20 nM Cu, 29 ± 24 nM ligand) and lowest in the marine rain events (11 ± 5 nM Cu, 11 ± 7 nM ligand). In 7 of the 14 events sampled, ligand concentrations exceeded those of TDCu, leading to virtually complete complexation (>99.9%) of Cu and concentrations of free Cu^{2+} of $< 10^{-13}$ M as calculated using values for excess ligand and K'_{CuL} (Bruland et al. 2000). TDCu concentrations in the remaining samples were lower than those of ligands, leading to a lesser degree of very strong complexation (55 to 92%) implying that a greater proportion of TDCu resided in organic complexes weaker than those detected at the competition level utilized. Higher levels of

Table 2 Characteristics of rain samples collected at UNCW for photochemical experiments

Event no.	Rain date	Storm type	Amount (mm)	pH	DOC/ μM	[Cu]/nM	% CuL ^a	[Ligand]/nM		
								Initial	Dark control	Final
496	3-May-04	Marine	28.7	4.69	13.3	23.6 \pm 2.6	>99.9	24.1 \pm 2.1	NA	26.0 \pm 0.7
553	14-Jan-05	Marine	23.9	4.98	14.3	10.2\pm2.8	63.0	6.5\pm0.3	NA	9.8\pm0.9
578	2-Jun-05	Marine	50.8	4.89	19.7	4.4\pm1.8	86.4	3.8\pm0.8	3.4\pm0.4	19.8\pm0.8
567	14-Apr-05	Coastal	21.1	4.86	41.8	37.8 \pm 5.2	91.5	34.6 \pm 10.6	31.2 \pm 6.3	28.8 \pm 2.7
572	13-May-05	Coastal	3.8	3.96	500.4	12.9\pm1.1	71.3	9.2\pm0.2	11.5\pm1.4	16.5\pm2.1
580	4-Jun-05	Coastal	28.5	4.66	49.7	3.4 \pm 0.1	>99.9	13.3 \pm 4.0	10.9 \pm 0.1	7.1 \pm 0.2
534	11-Sep-04	Mixed	19.8	3.99	177.0	78.5 \pm 7.6	82.2	64.5 \pm 22.3	NA	52.9 \pm 4.5
540	1-Oct-04	Mixed	21.8	4.34	113.5	11.4 \pm 0.7	>99.9	13.1 \pm 1.0	NA	7.8 \pm 0.2
554	30-Jan-05	Mixed	10.7	4.99	NA	55.1\pm1.8	55.2	30.4\pm1.8	29.5\pm5.2	43.0\pm1.4
563	27-Mar-05	Mixed	18.5	4.95	46.0	21.0 \pm 2.2	>99.9	23.1 \pm 0.4	NA	17.8 \pm 2.6
577	30-May-05	Mixed	4.8	4.16	310.1	10.0\pm0.5	62.0	7.6\pm0.3	6.1\pm0.6	9.4\pm2.5
559	28-Feb-05	Mixed	23.1	4.83	15.3	2.1 \pm 0.3	>99.9	8.3 \pm 0.5	8.2 \pm 2.4	5.8 \pm 1.1
488	10-Mar-04	Terrestrial	9.4	4.96	78.0	80.0 \pm 1.9	>99.9	82.2 \pm 11.1	NA	59.8 \pm 6.1
493	27-Apr-04	Terrestrial	12.7	4.55	NA	23.5 \pm 4.3	>99.9	32.4 \pm 2.5	NA	22.2 \pm 1.0

Uncertainties in concentrations of Cu and ligands are based on duplicate determinations. The conditional stability constants of the Cu-organic complexes are ≥ 15 . Samples where photoproduction of ligand was observed are shown in bold. Dark control shows ligand concentration after sample has been stored for 6 h at room temperature in the dark. Final ligand concentration shows concentration after 6.5 h exposure to simulated solar radiation.

NA = Not analysed

^a% CuL indicates percentage of total dissolved Cu occurring in organic complex of strength indicated.

TDCu in these cases should reside in weaker organic complexes with correspondingly higher levels of labile Cu, including inorganic complexes and free hydrated Cu²⁺.

Changes in ligand concentration relative to initial values caused by exposure to simulated sunlight are presented in Table 3. Titrations carried out on dark controls showed no significant differences over the experimental time period indicating that changes in ligand concentrations are primarily photochemically driven. In a number of experiments where irradiation time was increased to 24 or 48 h, an increase in DOC was also observed. Growth of bacterial material was suspected as the cause of this increase in DOC, therefore experiments were subsequently limited to 6.5 h. Unfortunately, instrumental difficulties and sample volume limitations precluded the collection of final DOC or CDOM data available for all of the samples in Table 3. In two of the rain samples, e567 and e563, a small increase in DOC concentration was observed following 6.5 h irradiation. This increase suggests there may have been some contamination of these samples, but they are included in the following discussion for comparison as the results of these rains are consistent with other samples. Six rain events (580, 540, 567, 559, 488, 493) show clear evidence of ligand loss, ranging from 1.7 to 22 nM or 8 to 47% of the initial ligand concentrations. Four events (553, 554, 572, 578) displayed increases in ligand concentration after irradiation ranging from 1 to 16 nM (11 to 420% relative to initial concentrations). Examples of photochemically induced destruction and production of Cu-complexing ligands as a function of irradiation time in two different rain events are illustrated in Fig. 3. Changes in ligand concentration caused by photolysis in the remaining four events were too small to unambiguously assign loss or gain. The loss, gain, or lack of change in ligand concentration

Table 3 Response of Cu complexation to exposure to 6.5 h of simulated sunlight

Event no.	[Ligand] _{Final} / nM	ΔLigand/ nM ^a	% Ligand change	Ligand A	CDOM	CDOM Total ^b	CDOM/ [Ligand] ^{b,c}	[DOC]/ μM	[DOC]/ [Ligand]		
				peak ^b	Initial	Final	Initial	Final	Initial	Final	
496	26.0±0.7	1.8	7.6	1 717	9 235	NA	299	NA	13.3	NA	428
553	9.8±0.9	3.3	50.6	7 201	41 618	41 589	6 403	6 398	14.3	NA	1 810
578	19.8±0.8	16.0	421.1	2 500	13 086	15 287	3 444	4 023	19.7	18.2	518 919
567 ^d	28.8±2.7	-2.7	-7.8	5 642	36 647	27 668	1 059	800	41.8	52.3	1 208 1 816
572	16.5±2.1	1.0	10.9	13 236	106 096	108 750	11 532	6 590	500.4	NA	54 391
580	7.1±0.2	-6.3	-47.4	3062	15 181	17 915	1 141	1 347	49.7	45.1	3 737 6 352
534	52.9±4.5	-11.7	-18.1	3 949	23 779	59 391	369	921	177.0	91.8	2 744 1 735
540	7.8±0.2	-5.3	-40.5	4 733	25 382	NA	1 938	NA	113.5	NA	8 664
554	43.0±1.4	12.6	41.4	2 598	15 851	66 213	2 432	2 178	NA	NA	
563 ^d	17.8±2.6	-5.4	-23.2	6 571	40 637	3 646	1 759	120	46.0	49.1	1 991 2 758
577	9.4±2.5	3.2	51.6	5 458	29 603	77 963	3 895	10 258	310.1	299.1	40 31 819
559	5.8±1.1	-1.7	-20.5	1 589	8 849	18 777	1 066	2 262	15.3	12.4	1 843 2 138
488	59.8±6.1	-22.4	-27.3	23 682	149 679	12 572	1 821	153	78.0	NA	949
493	22.2±1.0	-7.3	-22.5	1 992	13 803	NA	426	NA	NA	NA	

Samples where photoproduction of ligand was observed are shown in bold. Uncertainties in rates are based on duplicate determinations.

NA = Not analysed

^a ΔL indicates change in ligand concentration following 6.5 h irradiation.

^b CDOM fluorescence is given in quinine sulphate equivalents (Coble et al. 1998).

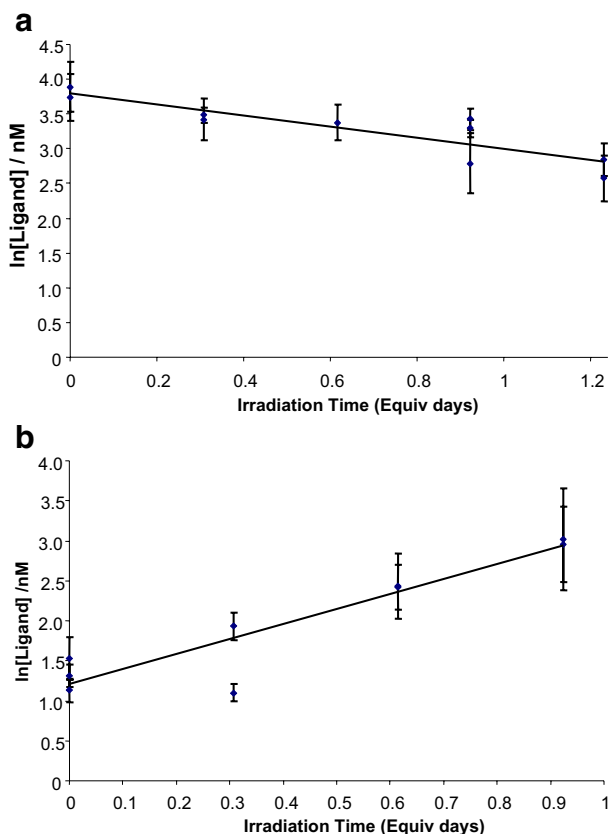
^c [Ligand] in nM

^d Increase in DOC samples observed in rain sample following irradiation.

in each case should be interpreted as a net difference resulting from simultaneous degradation and production from pre-existing material.

The mixed response of Cu ligands to irradiation presented in Table 3 can be used to interpret earlier field studies investigating Cu speciation in rainwater. Witt et al. (2007) found there were no clear seasonal or diurnal trends in ligand concentration in a series of rain samples analyzed in an earlier Cu speciation study. This would occur if ligands were photoproduced in some events and destroyed in others upon exposure to sunlight similar to what was observed in Table 3. Seasonal and diurnal influences on Cu speciation may be further complicated by the impact of storm origin. Two of the three marine events photolyzed in Table 3 showed net increases in ligand concentrations, possibly suggesting that compositional characteristics of CDOM in rains of marine origin favour photoproduction. In studies of humic-rich organic matter from a bog lake, Brinkmann et al. (2003) observed that hydrophobic components of CDOM were less affected by degradation and could even be formed whereas hydrophilic components were preferentially degraded after irradiation by simulated sunlight. Differences in response to sunlight irradiation of rainwater CDOM might therefore suggest that samples showing photodegradation might contain relatively more hydrophilic moieties whereas samples showing net production (including two marine rains) might be dominated by hydrophobic material. There is preliminary evidence from ¹H-NMR analysis in our laboratory that CDOM-like substances

Fig. 3 Change in ligand concentration with time for (a) e567, (b) e578. The uncertainty in [Ligand] values were calculated from the standard error in the gradient and intercept of the linearised data using standard error propagation methods. Ligand rate e567: $1.87 \pm 0.3 \ln(\text{nM}) \text{ day}^{-1}$, r^2 0.864, ligand rate e578: $-0.79 \pm 0.15 \ln(\text{nM}) \text{ day}^{-1}$, r^2 0.778



in marine rain contains relatively more aromatic moieties compared to terrestrial rain, an observation consistent with this hypothesis.

Samples showing clear photodegradation tended to have a higher degree of complexation of Cu by strong organic ligands (92 to >99.9%) compared to samples showing photoproduction (55 to 86%) (Table 3). This implies that a larger percentage of TDCu in samples showing no significant changes or net photoproduction would be bound in weaker organic complexes. Recent evidence suggests that CDOM like substances can be both photodegraded and photoproduced as the result of a complex and dynamic set of in situ photochemical processes occurring in atmospheric waters (Graber and Rudich 2006 and references therein). Based on these earlier studies the observed production of Cu ligands presented here could result from two possibilities. The first is that large non Cu active CDOM complexes could photodegrade by exposure to UV radiation and radicals into molecules which subsequently complex Cu. Alternatively small non Cu active molecules such as certain organic acids could polymerize into larger Cu responsive molecules. This scenario is unlike that in surface waters where exposure to sunlight was seen only to degrade Cu ligands (Shank et al. 2006). Voelker et al. (2000) showed that O_2^- photoproduced in the presence of CDOM is very reactive with these weaker organic complexes and relatively unreactive to strongly complexed Cu. Therefore it is plausible that reactions with photoproduced radicals such as O_2^- react with weaker Cu complexes to form additional strong Cu-complexing ligands. Such transformations may include cleavage of

moieties containing effective Cu-complexing groups such as carboxylic acids from aromatic-rich CDOM like materials, resulting in net production of ligands.

3.3 Rates of photochemical loss or gain of Cu-complexing ligands

Variability in the photochemical response of Cu-complexing ligands in rainwater upon photolysis may be viewed as the result of two competing reactions represented by equations 1 and 2 below:



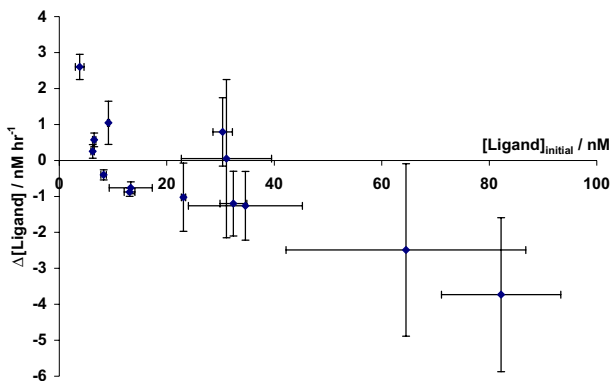
In reaction 1 ambient rainwater CDOM is cleaved or photooxidised by light to DOM* (which may or may not be chromophoric itself), producing Cu-complexing ligands (L) as a by-product. Reaction 2 describes photooxidation of the Cu ligand to L* which may or may not bind Cu. Support for a mechanism involving these competing reactions can be found in the ratio of CDOM abundance (indicated by CDOM fluorescence) to ligand initially present in samples. The five rain events with the highest ratio of CDOM fluorescence to organic ligands (Table 3) all had net production of ligand upon irradiation as the rate of ligand production via Eq. 1 was faster than photodegradation of ligand via Eq. 2. When the ratio of CDOM to ligand was relatively smaller, photodegradation via Eq. 2 was faster than production resulting in a net loss of ligands with time. Following irradiation, the CDOM: ligand ratio remained relatively high in samples showing photoproduction and in most of these the amount of CDOM fluorescence also increased.

The importance of initial concentration of ligands, which would impact the loss rate via Eq. 2, was further evaluated by examining the relationship between the rate of ligand change relative to initial ligand concentration (Fig. 4). Samples with the highest initial ligand concentrations (events 488, 534, 567, 493) had the fastest rate of ligand loss with time whereas the sample with the lowest ligand concentration (event 578) had the largest ligand production. Rate of ligand change upon photolysis in samples with intermediate initial ligand concentrations were much more variable most likely because the rate of production via Eq. 1 was near the rate of loss via Eq. 2.

3.4 Role of UV radiation on changes in ligand concentrations

A number of experiments were carried out at different electroanalytical detection windows with selected cut-off filters in order to determine which wavelengths in the solar spectrum were most effective at initiating photochemical changes in Cu speciation (Fig. 5). The response of ligands to the full solar spectrum was compared to photosynthetically active radiation alone (PAR; 400–700 nm). In rain events 578, 581 and 589, a greater increase in ligand concentration was observed in the presence of full spectrum sunlight containing UV radiation. Rain event 589 had the unusual feature of having a greater concentration of the stronger ligand class indicated by the titration. Interestingly, there was still a larger concentration of the stronger ligand following irradiation with PAR only, and following irradiation with the full solar spectrum the concentrations of the two ligand classes were of a similar magnitude. In rain event 585 the weaker ligand class ($\log K'_{\text{CuL}}=13$) showed a smaller concentration increase when UV radiation was eliminated whereas the stronger class of ligand

Fig. 4 Rate of ligand change as a function of initial ligand concentration. Samples titrated at $\log \alpha - \text{Cu}_{(\text{SA})_2} 7.5$ at a number of time points during 6.5 h irradiation, $n=14$, $r^2 0.65$. Error bars represent ± 1 standard deviation



($\log K'_{\text{CuL}}=14$) increased more in concentration following irradiation by PAR only rather than following irradiation by full spectrum sunlight. This results from competing photoproduction (Eq. 1) and photodestruction (Eq. 2) of ligand with the latter process being more favoured by UV radiation. Photochemical changes of strong Cu ligands ($\log K'_{\text{CuL}} > 16$) caused by UV radiation has also been observed in a lake water sample irradiated for several days (Sander et al. 2005). A similar study on an estuarine sample reported that photodestruction of Cu ligands ($\log K'_{\text{CuL}} \sim 13.5$) was not greatly affected by UV radiation over 5 h, although after several days photodestruction of the ligands was increased by exposure to UV light (Shank et al.

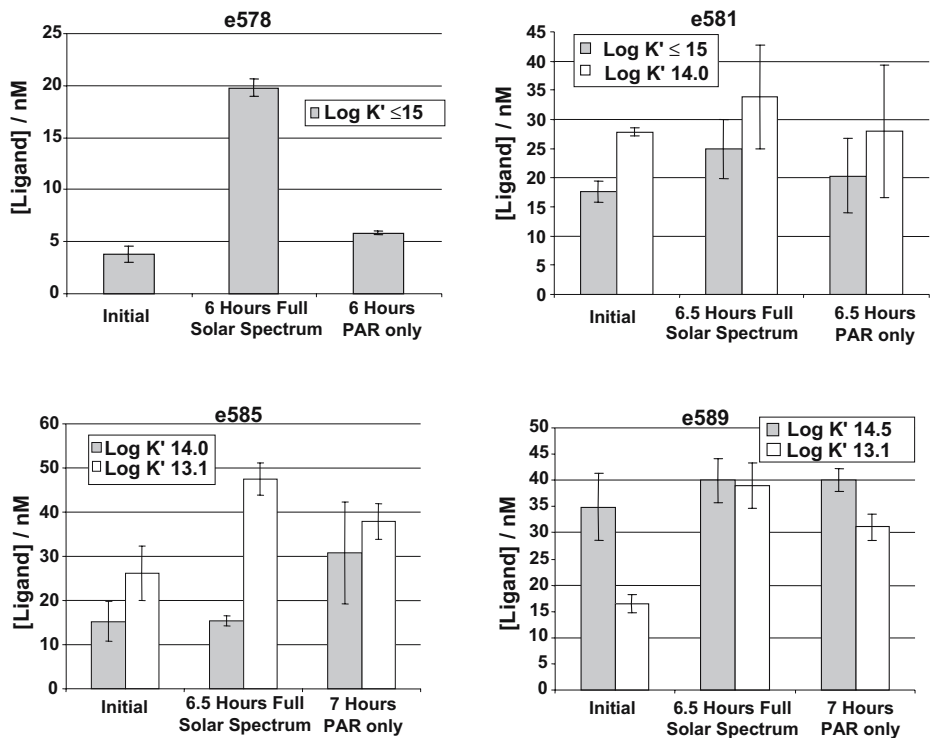


Fig. 5 Ligand concentration in rain events before and after photolysis with full spectrum sunlight and PAR. Conditional stability constants shown in legend for each rain event

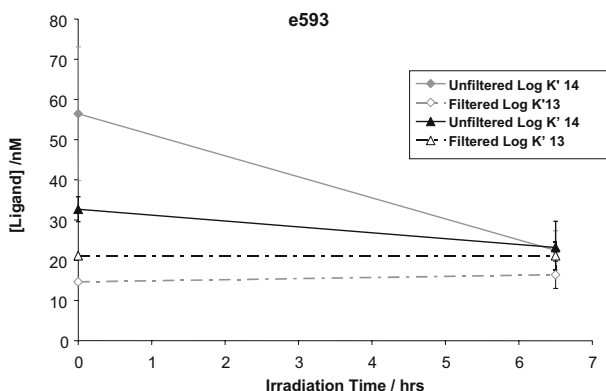
2006). Equivalent studies have not been carried out previously on rainwater. While there are complications in comparing the strength of copper complexes in fresh, estuarine and seawater due to the increase in side reactions due to the increase in side reactions with the addition cations, these studies are the closest available studies at present. Results presented in Fig. 5 and in earlier literature studies with surface waters are significant because they suggest that the photochemical response of Cu ligands in environmental samples is most effectively induced by exposure to UV and PAR in combination but a significant fraction of the photochemical response could also be caused by PAR alone.

3.5 Effect of particles on photochemistry of complexation

The effect of ambient particles on the photochemistry of Cu ligands was examined by photolyzing filtered and unfiltered portions of one rain sample (Fig. 6). At the competition level used for these analyses ($\log \alpha_{\text{Cu}(\text{SA})_2} = 6.2$), two ligand classes could be discerned, with values of $\log K'_{\text{CuL}}$ of ~ 12 and ~ 13 . The unfiltered sample started with significantly higher initial ligand concentrations for both classes as compared to the filtered sample suggesting a large fraction of the Cu ligands in this sample existed on particles. This is similar to an earlier study of Cu speciation in rainwater by Witt and Jickells (2005) who found higher Cu and ligand concentrations in the presence of particles.

Following photolysis ligand concentrations dropped to values close to initial filtered values. The filtered sample showed little or no change in complexation characteristics following irradiation. This suggests that the Cu complexing ligands adsorbed or otherwise associated with particles are photodegraded relatively more rapidly than dissolved ligands. Due to sample volume limitations a dark control was not available for this sample. However, in an earlier investigation, organic complexation parameters in unfiltered rain samples did not change significantly following storage for several weeks in the dark at 4°C (Witt and Jickells 2005) suggesting that changes in ligand concentration in unfiltered rain are not significantly impacted by dark storage. These are preliminary results from an experiment on a single rain sample, and more investigation is required before clear conclusions can be drawn. The results suggest that the particles in the rain play an important role in the photochemistry of copper complexation. The rain samples investigated

Fig. 6 Ligand concentration as a function of irradiation time in filtered and unfiltered rainwater. Error bars represent 1 standard deviation from value. *Solid line* shows unfiltered rain, *broken line* filtered (0.2 μm)

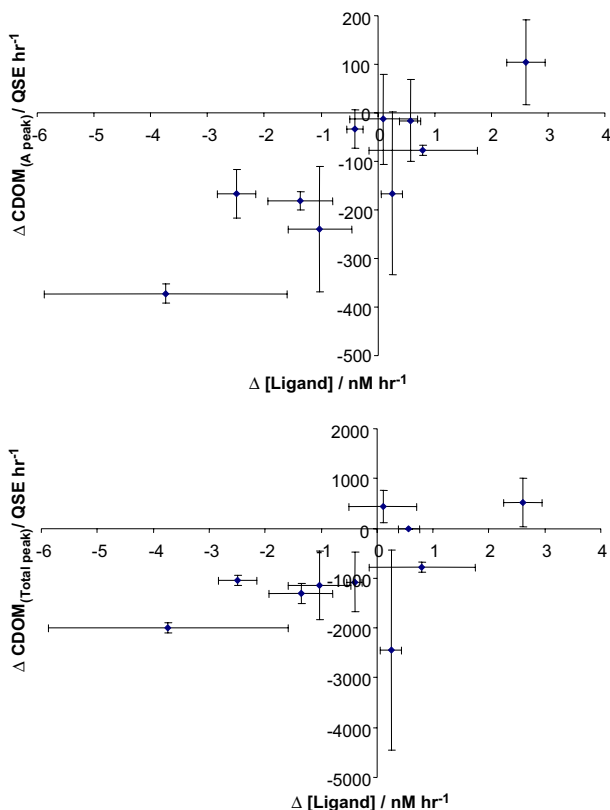


in the rest of this study were filtered prior to analysis and a range of both photoproduction and photodestruction of ligands was observed. Given a greater sample volume it would be of interest to investigate whether the inclusion of particles during photochemical reactions would lead to a similar distribution of photochemical behaviour.

3.6 Photochemistry of CDOM and strong ligands in rain samples

The relationship between the photochemistry of CDOM and of strong ligands ($K_{CuL} \geq 10^{15}$) in rain samples was compared by examining the rates of change in ligand concentration as a function of the rates of changes in peak A and of total integrated fluorescence (Fig. 7). Rate of change in the A peak and total integrated fluorescence of samples correlates positively ($p < 0.01$) with that of the change in strong ligands. There was no significant correlation between the rate of ligand change and the *M* or *T* peak rates ($p > 0.5$) suggesting that the majority of the photolabile CDOM Cu ligand resides in the A peak. There is a stronger correlation between the ligand rate of change and that of the A peak observed than that between the change of ligand and the change in total fluorescence. The A peak is associated with terrestrial humic material, and these results suggest this type of humic matter plays an important role in the complexation of copper in rainwater. The weak correlation with the total fluorescence rate may be because peak A only comprised between 12 and 20% of the total fluorescence intensity in the rain samples. While the A peak appears to be linked to the photochemistry of the copper complexes, the initial ligand concentration did not correlate

Fig. 7 Rate of change of ligand concentration as a function of rate of change of CDOM A peak and total integrated fluorescence. Error bars represent the standard error in the slopes of Ligand/Time or CDOM/Time



with the initial A peak intensities in the rains, suggesting they are not solely responsible for the complexation of copper.

There is a poor correlation between the [DOC] in the sample and its CDOM fluorescence (Table 2). This suggests there are variations in the composition of the DOM in the rain samples and that they contain differing fractions of chromophoric material. Organic material which does not contain conjugated double bonds such as oxalic acid or malonic acid can be found in the atmosphere (Kerminen et al. 2000; Khwaja 1995; Warneck 2003). Such organic material may also be capable of forming strong bonds with copper ions (Chen et al. 2001; Okochi and Brimblecombe 2002), and contribute to the CDOM copper complexing capacity without affecting fluorescence. Previous studies have observed photodegradation of some carboxylate copper complexes such as malonate and oxalate complexes, while others such as formate complexes were unaffected by visible irradiations (Ferraudi and Muralidharan 1981). This would lead to a complicated relationship between the amount of DOC present and the photochemical response of copper complexes. The initial amount of CDOM in each sample was not correlated to the ligand concentration or the ligand rates ($p > 0.6$). The rate of change of weaker ligand classes (rain titrated at $\log \alpha_{\text{Cu}(\text{SA})_2} < 7$) was not correlated with the CDOM rates ($p > 0.1$) suggesting the photolabile CDOM resides in the strong ligand class. The function of photochemically reactive strong Cu-complexing substances has also been recognized in estuarine waters (Shank et al. 2004; Shank et al. 2006).

4 Conclusions

In summary, chromophoric dissolved organic matter (CDOM) appears to be an important and perhaps the dominant ligand of Cu in rainwater. Extracted CDOM was able to form complexes with Cu with similar conditional stability constants to those observed in authentic rain samples. The organic Cu-complexing ligands in rain water undergo both photodestruction and photoproduction through two competing processes. Samples with higher ligand concentrations tend to experience an overall loss in ligand concentration through irradiation, whereas high CDOM samples result in photoproduction of ligands. Gain or loss may also depend on the nature and composition of ligands including their relative hydrophobicity and if they are adsorbed or otherwise associated with particles as these are photodegraded more rapidly. UV radiation was responsible for some, but not all the photochemical changes in ligands, indicating PAR is also able to induce changes in the distribution of ligand sites in rains.

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