Characterization of proton and copper binding properties of natural organic matter from an Australian drinking water source by differential absorbance spectroscopy

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ABSTRACT

This study examined the effects of changes in pH and copper concentration on the absorbance spectra of natural organic matter (NOM) from a reservoir in Western Australia. Differential absorbance spectra generated for this NOM under changing pH and copper concentration conditions revealed features that could be correlated to the activity of distinct types of chromophores. A comparison of results with those generated for experiments with standard Suwannee River fulvic acid highlighted important differences in chemistry between the two samples.

Key words | differential absorbance, copper, complexation, chromophore

INTRODUCTION

Natural organic matter (NOM) is an important factor in determining the speciation and distribution of metal species in environmental systems. Similarly, NOM can influence the release of metals into drinking water systems through its effect on corrosion processes (Edwards & Sprague 2001; Korshin et al. 2005). The complex nature of NOM and the strong dependence of NOM properties on local biogeochemical conditions complicate the study of metal-NOM interactions and make precise assessment of binding capacity and stability constants difficult. This study utilized differential absorbance spectroscopy to examine the copper and proton binding properties of an Australian drinking water source under the low NOM and copper concentrations relevant to actual systems.

The Mundaring Weir is a reservoir located approximately 40 km outside of the city of Perth in Western Australia. This reservoir is the source for the Goldfields Water Supply Scheme, which is the sole source of drinking and irrigation water to the region east of Perth. This area includes the region’s main agricultural areas and extends as far inland as the gold-mining town of Kalgoorlie, 560 km inland. The reservoir contains water from local surface water sources, but during the dry Perth summer, this is often insufficient to keep reservoir levels high enough to meet demand. In this case, groundwater from a nearby treatment facility is pumped back into the reservoir. This groundwater has been treated and is pre-chlorinated before addition to the reservoir. The reservoir contents, containing variable percentages of already treated water, are then pumped throughout the region. Along the way, the water is treated at several chlorination stations to maintain an adequate residual disinfectant concentration.

The majority of the pipeline used to transport this water supply throughout the region is located aboveground and is less than a metre in diameter. The water is thus susceptible to the very high average temperatures in the region, and these high temperatures can cause a rapid loss of chlorine residual in the system. The use of chloramine (NH2Cl) may provide longer-lasting disinfectant residuals at these elevated temperatures, but it also causes an elevated ammonia concentration which facilitates the growth of nitrifying bacteria in pipeline biofilms. The nitrification process produces nitrate, which exacerbates the consumption of chlorine and results in a further acceleration of disinfectant loss. The presence of
low copper concentrations may inhibit this nitrification, as copper has known algicidal and bactericidal properties and has been used to control algal blooms in reservoirs (Flemming & Trevors 1989; Burch et al. 2001).

In order to assess the fate of the copper in the system, it is necessary to adequately understand the interaction of copper with NOM. It is known that the majority of copper in environmental systems exists in forms complexed with humic materials and NOM (Weber 1988; Kungolos et al. 2006). The proton-binding behaviour of NOM is important in determining the metal-binding properties of that sample, and this study used differential absorbance spectroscopy to compare the proton-binding of Mundaring NOM to that for standard Suwannee River fulvic acid (SRFA) samples. The same differential absorbance technique was also used to illustrate the effects of copper binding on NOM chromophores and presents a new application for differential absorbance spectroscopy.

**MATERIALS AND METHODS**

Water samples were collected from the outlet of the Mundaring Weir in December 2006, and were concentrated through reverse osmosis to final DOC concentrations of approximately 25 mg/L. The concentrate was filtered through 0.45 μm filters to remove particulate matter. A sample of Suwannee River fulvic acid (SRFA) was obtained from the International Humic Substances Society (Sample # 1S101F).

Titrations were performed by changing concentrations of protons (pH) and copper in solution. For pH titrations, samples were prepared at 5 mg/L DOC and a background electrolyte concentration of 0.01 M NaClO₄ in a volume of 100 mL. The pH of these samples was lowered to an initial value of approximately 2 with HClO₄. Titrations were performed in both the forward (increasing pH) and backward (decreasing pH) directions. Appropriate volumes of stock solutions of 0.01 M, 0.1 M, or 1.0 M perchloric acid and sodium hydroxide were added to change the pH in approximately 0.25 pH unit increments. After stabilization of each pH point, measurements of absorbance were performed. Absorbance was recorded in a 5 cm quartz cell between 200 and 600 nm with a Perkin-Elmer Lambda 18 UV/Vis Spectrophotometer.

Copper titrations were conducted in a similar manner. Initial Mundaring NOM solutions of 5 mg/L DOC and 0.01 M NaClO₄ were prepared in 100 mL volumes, and the pH was adjusted to a specific value (5, 6, 7, or 8). Copper titrations were performed through the addition of a CuSO₄ stock to final concentrations of 0 to 1,000 μg/L as Cu at constant pH. At each copper addition point, absorbance measurements were performed as described above.

**RESULTS AND DISCUSSION**

Absorbance spectra recorded for a Mundaring NOM solution at varying pH are shown in Figure 1. These spectra exhibit the characteristic broad featureless shape of NOM absorbance spectra. A small but consistent increase in absorbance with increasing pH is also visible, but no additional spectral features are apparent.

Differential absorbance spectra were calculated as the difference between the absorbance recorded at a pH of interest compared to a chosen reference pH, according to the following equation, which also includes terms for normalization to DOC concentration and cell length:

\[ \Delta A_{pH}(\lambda) = \frac{1}{l_{cell} \cdot DOC} \cdot \frac{A_{pH}(\lambda) - A_{pH_{ref}}(\lambda)}{2} \]

Selected differential spectra recorded for Mundaring NOM are shown in Figure 2. In this case, the lowest pH spectrum was selected as the reference in order to examine the proton-binding behaviour of Mundaring NOM throughout the entire pH region.

The differential spectra of Mundaring NOM reveal features which are not apparent in the raw absorbance spectra.
Most notably, a peak centred around approximately 280 nm appears prominently in the differential absorbance spectra. This pattern of differential spectra can be compared to those generated for SRFA under similar experimental conditions, which are shown in Figure 3. While the SRFA differential absorbance spectra also exhibit a peak near 280 nm, that peak is eclipsed by a much larger broad peak centred around 330 nm. This suggests that the Mundaring NOM is lacking a type of chromophore present in the SRFA.

By selecting reference spectra calculated at different pHs, it was possible to further probe these differences. In the region of pH 3–5, it is assumed that primarily carboxylic-type chromophores are active in proton-binding, whereas phenolic-type chromophores are likely to become engaged above approximately pH 8 (Perdue et al. 1984; Ritchie & Perdue 2003). By selecting appropriate reference spectra, it was possible to generate differential absorbance spectra for the carboxylic and phenolic regions separately. The average resulting differential spectra for the carboxylic and phenolic regions for each of SRFA and Mundaring NOM are shown in Figure 4.

Several key differences between the differential spectra of Mundaring NOM and SRFA are apparent. The DOC-normalized intensity of the differential absorbance is significantly lower for Mundaring NOM than for SRFA in both the carboxylic and phenolic pH ranges. The carboxylic region of both NOM samples has a similar shape and location. However, while the differential absorbance spectra of SRFA are dominated by the contribution from phenolic chromophores, the phenolic contribution to the differential absorbance spectra of Mundaring NOM are largely absent. This is potentially attributable to the treatment of a fraction of the Mundaring NOM before its arrival in the reservoir. Water treatment processes preferentially remove the hydrophobic fraction of NOM, of which phenolic chromophores would likely be an important constituent.

The binding of copper to NOM samples is similar in nature to the binding of protons, and the binding of copper to NOM functional groups proceeds by displacing these carboxyl and phenolic protons (Gamble et al. 1985). A similar approach to that used above for proton-binding to Mundaring NOM and SRFA could be used to assess the character of copper-binding chromophores in these samples. The differential absorbance was calculated in the same manner as above for experiments with varying pH, except the reference spectrum was that for which no copper was present. Differential absorbance spectra for Mundaring NOM at select copper concentrations are shown in Figure 5, and the corresponding differential absorbance spectra for SRFA with copper are shown in Figure 6.
For both NOM samples, changes in absorbance due to interactions with very small concentrations of copper (5 µg/L) are readily observable. The different characters of the Mundaring NOM and the SRFA are visible in the dissimilar shapes of their resulting spectra. The Mundaring NOM differential spectra are dominated by a peak at 220 nm, with a hint of a shoulder near 250 nm appearing only at high Cu concentrations. The SRFA, on the other hand, has several visible peaks, the largest located near 240 nm, with smaller broad bands located near 320 and 390 nm. Recalculating the differential spectra choosing different low and high copper concentrations as reference spectra can reveal the presence of weak and strong binding sites in the NOM samples.

CONCLUSIONS

This study applied differential absorbance spectroscopy to the examination of proton-binding and copper-binding in NOM from an Australian drinking water source. Differential absorbance spectra revealed important features which are absent in the conventional absorbance spectra. Analysis of these features and comparison to spectra generated for standard Suwannee River fulvic acid clearly demonstrated the differences in chemistry between the NOM and the fulvic acid samples. The Mundaring NOM was significantly depleted in phenolic-type chromophores relative to the standard fulvic acid sample. Differential absorbance spectroscopy was able to clearly differentiate between the two types of NOM, suggesting that differential absorbance spectroscopy may allow for the detection and differentiation of NOM from different sources in the environment. A similar analysis was applied to spectra recorded for Mundaring NOM samples in the presence of copper and revealed information about the involvement of copper-binding chromophores. Differential absorbance spectroscopy can be a useful technique for the characterization of copper-binding to NOM at low Cu and NOM concentrations which are not accessible by other techniques.

REFERENCES