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Using Cadmium-113 NMR Spectrometry To Study Metal Complexation by Natural Organic Matter

JIAN LI,† E. MICHAEL PERDUE,*,† AND LESLIE T. GELBAUM‡

School of Earth and Atmospheric Sciences and Biosciences Center, Georgia Institute of Technology, Atlanta, Georgia 30332

Because of its relatively high natural abundance and the broad range of chemical shifts (900 ppm), ^{113}Cd is a potentially excellent istope for NMR studies of metal binding sites of natural organic matter (NOM). This paper presents a ^{113}Cd NMR study of the effects of pH and, to a lesser extent, Cd/C molar ratio on the complexation of cadmium ion by Suwannee River NOM. Spectra are presented for solutions ranging in pH from 3.6 to 9.0 and ranging in Cd/C ratio from 0.0013 to 0.0068. At acidic pH, a single somewhat sharp peak is observed, but more complex spectra are obtained at alkaline pH. These changes indicate that Cd−NOM exchange rates are much faster at acidic pH, where the concentration of free Cd^{2+} is greatest. Under nearly all the conditions of Cd/C ratio and pH that were used, Cd^{2+} is primarily coordinated by O donor atoms, probably in carboxyl groups. At high pH, some evidence of Cd^{2+} coordination by N donor atoms is observed. No evidence of Cd^{2+} ions coordinated by S donor atoms was observed in the NMR spectra, even at Cd/C ratios that were significantly lower than the S/C ratio of the NOM.

Introduction

The distribution of a trace metal cation between free and complexed forms can be controlled by its reactions with natural organic matter (NOM), most of which is known as humic substances. The study of metal complexation by NOM presents a tremendous technical challenge because NOM is an unresolvably complex mixture of organic compounds that is necessarily studied as a mixture (*1*). NOM includes molecules containing many types of functional groups, with molecular weights that range from a few hundred to many thousands. A typical NOM molecule may contain aromatic rings and aliphatic chains that host numerous carboxylic, phenolic, hydroxyl, carbonyl, and alkoxyl groups. Although oxygen-containing functional groups are the most numerous, NOM also contains small percentages of N and S that may be important ligand atoms (*2*). As our understanding of the abundance, nature, and strengths of metal binding sites in NOM increases, better models of the aquatic chemistry of trace metal cations can be developed.

An ideal analytical method for studying metal−NOM complexation would simultaneously quantify the free metal ion and each metal−NOM complex in a sample; however, given the complexity of NOM, this goal is probably not attainable. In existing analytical methods, either "free" metal or "bound" metal is generally measured (*3*), and the other form is calculated from the mass balance equation (total metal = free metal + bound metal). No information is provided about the distribution of metal−NOM complexes within the bound metal fraction. Furthermore, because a metal ion reacts with NOM to form complexes with different kinetic and thermodynamic properties (*4*), different experimental methods often yield different estimates of the relative concentrations of free and bound forms of a metal (*5*).

For some metal cations, nuclear magnetic resonance (NMR) spectrometry can potentially detect the free metal ion and each metal−NOM complex in a sample. NMR can simultaneously provide information regarding the relative proportions of individual complexes and their electronic environments (i.e., the nature of the donor atoms in the primary coordination shell of the metal ion). Cadmium-113, which is one of the common isotopes of cadmium, is readily observed by NMR, and the free cadmium ion produces a single sharp peak in an NMR spectrum (*6, 7*). Because of the relatively high natural abundance of the spin $I = {}^{1}/_{2}$ isotope (12.26%) and the broad range of chemical shifts (900 ppm), ^{113}Cd NMR has been shown to be an excellent technique to probe metal binding sites of biomolecules (*6, 7*).

Ligands that coordinate with Cd^{2+} via oxygen donor atoms (SO_4^{2-}, NO_3^-, NO_2^-, HCO_2^-, CH_3COO^-) generally cause increased shielding of the cadmium nucleus ($\delta_{ppm} = -180$ to $+40$ ppm). Ligands that bind via nitrogen donor atoms (NH_3, C_5H_5N, N_3^-, $H_2NCH_2CH_2NH_2$) cause substantial deshielding of the cadmium nucleus ($\delta_{ppm} = +40$ to $+300$ ppm), and ligands that bind via sulfur donor atoms (S^{2-}, HS^-, thiourea, thiocyanate) very strongly deshield ($\delta_{ppm} = +400$ to $+800$ ppm) the cadmium nucleus (*8*).

Cadmium-113 NMR has been used in a few studies of cadmium binding by solid-phase environmental samples (*9*−*13*). This method has also been applied to study cadmium binding by dissolved organic matter, including Suwannee River NOM (*14*−*16*), Suwannee River fulvic acid (*17*), and a soil fulvic acid (*18*). All the previous studies of aqueous-phase complexation reactions examined the effect of the Cd/C ratio on NMR spectra at approximately pH 5−6. This paper presents a ^{113}Cd NMR study of the effects of pH and, to a lesser extent, Cd/C ratio on the complexation of cadmium ion by Suwannee River NOM.

Technical Background

(A) Aqueous Speciation of Cadmium. In ^{113}Cd NMR spectrometry, the most common reference material is aqueous $Cd(ClO_4)_2$, at concentrations ranging from 0.1 to 1.0 mol/L. In practice, the observed chemical shift of cadmium is essentially constant over this concentration range of $Cd(ClO_4)_2$ (*8*). In such solutions, standard chemical equilibrium calculations that consider the formation of cadmium perchlorate complexes, cadmium hydroxy complexes, and the insoluble solid cadmium hydroxide predict that greater than 99% of cadmium is in the form of the Cd^{2+} aquo ion, i.e., the free cadmium ion. Accordingly, in these reference solutions, the chemical shift of the free Cd^{2+} ion is identical with the observed chemical shift of the reference $Cd(ClO_4)_2$ solutions.

(B) Competitive Binding of Cadmium and Hydrogen Ions. Most of the O donor atoms in Suwannee River NOM are in carboxyl groups, which are more than 50% deprotonated above pH 4 (*19*). In contrast, any N and S donor atoms

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* Corresponding author e-mail: mperdue@eas.gatech.edu; tel: (404) 894-3929; fax: (404) 894-5638.

† School of Earth and Atmospheric Sciences.

‡ Biosciences Center.

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that can bind Cd^{2+} are probably present in amine and thiol groups, both of which are typically protonated below about pH 9. Therefore, the extent to which Cd^{2+} can be bound by O, N, or S donor atoms is expected to be a function of pH, with the contributions of N- and S-containing binding sites potentially becoming more important at alkaline pH values. Even at alkaline pH values where Cd^{2+} is expected to bind preferentially to N and S donor atoms (*20*), the extent to which N- and S-containing binding sites can dominate Cd^{2+} complexation by NOM is strictly limited by their low abundances relative to carboxyl and other O-containing groups.

(C) Metal−Ligand Exchange Kinetics and Relaxation Kinetics. If metal−ligand exchange kinetics are sufficiently fast, then only one weighted-average peak will be observed in the NMR spectrum of Cd^{2+}. At intermediate metal−ligand exchange rates, broad poorly resolved peaks may be obtained. If metal−ligand exchange rates are very slow, then each Cd-containing species can potentially be observed. Spectra are also affected by differential relaxation rates of free and complexed forms of cadmium. The free Cd^{2+} ion has a relaxation time of more than 1 min, but complexes with NOM have relaxation times of less than 1 s (*21*). Because many scans are required to obtain usable spectra of dilute aqueous solutions of cadmium, it is seldom experimentally practical to use pulse delays that are sufficient to allow complete relaxation of the free Cd^{2+} ion. Accordingly, the relative abundance of the free Cd^{2+} ion may be underestimated whenever both free and complexed forms of cadmium are present in solution.

Experimental Approach

(A) Reagents. NOM for this research was obtained from the Suwannee River near Fargo, GA, by reverse osmosis. The concentrated NOM solution was desalted using an H^+-saturated cation-exchange resin and then lyophilized (*22*). The dry, ash-free elemental composition of the NOM (as molar ratios) is H/C = 0.95, O/C = 0.622, N/C = 0.017, and S/C = 0.004 (*23*). In all following references to NOM, its concentration will be given as the molar concentration of dissolved organic carbon (DOC).

A 0.5 M solution of reagent-grade $Cd(ClO_4)_2$ in D_2O was used as an external standard in all experiments to set the zero ppm chemical shift. As stated previously, more than 99% of the cadmium in this solution is calculated to be in the form of the Cd^{2+} aquo ion. For the experiments with NOM that are discussed in this paper, enriched ^{113}CdO (95.1%) was dissolved stoichiometrically in 70% $HClO_4$ to obtain $Cd(ClO_4)_2$., which was diluted as needed with D_2O in all NMR experiments. Because Na^+ and ClO_4^- do not complex strongly with Cd^{2+} or NOM, reagent-grade NaOH and $HClO_4$ were used to adjust pH values of sample solutions, and $NaClO_4$ was used to adjust the ionic strength of standard solutions that were used to calibrate the cadmium ion selective electrode (see next section).

(B) Instruments and Measurements. Cadmium-113 NMR spectra were obtained using either a Varian XL-400 or a Brucker AMX-400 NMR spectrometer (during this study, the Varian XL-400 NMR spectrometer was replaced by a Brucker AMX-400 NMR spectrometer). Each sample was prepared in a 10-mm borosilicate tube. NMR spectra were recorded on freshly prepared samples, and spectra were obtained using the following conditions:

frequency	88.6949 MHz
pulse width	15 μs (90°)
spectral width	80000 Hz
acquisition time	0.33 s
relaxation delay	0.20 s

The activity of free uncomplexed Cd^{2+} ion was measured using an Orion Cd^{2+} ion selective electrode (ISE) and an Orion double-junction reference electrode. The ISE was calibrated using $10^{-3}-10^{-6}$ M $Cd(ClO_4)_2$ solutions in 0.1 M $NaClO_4$. The ionic strengths of samples containing $Cd(ClO_4)_2$ and NOM were estimated from the concentration of added $Cd(ClO_4)_2$. An Orion pHmeter equipped with a glass electrode and an Orion double-junction reference electrode was used to measure apparent pH values. Because the standard buffer solutions are in H_2O and the solutions containing $Cd(ClO_4)_2$ and NOM were in D_2O, pH values of the samples were estimated to be about 0.4 higher than the readings of the pHmeter (*24*). The Davies equation was used to interconvert activities and concentrations (*25*).

The adjusted pH (meter reading + 0.4) and pCd values were used subsequently to calculate the equilibrium concentrations of known cadmium hydroxy complexes and to determine the saturation index (SI) of each solution with respect to amorphous cadmium hydroxide. Organically complexed cadmium was calculated as the total cadmium concentration minus the measured concentration of free Cd^{2+} and the sum of the calculated concentrations of all known cadmium hydroxy complexes.

(C) Experimental Strategy. Ideally, the NMR experiments would have been conducted under experimental conditions that correspond to those in natural waters, insofar as pH, DOC, and total cadmium concentrations are concerned. Two experimental constraints prohibit the use of such experimental conditions. First of all, the lowest concentration of Cd that could be observed by NMR in a 60-h experiment, particularly at alkaline pH values, was around 0.001 M. Second, the maximum attainable concentration of DOC from Suwannee River NOM is about 0.8 M. Accordingly, the lowest practical Cd/C ratio is about 0.0013. The actual concentrations of Cd^{2+} and DOC used in the NMR experiments are 5 and 3 orders of magnitude, respectively, above natural levels; however, the lowest Cd/C ratio is within about 1−2 orders of magnitude of a typical Cd/C molar ratio in natural systems.

Given the above constraints, the basic experimental plan was structured to maximize the possibility of observing any binding of cadmium by N or S donor atoms. For example, the molar Cd/C ratios were maintained in the range of 0.0013−0.0068, well within the range of the N/C and S/C molar ratios of the NOM (0.017 and 0.004, respectively). Under such conditions, it is at least possible, in principle, for most of the cadmium to react with N or S donor atoms. The pH dependence of ^{113}Cd NMR spectra at selected Cd/C ratios was examined in the pH range of 3.6−9.0, with the expectation that the relative contribution of N and S donor atoms might become more important at the higher pH values.

Because the NMR experiments must be conducted at high absolute concentrations of both Cd^{2+} and NOM, it is essential to demonstrate that chemical properties that are observed under such conditions are also representative of more dilute solutions. To verify that the fraction of binding sites containing Cd^{2+} depends only on the activity of Cd^{2+} (at constant pH), cadmium binding titrations were conducted at DOC concentrations of 0.0079 and 0.79 M. In these titrations, each solution of Suwannee River NOM was titrated by stepwise addition of 0.0049 M $Cd(ClO_4)_2$. After each addition of titrant, the activities of H^+ and Cd^{2+} ions were measured as described previously, and pH was carefully readjusted to pH 5.20 ± 0.02.

Results and Discussion

The cadmium binding curves at pH 5.20 at DOC concentrations of 0.0079 and 0.79 M are given in Figure 1. The results are consistent with the results of previously published proton (*19*), calcium (*26*), and copper (*27*) binding titrations. In particular, if the concentration of complexed Cd^{2+} is nor-

TABLE 1. Chemical Speciation in Solutions Containing Cadmium Perchlorate and Suwannee River Natural Organic Matter at Selected pH Values[a]

spectrum	$Cd(ClO_4)_2$	DOC	Cd/C	pH[b]	pCd	$[Cd^{2+}]$	$\Sigma_i[Cd(OH)_i]$	log SI[c]	[Cd−NOM]
Figure 2a	5.5×10^{-3}	0.804	0.0068	3.6	3.2	1.1×10^{-3}	2.3×10^{-10}	−9.6	4.4×10^{-3}
Figure 2b	5.5×10^{-3}	0.804	0.0068	4.3	3.6	4.3×10^{-4}	4.6×10^{-10}	−8.6	5.1×10^{-3}
Figure 2c	5.5×10^{-3}	0.804	0.0068	6.4	3.8	2.7×10^{-4}	3.7×10^{-8}	−4.6	5.2×10^{-3}
Figure 3a	5.5×10^{-3}	0.804	0.0068	9.0	6.1	1.2×10^{-6}	6.7×10^{-8}	−1.8	5.5×10^{-3}
Figure 3b	2.2×10^{-3}	0.804	0.0027	8.4	6.5	4.8×10^{-7}	6.7×10^{-9}	−3.4	2.2×10^{-3}
Figure 3c	1.1×10^{-3}	0.862	0.0013	8.7	7.2	7.4×10^{-8}	2.6×10^{-9}	−3.5	1.1×10^{-3}

[a] All concentrations are in mol/L; pH and pCd are negative logarithms of the activities of H^+ and Cd^{2+}, respectively. [b] Because samples are in D_2O, the tabulated pH values are 0.4 higher than the readings of the pH meter. [c] SI is the saturation index of the solution with respect to $Cd(OH)_2(s)$.

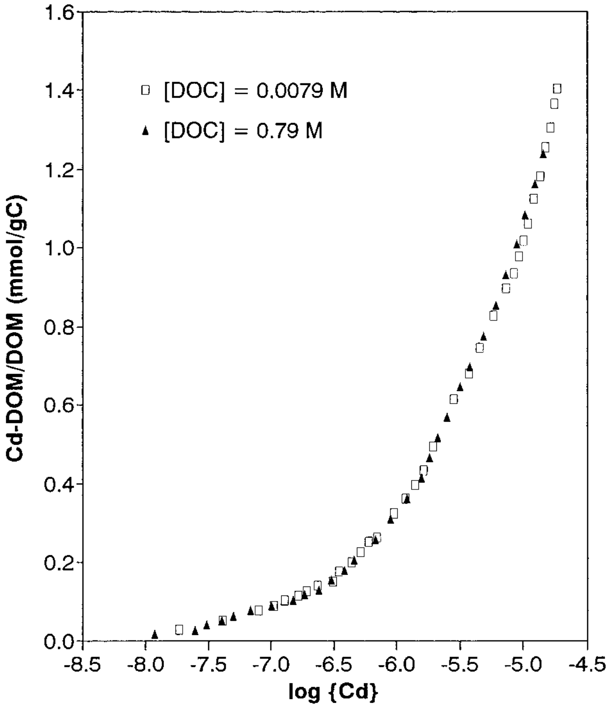

FIGURE 1. Cadmium binding titration curves of Suwannee River NOM at dissolved organic carbon concentrations of 0.0079 and 0.79 M at pH 5.20.

malized to the DOC concentration, then the Cd^{2+} binding curves from solutions with very different DOC concentrations are superimposable. This means that the fraction of binding sites that contain Cd^{2+} is solely a function of the activity of the free Cd^{2+} ion (at constant pH and in the absence of other competing cations). This being the case, the distribution of Cd^{2+} within the binding sites of NOM is expected to be comparable at both elevated and environmentally realistic concentrations of Cd^{2+} and DOC. Significantly, the Cd/C ratios used in the NMR experiments (typically 0.0013−0.0068) are well within the range of Cd/C ratios used in the titrations (0.00015−0.020). Accordingly, the chemical insight that is provided by the NMR studies at elevated concentrations of Cd^{2+} and NOM is expected to be applicable under environmental conditions.

Table 1 presents the ancillary chemical measurements and calculations for each sample whose NMR spectrum is to be presented. As described previously, the data in Table 1 describe the equilibrium composition of each solution. Together, these ancillary chemical measurements and chemical equilibrium calculations provide useful insight that aids substantially in the interpretation of the ^{113}Cd NMR spectra. It is evident that none of the solutions is saturated with respect to amorphous $Cd(OH)_2(s)$ and that cadmium hydroxy complexes are not a major component of any of the solutions. In fact, the major cadmium-containing species in all the solutions are the Cd^{2+} ion and organically complexed cadmium. In the most acidic solution (pH 3.6), 80% of cadmium is organically complexed, and the degree of complexation approaches 100% at alkaline pH.

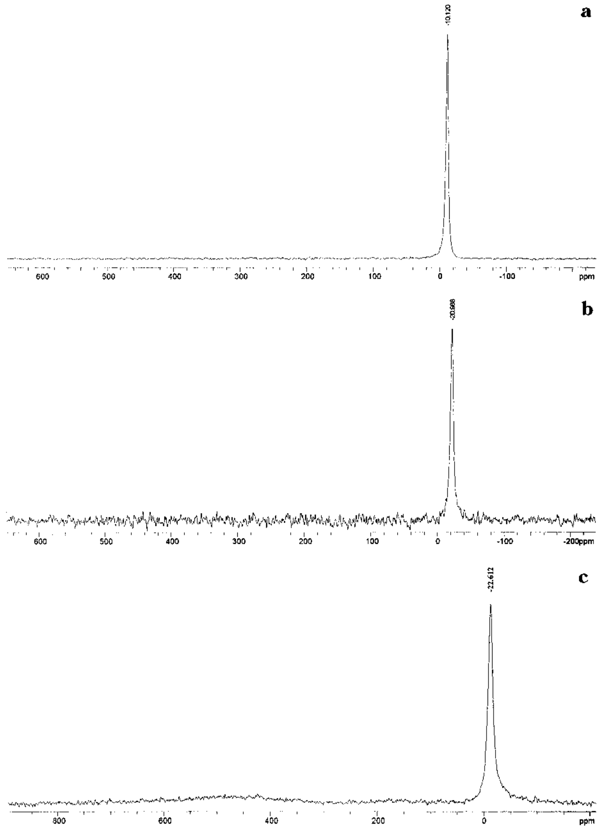

FIGURE 2. ^{113}Cd NMR spectra of solutions containing 0.0055 M $Cd(ClO_4)_2$ and 0.80 M dissolved organic carbon at pH values of (a) 3.6, (b) 4.3, and (c) 6.4.

The ^{113}Cd NMR spectra in Figure 2 were all obtained at a molar Cd/C ratio of 0.0068 and at acidic pH values that range from 3.6 to 6.4. It is immediately evident that only a single peak is observed in each spectrum, which means that metal−ligand reactions are sufficiently fast that only a weighted-average peak is observed. As pH is increased, the average chemical shift moves upfield from about −10.1 ppm to about −22.6 ppm. The total cadmium concentration is the same in all three spectra; however, as competitive binding of H^+ decreases at higher pH, a larger fraction of the cadmium is complexed by NOM. The movement of the weighted-average peak away from 0 ppm (the chemical shift of the free Cd^{2+} ion—see Technical Background) to more a negative chemical shift is a consequence of the decreased mole fraction of free Cd^{2+} ion with increasing pH. The fact that the weighted-average chemical shift is negative in each of the spectra in Figure 2 is consistent with the hypothesis that

Cd^{2+} is primarily bound to oxygen donor atoms in the NOM, probably in COOH groups, which are largely deprotonated above pH 4.0 (*19*). Because only a weighted-average peak is observed, the possibility that a small fraction of the Cd^{2+} may be bound by N and/or S donor atoms cannot be excluded.

The results in Figure 2 are in excellent agreement with the results that have been obtained for cadmium binding by soil fulvic acid (*18*). In that paper, experiments were conducted at pH 6.0, and the molar Cd/C ratio was varied from 0.0030 to 0.0227 by varying the concentration of Cd^{2+} in solutions containing 1.35 mol/L organic carbon as soil fulvic acid. The weighted-average chemical shift varied from -15.6 to -20.4 ppm as the Cd/C ratio was increased. The authors pointed out that these chemical shifts are farther downfield than would be expected for simple mono- or dicarboxylate complexes of cadmium, so they suggested that other donor atoms, including N, might be coordinated to Cd^{2+} in their experiments.

The results for cadmium binding by soil fulvic acid (*18*) and the results in Figure 2 are in strong disagreement with the results that have been obtained for cadmium binding by Suwannee River fulvic acid (*17*). In that paper, experiments were conducted at pH 6.4, and the molar Cd/C ratio was varied from 0.0020 to 0.0445 by varying the concentration of Suwannee River fulvic acid in solutions containing 4.38×10^{-3} M Cd^{2+}. So the experimental conditions were comparable to those in this study and in the study of soil fulvic acid (*18*). The results, however, are strikingly different. As the Cd/C ratio was varied from 0.0020 to 0.0445, the weighted-average chemical shift varied from -11.90 to $+25.36$ ppm. The downfield movement of the weighted-average chemical shift with increased Cd/C ratio at constant pH is opposite to that which was observed for cadmium binding by soil fulvic acid. Furthermore, the strongly deshielded (positive) chemical shifts that were reported in the study of cadmium binding by Suwannee River fulvic acid were not found in this study or in the study of cadmium binding by soil fulvic acid (*18*).

There is a very likely explanation for the unusual results for cadmium binding by Suwannee River fulvic acid (*17*). By dissolving ^{113}CdO(s) in a "small volume" of 35% DCl, the authors introduced Cl^{-} ion into their samples. Significantly, Cl^{-} ion was not present in the study of cadmium binding by soil fulvic acid (*18*) or in this study. Chemical equilibrium calculations predict that a pH 6.4 solution containing 4.38×10^{-3} mol/L cadmium and a 2–3-fold excess of Cl^{-} beyond the stoichiometric amount of DCl needed to dissolve the ^{113}CdO(s) should contain between 53 and 43% free Cd^{2+}, between 45 and 53% CdCl^{+}, and between 2 and 4% CdCl$_2$(aq). Given the chemical shift of 0 ppm for the Cd^{2+} ion (see Technical Background) and the published chemical shifts of CdCl^{+} and CdCl$_2$ of $+89$ and $+114$ ppm, respectively (*7*), the weighted-average chemical shift of this solution should lie between $+43$ and $+51$ ppm.

In the study of cadmium binding by Suwannee River fulvic acid (*17*), the authors interpreted their NMR data in terms of a simple 1:1 metal–ligand complex, and they estimated the chemical shifts of the free Cd^{2+} ion and the "pure" complex to be $+48.3$ and -13.6 ppm, respectively. They apparently did not realize that cadmium exists almost entirely as the free Cd^{2+} ion in 1 M Cd(ClO$_4$)$_2$, which was used as an external standard solution to define a chemical shift of zero ppm. In actuality, the chemical shift of $+48.3$ ppm is attributable to a mixture of the free Cd^{2+} ion and its chloro complexes, as described in the preceding paragraph. The chemical shift of -13.6 ppm is likewise some kind of weighted-average value for solutions containing mainly chloro complexes and fulvic acid complexes of cadmium. Under similar conditions of pH and Cd/C ratio (but in the absence of Cl^{-}) that were used in this study and in the study of cadmium binding by soil fulvic acid (*18*), the weighted-average chemical shift of organically complexed cadmium was more shielded.

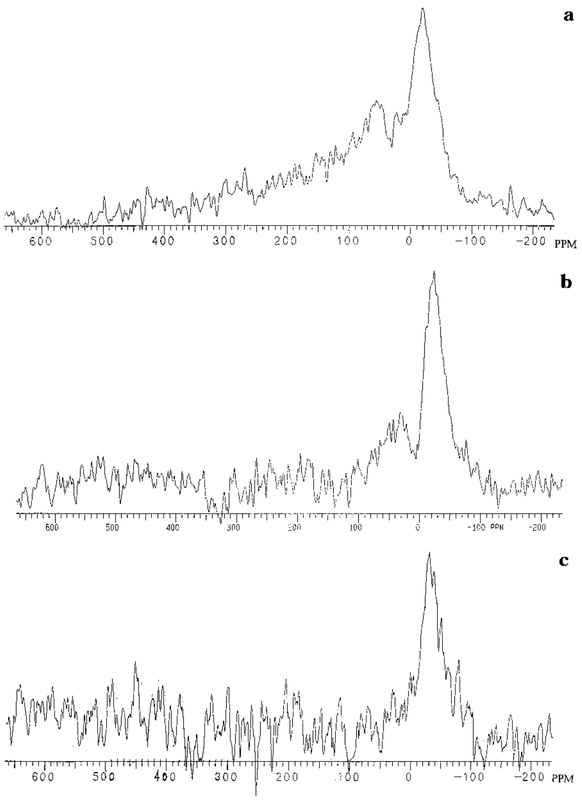

FIGURE 3. ^{113}Cd NMR spectra of solutions containing (a) 0.0055 M Cd(ClO$_4$)$_2$, 0.80 M dissolved organic carbon (DOC), pH 9.0; (b) 0.0022 M Cd(ClO$_4$)$_2$, 0.80 M DOC, pH 8.4; and (c) 0.0011 M Cd(ClO$_4$)$_2$, 0.86 M DOC, pH 8.7.

In contrast to the simple weighted-average NMR spectra that are obtained at acidic pH values, where metal–ligand reactions are relatively fast (Figure 2), the NMR spectra at alkaline pH (Figure 3) are much more complex. The three samples whose NMR spectra are given in Figure 3a–c differ slightly in pH (9.0, 8.4, and 8.7, respectively) and in DOC concentration (0.80, 0.80, and 0.86 mol/L, respectively), but the main difference in the solutions is the total cadmium concentration (5.5×10^{-3}, 2.2×10^{-3}, and 1.1×10^{-3} mol/L, respectively).

The spectrum in Figure 3a was measured at the same Cd/C ratio as the spectra in Figure 2. The difference is striking. The broad maximum at about -10 to -30 ppm confirms that Cd^{2+} is largely bound to oxygen donor atoms, just as was the case at acidic pH. The significant peak area at positive chemical shifts (especially between $+40$ and $+70$ ppm) provides direct evidence that a significant fraction of the Cd^{2+} is probably bound by N donor atoms. The samples whose spectra are shown in Figure 3, panels b and c, contain progressively less Cd^{2+}, and the downfield peak between $+40$ and $+70$ ppm gradually disappears. This may indicate that, even at pH 8.4–9.0, Cd^{2+} still reacts preferentially with carboxylate ions, presumably due to competitive binding of H^{+} by N and S donor atoms.

Despite the poor signal-to-noise ratio of the spectra in Figure 3, it is evident from the complexity of these spectra that metal–ligand reactions at alkaline pH are simply too slow to yield weighted-average NMR spectra. Among the factors that might contribute to slower reaction rates is the much lower concentration of free Cd^{2+} in the alkaline solutions. Reaction rates that are proportional to the concentration of free Cd^{2+} would decrease by several orders of magnitude as pH is increased from 3.6 to 9.0. Of course, other factors may be involved, but, whatever the explanation, the reaction rates are definitely slower at alkaline pH values.

Probably the greatest surprise in this study is the lack of evidence for coordination of Cd^{2+} by S donor atoms, even in samples where the Cd/C ratio is only one-fourth the S/C ratio of the NOM and at alkaline pH values where competitive binding of H^+ should be less important. A probable explanation is found in the very recent publication of Morra et al. (*28*), who, using XANES spectroscopy, have determined that most of the S in Suwannee River fulvic acid is in the +5 or +6 oxidation state. The Suwannee River NOM used in this research is very similar to Suwannee River fulvic acid in many respects, so the abundance of reduced S may be so low that its interaction with Cd^{2+} could not be observed in this study.

This study provides direct evidence regarding the nature of cadmium binding sites in NOM. At Cd/C ratios of about 0.001−0.007 in the pH 3−9 range, Cd^{2+} is primarily complexed via O donor atoms, probably in carboxyl groups. At alkaline pH values, Cd^{2+} is also definitely present in binding sites that contain N donor atoms. No evidence of Cd^{2+} ions coordinated by S donor atoms was observed in the NMR spectra, even at Cd/C ratios that were significantly lower than the S/C ratio of the NOM. Cadmium−NOM exchange rates are affected by the concentration of free Cd^{2+} ion. At acidic pH values, where the concentration of the free Cd^{2+} ion is higher, cadmium−NOM exchange rates are relatively fast, and only a single weighted-average peak is observed in the NMR spectra. At alkaline pH, Cd−NOM exchange rates are much slower, and broad, complex NMR spectra are obtained.

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