

Comparison of zinc complexation properties of dissolved organic matter from surface waters and wastewater treatment plant effluents

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Abstract: Unlike natural organic matter (NOM), wastewater organic matter (WWOM) from wastewater treatment plant effluents has not been extensively studied with respect to complexation reactions with heavy metals such as copper or zinc. In this study, organic matter from surface waters and a wastewater treatment plant effluent were concentrated by reverse osmosis (RO) method. The samples were treated in the laboratory to remove trace metals and major cations. The zinc complexing properties of both NOM and the WWOM were studied by square wave anodic stripping voltammetry (SWASV). Experimental data were compared to predictions using the Windermere Humic Aqueous Model (WHAM) Version VI. We found that the zinc binding of WWOM was much stronger than that of NOM and not well predicted by WHAM. This suggests that in natural water bodies that receive wastewater treatment plant effluents the ratio of WWOM to NOM must be taken into account in order to accurately predict free zinc activities.

Keywords: zinc complexation; organic matter; SWASV, wastewater

Introduction

A complicated composition of organic matter is often encountered in soil, natural waters, and wastewater effluents. Complexation of trace metals by those organic matters has important influence on the speciation of trace metals in soil and waters. The primary forms of bound zinc in natural waters and soil are zinc complexed by organic (natural organic matter (NOM) or waste water organic matter (WWOM)) and inorganic ligands, and zinc that is sorbed onto particulate matters. Zinc complexation with organic matters in natural waters can markedly lower the free zinc activity relative to total dissolved Zn, leaving only a small fraction of the total zinc as "free" zinc, which is considered to be bioavailable, or toxic (Allen, 1996). Therefore, in order to understand zinc toxicity in water bodies, we need to understand zinc complexation characteristics of organic matters.

There are a number of models available that predict metal complexation with inorganic and organic compounds with defined chemical nature. However, neither NOM nor WWOM has been very well characterized due to their complicated nature, although the main functional groups that bind to metals in NOM are known. There exist a few models that model metal binding to NOM (e.g., WHAM, NICA) (Tipping, 1998; 1994; Benedetti, 1995). The Biotic Ligand Model (BLM), which uses WHAM to compute organic metal speciation, was recently proposed to predict acute toxicity of metals to aquatic organisms (Di Toro, 2001; Santore, 2001). The key assumption of all the above models is that metal complexation characteristics of NOM are independent of their origin, which has been partially confirmed by several recent studies for metals such as copper (Lu, 2002).

Many natural water bodies receive effluents from wastewater treatment plants. Yet, the metal binding characteristics of wastewater organic matter (WWOM) from wastewater treatment plants effluents is not well understood. This paper reports data from experiments conducted on both WWOM and NOM to determine zinc complexing properties. The data are analyzed to ascertain if both WWOM and NOM can be generalized to behave in a similar fashion or if the zinc

complexing properties of WWOM are different from those of NOM.

1 Materials and methods

All reagents used were analytical grade except the acids, which were optima grade. All reagents were obtained from Fisher Scientific (Pittsburgh, PA). "Better" buffers of MES (for pH 6.0), MOPS (for pH 7.0) and PIPBS (for pH 8.0) were used in zinc titrations to keep the pH constant. These buffers are non-complexing and do not interfere with the titrations (Kandegedara, 1999). The buffers were added to samples to achieve a 0.01 mol/L concentration of the buffers. During the titrations, 0.1 mol/L NaOH or HNO₃ was added as required to keep the pH change within ± 0.1 pH unit. Distilled de-ionized water was used in all experiments, for all dilutions for blanks.

NOM was sampled from the Big Moose Lake, a high elevation system in the Adirondack Mountains of New York State, in May 2000; from the Edisto River, a typical receiving water in South Carolina with a much larger watershed and longer residence time, in March 2001; and from the Suwannee River, Georgia, in June 1997. In addition, WWOM was collected in February, 2002 from the Wilmington Wastewater Treatment Plant (Wilmington, Delaware), a primarily domestic treatment plant effluent. The sampling procedures were similar to those described by Ma *et al.* (Ma, 2001). The samples were concentrated in the field using a reverse osmosis (RO) unit (Model PROS/2S, RealSoft, Norcross, GA) (Serkiz, 1990). The concentrated samples were stored in coolers with ice in the field and in a refrigerator at 4°C in the laboratory. The concentrated NOM or WWOM samples were passed through a H⁺-saturated cation-exchange resin (Dowex 50WX8, Fluka Chemical Co., Milwaukee, WI) column to remove both trace metals and major cations. To avoid losing humic acid (HA) on the resin due to the strongly acidic condition, HA was separated in advance by acidic precipitation (pH \approx 1) and was later recombined with the material that passed through the cation-exchange column. The NOM and WWOM samples thus treated were used in all the subsequent experiments.

1.1 Characterization of NOM and WWOM

We determined the concentration of total dissolved

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organic carbon(TOC) using a Tekmar-Dohrman DC-190 TOC analyzer and the metal content using a Spectro Flame-EOP ICP(Spectro Analytical Instrument, Kleve, Germany). The

metal concentrations and TOC for the GA-NOM and the DE-WWOM samples are reported in Table 1.

Table 1 Metal concentrations, total dissolved organic carbon(TOC), inorganic carbon(IC), and percentage of fulvic and humic acids of the GA-NOM and DE-WWOM

Conc., mg/L.(with 10 mg DOC/L)	Na	K	Ca	Mg	
GA-NOM	0.081	0.565	0.0372	<0.0018	
DE-WWOM	382.7	27.24	6.08	9.34	
Conc., mg/L (with 10 mg DOC/L)	Ni	Cu	Zn	Cd	Pb
GA-NOM	< 2.01	3.79	< 0.10	< 0.68	< 0.5
DE-WWOM	19.54	45.64	17.17	< 0.68	< 0.5
Organic and inorganic carbon	TOC, mg/L	IC, mg/L	Percentage of HA and FA, %		
			HA	FA	
GA-NOM	931.3	0.932	5	95	
DE-WWOM	1070	0.903	0	100	

1.2 Zinc titration

The NOM and WWOM samples were titrated against zinc using square wave anodic stripping voltammetry (SWASV) over a range of total zinc concentrations from 10^{-7} mol/L to 10^{-4} mol/L. Titrations were conducted in a clean room at room temperature of 22°C. Voltammetric measurements were performed using an analytical instrument systems AIS Model DLK-100A electrochemical analyzer with an EG and G Princeton Applied Research PARC 303A static mercury drop electrode in the hanging mercury drop electrode (HMDE) mode. The mercury drop size was "large" with a surface area of 2.83 mm². The reference electrode was Ag/AgCl/3M KCl. For each measurement, a new mercury drop was extruded and the sample solution to be measured was purged with ultrapure (grade 5.0) N₂ for 4 min to eliminate the possible interference of carbonate and O₂. SWASV mode was used to measure labile Zn concentration. For each SWASV measurement the deposition time was 30 s and deposition potential was -1.500 V without stirring; an equilibration time of 15 s followed; for the stripping step, the square wave mode was used, the pulse height was 0.025 V and the potential scan began from -1.500 V and ended at -0.800 V at a scan rate of 0.050 V/s. The NOM and WWOM samples were titrated with Zn at pH 6.0, 7.0, and 8.0. "Better" buffers were used to control the pH to the required value. For each titration, 10 mg/L of the dissolved organic carbon(DOC) was prepared by dilution of the concentrated NOM or WWOM samples. 1 mol/L NaNO₃ solution was added to adjust the ionic strength to 0.02 mol/L. The reactions were allowed to stabilize after each addition of zinc for at least 4 min. Our experiments on Zn-organic matter complexation reaction kinetics showed that the complexation reactions between Zn and organic matter reached equilibrium within 4 min under our experimental conditions (data not shown).

1.3 Computation of free zinc activities

The peak current measured by SWASV, I_p , which is proportional to the labile fraction of metal in the voltammetric measurement, is a weighted average of the diffusion of all metal species(free + complexed). For fully labile system, the peak current I_p is expressed as Equation (1) (van Leeuwen, 1989; de Jong, 1987a; 1987b; 1987c):

$$I_p = -\pi^{-1/2} nFA\bar{D}^{1/2} C_{M,T}^* \tau^{-1/2}, \quad (1)$$

where F is the Faraday constant, A is the electrode surface

area, n is the number of moles of electrons transferred per mole of metal oxidized or reduced, $C_{M,T}^*$ is the total soluble metal activity in the bulk solution, τ is characteristics time, which is constant in our experiments, and \bar{D} is the weighted average of the diffusion coefficient of all metal species(free + complexed), which is expressed as(van Leeuwen, 1989; de Jong, 1987a; 1987b; 1987c):

$$\bar{D} = \frac{[M]^*}{C_{M,T}^*} D_M + \frac{[ML]^*}{C_{M,T}^*} D_{ML}, \quad (2)$$

where $[M]^*$ is the free metal ion activity in bulk solution, $[ML]^*$ is the complexed metal activity in bulk solution, D_M and D_{ML} are the diffusion coefficient of the free and complexed metal ion.

The mass balance of metal in bulk solution is,

$$[M]^* + [ML]^* = C_{M,T}^*. \quad (3)$$

Defining normalized current Φ as the ratio of peak current in the presence ligands to that of ligand-free reference,

$$\Phi = \frac{I_p^l}{I_p} = \left(\frac{\bar{D}}{D_M} \right)^{1/2}, \quad (4)$$

where Φ is the normalized current, I_p^l is the peak current in the presence of ligands and I_p is that of ligands free reference. Combining Equations (2), (3), and (4), the free metal ion activity in bulk solution is expressed as,

$$[M]^* = \frac{\left(\left(\frac{I_p^l}{I_p} \right)^2 - \frac{D_{ML}}{D_M} \right)}{\left(1 - \frac{D_{ML}}{D_M} \right)} C_{M,T}^*. \quad (5)$$

Equation (5) was used to compute free zinc ion activity for fully labile Zn-organic matter systems in our experiments. Normalized current was obtained by comparing the peak current in the present of ligands and that of ligand-free reference. Total zinc concentration was determined by ICP. The value of D_{ML}/D_M was estimated under conditions in which the ligand concentration was in large excess of the total zinc concentration so that $[M]^* \ll [ML]^*$ and the weighted average \bar{D} tended to D_{ML} (Equation 2).

1.4 Models

WHAM(Windermere humic aqueous model) version VI (Tipping, 1998) was used to calculate speciation of zinc in the presence of organic ligands. The free zinc data predicted by WHAM were compared to experimental data to determine if WHAM gave an accurate description of Zn-organic matter

complexation.

Nonlinear curve fitting program FITEQL 4.0 (Herbelin, 1999) was used to calculate stability constants of Zn-organic matter complexes and site concentrations of the organic matter. For the zinc titration data, a 2-site model gave good fit.

2 Results and discussion

2.1 Humic and fulvic fraction of the NOM and WWOM samples

DOC was determined on samples both before and after the precipitation of the humic acid. All the organic matter that was not humic acid was considered fulvic acid when calculating speciation using WHAM. The NOM from Edisto River, SC, Big Moose Lake, NY, Suwannee River, GA, and the WWOM from DE were found to contain 81%, 90%, 95%, and 100% fulvic acid, respectively. This assumption however is likely to be inaccurate for the samples, but particularly for the DE-WWOM because of the varied nature of organic matter present in wastewater effluents.

2.2 Zinc titration

Concentrated NOM or WWOM were added to solutions of fixed total Zn concentration of 7.37×10^{-7} or 1.40×10^{-6} mol/L buffered at pH = 7.0. For each addition of organic matter, voltammetric measurement was made and normalized current and peak potential were plotted against DOC concentration. The titration curves for GA-NOM and DE-WWOM are shown in Fig.1. The normalized current attained a limiting value at high DOC concentrations and the peak potential tended to more negative value during the titration, indicating the full lability of the systems. The D_{ZnL}/D_{Zn} values determined for the NOM samples using Equation (4) were: SC-NOM, 0.04; NY-NOM, 0.06; GA-NOM, 0.014. These values of D_{ZnL}/D_{Zn} for the NOM samples were close to

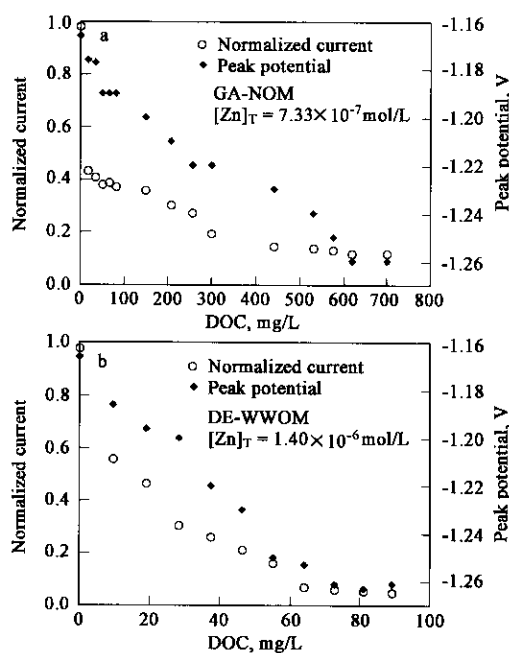


Fig.1 Estimation of D_{ZnL}/D_{Zn} value by titration of Zn with organic matter
pH = 7.0, $T = 22^\circ\text{C}$; a: GA-NOM, total Zn concentration was 7.33×10^{-7} mol/L; $D_{ZnL}/D_{Zn} = 0.014$; b: DE-WWOM, total Zn concentration was 1.40×10^{-6} mol/L; $D_{ZnL}/D_{Zn} = 0.002$

the reported value of 0.05 for NOM from some European river water (Jansen, 1998). However, the value of D_{ZnL}/D_{Zn} determined for the DE-WWOM sample was 0.002, much lower than those of NOM, indicating difference in diffusion coefficients between Zn-NOM complexes and Zn-WWOM complexes.

Zinc was added to the SC, NY, GA-NOM samples as well as the DE-WWOM sample having 10 mg/L DOC and the labile zinc was determined following each change in total zinc. Representative titration curves are shown in Fig. 2. With increase in pH, decrease in labile zinc concentration was observed for the same total zinc concentration. The free zinc activities were computed using Equation (5) and comparison of zinc titrations expressed as free zinc activities against total soluble zinc concentrations demonstrated that NOM from different surface water sources were similar in complexation of zinc under the same pH, ionic strength, and Ca concentrations (Cheng, 2003). However, under similar conditions, the WWOM bound to zinc more strongly than NOM, especially at low total zinc concentrations as shown in Fig.3, indicating stronger zinc binding of WWOM relative to that of NOM. Fig.3 compares the WHAM VI prediction of free zinc activities of the GA-NOM and DE-WWOM titration with our experimental data. While WHAM under-predicted the free zinc ion activity for Zn-NOM system, it over-predicted the free zinc ion activity for Zn-WWOM system, especially at low Zn concentrations. A few recent studies compared experimentally measured Zn-organic matter complexation with WHAM simulations and observed that WHAM tended to over-estimate Zn-NOM complexation (Christensen, 1999; 2000), which agreed with our results. It was suggested that this over-estimation was caused by the overestimation of Zn-NOM stability constant in the default database of WHAM, which was the "best average" from a limited number of published data. By using a lower Zn-NOM stability constant, instead of the default value in WHAM, better agreements between experimentally measured free Zn activities and WHAM prediction were found (Christensen, 1999; 2000). The under-estimation of Zn-WWOM complexation observed in our experiments suggested the existence of strong sites of low concentration for metal complexation in WWOM not accounted for in the current version of WHAM (WHAM VI). Similar observations were made on copper binding properties of WWOM and copper binding by sulfide was proposed to explain the strong binding at low metal concentrations by WWOM (Sarathy, 2002).

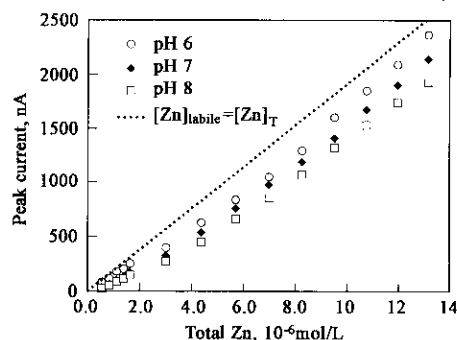


Fig.2 Zn titration curves of the DE-WWOM sample at pH 6.0, 7.0 and 8.0. DOC = 10 mg/L, $I = 0.02$ mol/L, $T = 22^\circ\text{C}$

However, metal binding by sulfide only accounted for the strong binding by WWOM partially and there is definitely the possibility that other strong binding ligands (e. g., proteins and other biological macromolecules) might be present in the WWOM.

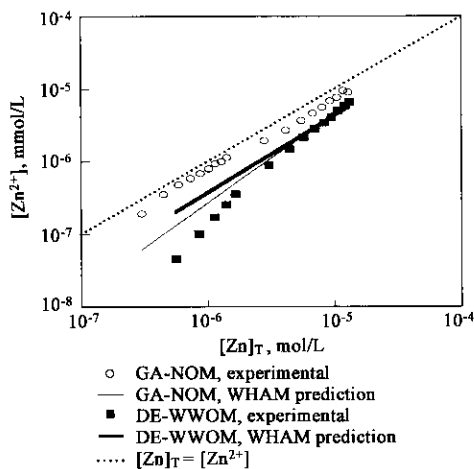


Fig. 3 Zn titration curves of GA-NOM and DE-WWOM samples at pH 7.0, DOC = 10 mg/L, $I = 0.02$ mol/L, $[Ca]_T = 1.5 \times 10^{-4}$ mol/L, $T = 22^\circ\text{C}$

2.3 Zinc-organic matter binding constants and site concentrations

Table 2 lists the conditional binding constants ($\log K_{znl}$) and the concentrations of the binding sites for GA-NOM and DE-WWOM obtained by nonlinear curve fitting program FITEQL 4.0. The ionic strength was 0.02 mol/L, pH = 7.0, $T = 25^\circ\text{C}$, and the total Ca concentration was 1.5×10^{-4} mol/L. For the DE-WWOM, a 2-site model with conditional stability constants of $\log K_1 = 5.47$, $\log K_2 = 6.93$ and site densities of $L_1 = 0.71$ mmol/gC and $L_2 = 0.10$ mmol/gC gave good fit. For the GA-NOM, curve fitting by FITEQL 4.0 using a 2-site model did not converge, so 1-site model with $\log K = 4.91$, $L = 0.84$ mmol/gC obtained by FITEQL 4.0 was used. In order to directly compare the binding constants and site concentrations of the NOM and WWOM, 1-site model was also used to fit the DE-WWOM titration data and the binding constant and site concentration obtained were: $\log K = 5.54$, and $L = 0.89$ mmol/gC. At the same pH, ionic strength, and Ca concentration, the WWOM had a higher Zn binding constant and similar site concentration compared to those of NOM, resulting in lower free zinc activities at the same DOC concentration.

Table 2 Conditional stability constants and site concentrations of GA-NOM and DE-WWOM obtained by nonlinear curve fitting program FITEQL 4.0

Sample	$\log K_1, \log K_2,$ (mol/L) ⁻¹		$L_{1,T}, L_{2,T},$ mmol/gC		$L_T,$ mmol/gC	Percentage of $L_{1,T}/L_T$	
	1	2	1	2			
2-site model							
DE-WWOM	5.47	6.93	0.71	0.10	0.82	0.87	0.13
1-site model							
DE-WWOM	5.54	NA	0.89	0	0.89	100	0
GA-NOM	4.91	NA	0.84	0	0.84	100	0

Notes: The ionic strength was 0.02 mol/L, pH = 7.0, $T = 22^\circ\text{C}$, total Ca concentration was 1.5×10^{-4} mol/L

To demonstrate the importance of the fraction WWOM in a mixture of WWOM and NOM in controlling free zinc activities, the following simulation was performed. Assuming

the total DOC contributed by both WWOM and NOM was 10 mg/L, total Zn concentration was 10^{-6} mol/L, pH = 7.0, $I = 0.02$ mol/L, and total Ca concentration was 1.5×10^{-4} mol/L, the percentage of free zinc in total zinc as a function of the fraction of WWOM was calculated by using MINEQL⁺ (Schecher, 1991). In calculating the free zinc activities, the 2-site model was used for the WWOM and the 1-site model was used for the NOM. The zinc binding constants and the site concentrations used in the calculation are listed in Table 2 and the simulation results are shown in Fig. 4. The fraction of WWOM in a mixture of WWOM and NOM had a remarkable effect on free zinc activities. When all DOC was contributed by NOM, about 60% of total Zn was free, while at the other extreme, when all the DOC was contributed by WWOM, only 16% of the total Zn was free, as predicted by the model. The dashed line is linear regression using two experimentally measured data points. It is seen that in the presence of NOM our model calculation might have underestimated the percentage of free Zn by as much as 20%. However, considering the low total Zn concentration ($[Zn]_T = 1.0 \times 10^{-6}$ mol/L) used in the simulation, the disparity between the experimentally measured and the model simulated free Zn activities was actually small. Both our model simulation and experimental data revealed that the WWOM had a much stronger Zn binding affinity than that of NOM from surface waters and this difference in Zn binding between WWOM and NOM must be taken into account when a significant fraction of DOC is contributed by WWOM.

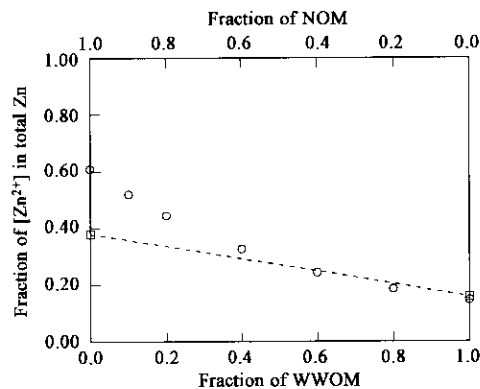


Fig. 4 Percentage of free zinc in total Zn as a function of fraction of WWOM in a mixture of WWOM and NOM DOC = 10 mg/L, pH = 7.0, $I = 0.02$ mol/L, $[Ca]_T = 1.5 \times 10^{-4}$ mol/L, $[Zn]_T = 10^{-6}$ mol/L. Open circles are model calculation by MINEQL⁺, open squares are experimental measurements. Dashed line is linear regression using the two experimental data points

3 Conclusions

WWOM and NOM demonstrated different zinc binding properties. At the same pH, ionic strength, Ca concentration, and temperature, WWOM bound to zinc more strongly than NOM. The 1-site model indicated a conditional zinc binding constant of $\log K = 4.91$, and site concentration of $L = 0.84$ mmol/gC for the GA-NOM under our experimental conditions and $\log K = 5.54$, $L = 0.89$ mmol/gC for the DE-WWOM under the same conditions. Comparison of titration curves with those predicted by WHAM VI indicated that at high zinc concentrations the disparity between WHAM

prediction and experimental data was relatively small. Yet, at low zinc concentrations, WHAM largely under-predicted the free zinc ion activity for Zn-NOM system and over-predicted the free zinc ion activity for Zn-WWOM system. These observations revealed that zinc complexation characteristics of organic matter were dependent on their origin (e.g., natural sources or wastewater effluents) and one set of binding constants and site concentrations could not accurately represent Zn-organic matter complexation. In natural water bodies that receive effluents from wastewater treatment plants, the ratio of WWOM to NOM is an important factor in determination of free zinc activities.

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