Silver Speciation in Seawater: The Importance of Sulfide and Organic Complexation

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Introduction

Silver, one of the most toxic of the heavy metals in aquatic ecosystems, has a $^{6	ext{th}}LC_{50}$ level (concentration resulting in 50% mortality in 96 hours) for the American oyster, *Crassostrea virginica*, of about one-hundredth of that for zinc or copper. The toxicity of silver to aquatic organisms has been of little concern because concentrations in the environment were considered to be too low to produce adverse effects. However, the amounts of silver that continue to enter surface waters from industry and municipal sewage may result in increased accumulation of silver by various aquatic organisms in local environs and could result in toxic effects.

Studies with other heavy metals show that their toxicity is often more dependent upon the concentration of complexing ligands than on the total dissolved concentration of the metal. Assuming that this also applies to silver, its distribution among the various aqueous complexes and the thermodynamic activity of its bioavailable complex(es) will determine its bioaccumulation in and toxicity to aquatic organisms. The limited research on silver suggests, based on a plot of toxicity versus the aqueous complex activity, that the neutral complex, AgCl$^0$, may be the primary bioavailable species for yeast. Recently, the data of Andrew et al. on Cu toxicity to *Daphnia magna* has been reexamined using geochemical modeling and multivariate statistical testing. The results suggest that the hydroxide species of Cu are the most toxic species whereas the uncomplexed Cu$^{2+}$ and other highly correlated species, showed little toxicity in contrast to previous statements based on plotting that the Cu$^{2+}$ ion is the most toxic species. These results indicate that although AgCl$^0$ may be a toxic species, determining whether it is the primary toxic species will require consideration of all the aqueous species and application of a quantitation technique.

The inorganic composition of open ocean water shows minimal spatial and temporal variation in chemical constituents except in upwelling areas. For example, the pH of open ocean water varies over a very narrow range of 8.0 ± 0.7. In contrast, fresh water inflow may cause significant variations of dissolved constituents in coastal waters. For a small group of constituents of important to silver speciation, concentrations may vary notably both spatially and temporally even in the open ocean. For example, sulfide concentrations of 1.7 to >100 μg L$^{-1}$ have been measured in estuarine water columns and above anoxic coastal sediments. The disequilibrium coexistence of sulfide and oxygen is apparently due to a kinetic constraint on the oxidation of S[+II].

Dissolved organic carbon (DOC) concentrations in seawater varies spatially and temporally. For open ocean water, Duursma reported a DOC range of 1.32 to 3.32 mg L$^{-1}$ of C, Dawson gave 3.40 mg L$^{-1}$ of C as the average concentration and Stumm and Morgan state that the average DOC concentration in seawater is 5.00 mg L$^{-1}$ of C. Organic carbon concentrations of estuarine water compiled by Jenne range from 1.9 to 17 mg L$^{-1}$, although most values fall between 2 and 6 mg L$^{-1}$. Some of the dissolved organic compounds in the sea may
complex some heavy metals. However, the importance of this complexation for silver is unknown because of the difficulty of measuring complexation capacity at the observed concentrations of silver. Jenne et al. suggested that the calculated oversaturation of San Francisco Bay water with respect to Ag₂S(s) might be due, at least in part, to organic complexation.

Our immediate objective was to investigate the effect of several variables on the equilibrium distribution of silver complexes in coastal waters via sensitivity analysis using a comprehensive geochemical model. The longer range objective was to provide rational for the design of laboratory experiments for the evaluation of silver bioavailability in coastal marine waters including the identification of any additional analytical parameters needed.

Methods

Speciation and saturation indices were calculated with the MINTEQ (version K1) geochemical model. The following complexes were added temporarily to the thermodynamic data base for this study: Ag-amino acid, Ag-2 amino acid, Ag-carb, 2Ag-carb, Ag-2 carb, Ag-phenol. Silver concentrations of 0.5 and 1.0 ng L⁻¹, at pH values of 7.0, 7.5 and 8.2, S[II] concentrations of 0.0, 0.1, 1.0 and 10.0 μg L⁻¹ and DOC concentrations of 1.0 and 5.0 mg L⁻¹ for salinities of 27.0, 29.5 and 32.0 %, were used. The concentrations of other dissolved constituents at the indicated salinity levels were computed from their concentration at 35 % given in Nordstrom et al. In these sensitivity analyses, the concentration of one constituent was varied while the remaining constituents were held at their base concentrations (e.g., Ag = 0.5 μg L⁻¹, salinity = 30 %, pH = 8.2, DOC = 1 mg L⁻¹, S[II] = 1 μg L⁻¹).

Results

Acanthite, Ag₂S, calculates to be one-half to two orders of magnitude oversaturated at a sulfide and silver concentration of 0.1 to 10 μg L⁻¹ and 0.05 ng L⁻¹, respectively. All other silver solids calculate to be undersaturated.

Inorganic Complexes

The sensitivity analyses show that the aqueous species that constitute greater than 1% of the total dissolved Ag are AgHS⁻, AgCl₂⁻, AgCl₃⁻, AgCl₄⁻. The activities of Cl complexes increase with salinity as the Cl⁻ activity increases. The most abundant aqueous species is the silver bisulfide complex AgHS⁻, even at S[II] concentrations only slightly above 0.01 μg L⁻¹ is the activity of this complex of the same order of magnitude as the most abundant Cl complex.

Organic Complexes

No conditional stability constants for natural dissolved organic matter complexes of Ag were found. As a first approximation of the content of the organic matter, we used the available compilations of specific organic compound concentrations in seawater and compilations of stability constants for complexes of silver with organic compounds to obtain a series of representative reactions and stability constants. Stability constants for Ag are available for only a few of the many organic compounds whose concentrations have been determined in seawater.

Using the above data, the organic complexation with silver can be calculated by: 1) assuming three functional group categories for the organics, which form silver complexes and can be represented by the stability constants; 2) using the average molecular weight; and 3) using the percent distribution of the organic compounds by class calculated from Duursma and alternatively by Dawson.
The activities of the silver-organic complexes were very small, comprising much less that 1% of the total dissolved Ag. A five times increase in the total DOC from 1 mg L⁻¹ to 5 mg L⁻¹ resulted in a significant increase in the activities of silver-organic complexes but did not change the activity of the free metal ion or the chloride complexes. A dissolved organic matter concentration of several hundreds of milligrams per liter would be required to decrease the neutral Cl complex activity by even as much as 5% at S[-II] = 0 and a much higher concentration of DOC would be required at S[-II] concentrations above zero.

Discussion and Conclusions

The importance of the variables examined on the speciation of aqueous Ag decreased in the order S[-II], (0.0 to 10.0 μg L⁻¹), pH (7.0 to 8.2), salinity (27 to 32%), and dissolved organic carbon (1 to 5 mg L⁻¹). The overwhelming effect of even low S[-II] concentrations on speciation indicates the importance of accurate analytical determination of sulfide concentrations in order to reliably compute the Ag speciation. The aqueous speciation of Ag is also dependent on the pH and Cl concentration; predictably, the activity of the silver chloride complexes is dependent on the salinity of the solution. Assuming the AgCl⁰ is the principal toxic species, any decrease in pH to below 8.2 would result in a significant increase in toxicity for silver, because of the decrease in the silver hydroxide species and corresponding increase in the silver chloride species with decreasing pH. This suggests that pH must be closely monitored in toxicity studies with an accuracy of 0.05 pH units clearly required but an accuracy of 0.01 pH units desirable. Assuming that the AgCl⁰ complex is the one that is bioavailable, then the accumulation and toxicity of the Ag will decrease significantly with increases in S[-II] and will decrease significantly with decreases in salinity. We combined the limited available data on organic carbon content in marine waters with the available data on the stability constants of silver with organic compounds to obtain a series of reactions to represent the complexation of Ag and DOC in seawater. Using these reactions and constants, organic complexation of Ag was found to be insignificant.

Acanthite Ag₂S(s) was calculated to be oversaturated by 0.5 to ~ 2 orders of magnitude in waters containing S[-II] in the 0.1 to 10 μg L⁻¹ range. Jenne et al. similarly reported acanthite to be oversaturated by many orders of magnitude in Sacramento River water assuming a sulfide concentration of 0.01 μg L⁻¹. Although acanthite is a common silver mineral and known to form in hydrothermal veins, it is not clear if it forms at ambient temperatures. Although it is not known if acanthite or amorphic Ag₂S precipitates from seawater at ambient temperatures, the potential for acanthite formation further emphasizes the importance of determine the sulfide concentrations of waters used in studies of silver speciation and toxicity.

Reference
