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Competing ligand exchange-solid phase extraction method for the determination of the complexation of dissolved inorganic mercury (II) in natural waters

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Abstract

A method employing dual competitive ligand exchange followed by solid phase extraction (CLE-SPE) for characterizing the complexation of inorganic Hg(II) in natural waters is described. This method employs parallel use of two competing ligands: diethyldithiolcarbamate (DEDC), which forms hydrophobic complexes with Hg(II), and thiosalicylic acid (TSA), which forms hydrophilic complexes with Hg(II). Inorganic mercury complexed by natural and competing ligands are separated based on hydrophobicity using C_{18} solid phase extraction columns.

Data modeling allows for the calculation of the concentration and conditional stability constants of natural ligands capable of complexing Hg(II) in both the operationally defined hydrophilic and hydrophobic fractions. The use of multiple ligand concentrations, and thus multiple analytical windows, to characterize different ligand classes within both of these two fractions is described. Studies of the kinetics of the ligand exchange involved, potential for changes in the stability of natural ligands during freezing and thawing, potential breakthrough during solid phase extraction, as well as the method's precision and estimation of error, are presented and discussed.

Results from the application of the method to natural freshwaters demonstrated that in the limited samples collected over 99.99% of the ambient inorganic mercury is strongly complexed by ligands with conditional stability constants ($K_{\mathrm{HgL}}^{\mathrm{cond}}$, Hg^{2+}) on the order of 10^{30}, values similar to that of reduced sulfur ligands. At ambient conditions 85–90% of the mercury exists in hydrophobic complexes in these freshwaters, but strong Hg-binding ligands exist in both the hydrophobic and hydrophilic fractions.

Keywords: Mercury; Complexation; Speciation; Ligands; Freshwater

1. Introduction

Mercury is a toxic heavy metal and global pollutant originating from natural and, increasingly, anthropogenic sources [1,2]. Like other trace metals, mercury's bioavailability and toxicity are a function of its chemical speciation. Knowing merely the total dissolved concentration of inorganic mercury, Hg(II), provides only limited insight into its possible uptake at the base of the food chain and by microbes, including those responsible for the methylation of mercury to its more toxic form, monomethyl mercury [3–6]. To better understand and predict the biogeochemical cycling of mercury in aquatic environments requires knowledge of the chemical forms and species of mercury present.

The uptake of trace metals by phytoplankton and microbes has been shown to follow the biological ligand model in many cases [7–12]. This model assumes that the hydrated free ion and inorganic complexes with rapid exchange kinetics, relative to binding by membrane transporters, are the forms which are most bioavailable and involved in uptake; this has not proved to be the case for mercury. Instead, neutrally charged hydrophobic inorganic complexes, such as $\mathrm{Hg(Cl)_2}^0$ and HgS^0, have been shown to determine the rate of uptake of inorganic mercury via passive diffusion under some conditions by phytoplankton, as well as by sulfate reducing bacteria responsible for the methylation of mercury [4,5]. However, more recent studies have suggested that under other conditions microbial uptake of Hg(II) likely also involves facilitated and active transport into the cell [13–15].

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While uncertainty remains as to exactly how inorganic mercury is taken up across cell membranes and which chemical species are most important in this transport, there is little doubt as to the key role which complexation with both organic and inorganic ligands and chemical speciation play. As a result, methods which are able to characterize the speciation of Hg(II) in solution and provide information on the nature of the ligands complexing Hg(II) at ambient mercury levels in natural waters are highly desirable. Due to the ability of hydrophobic complexes of Hg(II) to passively diffuse through the phospholipid bilayer of cell membranes [4,5], information on the distribution of hydrophobic and hydrophilic natural complexes of Hg(II) in aquatic environments is also valuable.

Unfortunately, detailed studies of the complexation and speciation of mercury are relatively few in number compared to the abundance of such studies involving other trace metals. While this is due largely to analytical constraints precluding such mercury speciation studies until relatively recently, this is likely also due in part to the strong complexation of mercury by the inorganic ligands OH^- ($\log K_1 = 10.6$; $\log \beta_2 = 21.2$; $\log \beta_3 = 20.9$; [16]) and Cl^- ($\log K_1 = 7.3$, $\log \beta_2 = 14.0$, $\log \beta_3 = 15.0$; $\log \beta_4 = 15.6$; [16]) relative to other trace metals. Based on this information alone mercury was predicted to exist as hydroxide and mixed hydroxide–chloride complexes in oxygenated freshwaters at near neutral pHs, and as chloride complexes in brackish and saline waters [17]. Later studies demonstrated the importance of organic ligands associated with dissolved organic matter, especially those containing thiol functional groups, in binding mercury [18–20]. These have been substantiated by recent investigations of the complexation of dissolved Hg(II) that have employed competing ligand exchange, liquid–liquid extraction [21,22], competing ligand exchange with equilibrium dialysis [23], a reducible mercury method to determine “labile” Hg(II) [24], and voltammetry to directly assess electrochemically active $[\mathrm{Hg(II)}']$ [25].

The method described in this paper employs a dual competitive ligand exchange with solid phase extraction approach based on that of Hsu and Sedlak [26]. A number of important modifications and adjustments are described to optimize this method, and a novel method of data analysis is presented which allows for the simultaneous calculation of the concentration and conditional stability constants for natural ligands forming both hydrophobic and hydrophilic complexes with Hg(II), which has not previously been reported. We also describe the use of multiple ligand concentrations to widen the analytical window [27–29] over which information on different ligand classes within each of the two operationally defined fractions can be ascertained.

2. Experimental

2.1. Theory of competitive ligand exchange and data analysis

The theoretical basis for much of the data analysis and ligand fitting of the competing ligand exchange-solid phase extraction (CLE-SPE) results used for this study have been described elsewhere [30–32]. In a natural water sample the total speciation using the operationally defined hydrophobic and hydrophilic fractions relevant to this study can be described by the equation:

$$[\mathrm{Hg}]_\mathrm{T} = [\mathrm{Hg}^{2+}] + \Sigma[\mathrm{HgI}_i]_\mathrm{hpi} + \Sigma[\mathrm{HgI}_j]_\mathrm{hpo} + \Sigma[\mathrm{HgL}_k]_\mathrm{hpi} + \Sigma[\mathrm{HgL}_l]_\mathrm{hpo} \quad (1)$$

where $[\mathrm{Hg}]_\mathrm{T}$ is the total dissolved Hg(II), $[\mathrm{Hg}^{2+}]$ is the free aqua Hg(II) ion, $\Sigma[\mathrm{HgI}_i]_\mathrm{hpi}$ is the sum of hydrophilic complexes of Hg(II) with known inorganic ligands, such as chloride and hydroxide, and $\Sigma[\mathrm{HgI}_j]_\mathrm{hpo}$ is the sum of hydrophobic complexes of Hg(II) with known inorganic ligands, such as chloride and hydroxide. $\Sigma[\mathrm{HgL}_k]_\mathrm{hpi}$ is the sum of hydrophilic complexes of Hg(II) with unknown inorganic or organic natural ligands, and $\Sigma[\mathrm{HgL}_l]_\mathrm{hpo}$ is the sum of hydrophobic complexes of Hg(II) with unknown natural ligands. The use of the terms hydrophilic and hydrophobic refer to the operationally defined conditions of this study (i.e., hydrophobic species are retained by a C_{18} column, while hydrophilic species are not).

The reaction forming a hydrophilic natural complex involving ligand L_k, and assuming a 1:1 stoichiometry, with unknown charges omitted for simplicity can be represented by the equation:

$$\mathrm{Hg}^{2+} + \mathrm{L}'_k \leftrightarrow \mathrm{HgL}_{k\,\mathrm{hpi}} \quad (2)$$

which at equilibrium is described by the conditional stability constant:

$$K^\mathrm{cond}_{\mathrm{HgL}_k} = \frac{[\mathrm{HgL}_k]_\mathrm{hpi}}{[\mathrm{Hg}^{2+}][\mathrm{L}'_k]} \quad (3)$$

where $[\mathrm{L}'_k]$ is the natural ligand not bound to Hg, and $K^\mathrm{cond}_{\mathrm{HgL}_k}$ is the ionic strength corrected conditional stability constant for the complex $[\mathrm{HgL}_k]_\mathrm{hpi}$. This stability constant is conditional to the pH and concentration of all components in the system responsible for side reactions with the species of interest. After the addition of the competing ligand thiosalicylic acid (TSA), which forms predominately anionic bis hydrophilic complexes with Hg(II) under the conditions used, the expression above for total Hg(II) becomes:

$$[\mathrm{Hg}]_\mathrm{T} = [\mathrm{Hg}^{2+}] + \Sigma[\mathrm{HgI}_i]_\mathrm{hpi} + \Sigma[\mathrm{HgI}_j]_\mathrm{hpo} + \Sigma[\mathrm{HgL}_k]_\mathrm{hpi} + \Sigma[\mathrm{HgL}_l]_\mathrm{hpo} + \Sigma[\mathrm{HgTSA}]_\mathrm{hpi} \quad (4)$$

The stability constants for the complexes of Hg(II) with TSA^{2-} are

$$\beta_1 = \frac{[\mathrm{HgTSA}_{(aq)}{}^0]}{[\mathrm{Hg}^{2+}][\mathrm{TSA}^{2-}]} \quad (5)$$

and

$$\beta_2 = \frac{[\mathrm{Hg(TSA)}_2{}^{2-}]}{[\mathrm{Hg}^{2+}]\,[\mathrm{TSA}^{2-}]^2} \quad (6)$$

Combining and rearrangement of the above equations give

$$\Sigma[\mathrm{HgTSA}_x{}^{2-2x}] = [\mathrm{Hg}^{2+}]\,\Sigma(\beta_\mathrm{TSA}[\mathrm{TSA}^{2-}]^n) \quad (7)$$

As described above, TSA can bind to Hg(II) to form both a neutrally charged hydrophobic monocomplex, $\mathrm{HgTSA}_{(aq)}{}^0$,