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# Pseudopolarographic Determination of Cd<sup>2+</sup> Complexation in Freshwater

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Pseudopolarography was used to detect Cd<sup>2+</sup> complexes in samples collected at several locations along the Potomac River in June and September, 2004. Irrespective of site and sampling time, no weak inorganic Cd<sup>2+</sup> species were present. However, up to two stable Cd<sup>2+</sup>-organic complexes were detected at each site. These unknown Cd<sup>2+</sup> complexes were characterized by their half-wave potential ( $E_{1/2}$ ). The  $E_{1/2}$  values indicated certain Cd<sup>2+</sup> complexes were common at different sites during each sampling but different complexes were observed in June and September. A Cd<sup>2+</sup> chelate scale, generated from model ligands, was used to estimate the thermodynamic stability constants ( $K_{\text{THERM}}$ ) of the unknown complexes, which ranged from  $\log K_{\text{THERM}} = 21.5$ – $32.0$ . Pseudopolarography did not recover all Cd<sup>2+</sup> in the samples. This was partly attributed to highly stable Cd-sulfide species; owing to the presence of acid volatile sulfide at concentrations greater than total dissolved Cd<sup>2+</sup>. These electrochemically inert species may be multinuclear Cd-sulfide clusters and/or nanoparticles with  $K_{\text{THERM}}$  values that exceed the detection window of pseudopolarography ( $\log K_{\text{THERM}} > 34.4$ ).

## 1. Introduction

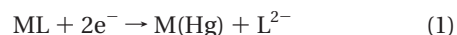
Cadmium is regarded as a priority contaminant in water bodies because it is a low level toxicant that has a strong tendency to bioaccumulate in the food web (1). The bio-availability and toxicity of Cd is mainly controlled by its dissolved free metal ion concentration (2). Decreasing the concentration of free metal ion by complexation with organic ligands diminishes toxicity (3). This is generally true for Cd (4); however, a few studies reported increased toxicity of Cd upon complexation as it facilitated Cd<sup>2+</sup> uptake by daphnid (5), phytoplankton, and zooplankton (6, 7).

Voltammetric stripping techniques are widely used to study metals in aquatic environments as they offer (sub)-nanomolar detection limits, extremely high sensitivity, and the ability to differentiate between different physicochemical forms (8). Anodic stripping voltammetry (ASV) has been widely used to investigate complexation of Cd<sup>2+</sup> (2, 8–20) as it is able to react directly on the electrode to form an amalgam [Cd(Hg)].

Pseudopolarography has been successfully used to study metal complexation with a variety of ligands in model

electrolyte solutions and natural waters (2, 9, 11, 21–29). This technique does not require addition of chemicals that would otherwise change the natural equilibrium and distribution of species; and thus allows the study of the actual metal complexes in solution. Previous studies (21, 24, 25, 30, 31) have fully described the theory of pseudopolarography and its application to metal speciation; a synopsis is given below (see the Supporting Information for more detail).

Pseudopolarography involves performing several successive ASV experiments; each with a different deposition potential ( $E_{\text{dep}}$ ) that is varied more negatively from the free metal reduction potential. The Cd<sup>2+</sup> complexes detected by pseudopolarography involve direct irreversible reduction of the complex at the electrode. This electrochemically destroys complexes by breaking metal–ligand bonds. The metal is subsequently reduced to an amalgam at the electrode surface (eq 1). Upon reoxidation during an anodic scan, the complex does not reform during the analysis as only the metal ion gives an anodic current on reoxidation. Thus, anodic currents are due to the reoxidation of Cd(Hg) to free/labile Cd<sup>2+</sup> and not to any complex. The plot of anodic peak currents against



$E_{\text{dep}}$  yields sigmoid curves analogous to a dc polarogram, and thus is called a pseudopolarogram (28). These curves reflect the thermodynamic and kinetic properties of the complex (21, 23); and are shifted toward more negative potentials relative to the reduction of the free metal ion (32). The magnitude of the shift is directly related to the thermodynamic stability constant ( $K_{\text{THERM}}$ ) of the complex (eqs 2 and 3). The more negative the half-wave potential ( $E_{1/2}$ ) of a sigmoid curve the more stable the complex (33).

$$E_{1/2} = E'_{1/2} - (0.0591/n)\log K_{\text{THERM}} \quad (2)$$

$E_{1/2}$  = observed reduction potential for the complex;  $E'_{1/2}$  = formal reduction potential for the divalent metal;  $n$  = number of e<sup>−</sup> transferred;  $K_{\text{THERM}}$  = stability constant for the metal–ligand complex (eq 3) where {} indicates activities of metal (M) and ligand (L). Thermodynamic stability constants

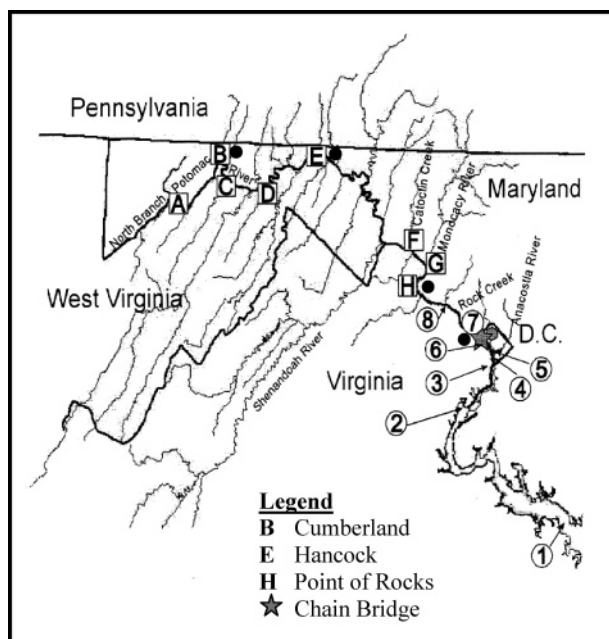
$$K_{\text{THERM}} = \text{ML}/\{\text{M}^{2+}\}\{\text{L}^{2-}\} \quad (3)$$

( $K_{\text{THERM}}$ ) for unknown ligands bound to Zn (22), Cu (25), and Pb (27) in natural waters have been determined from chelate scales for each metal. These were constructed from plots of known  $\log K_{\text{THERM}}$  values, for selected metal(II) complexes, against corresponding  $E_{1/2}$  values determined by pseudopolarography. The detection window of this method is limited by Na<sup>+</sup> reduction that starts to occur at  $E_{\text{dep}}$  about −1.7 V (27). Hence information on discrete metal complexes using pseudopolarography is limited to  $E_{\text{dep}}$  equal to and more positive than −1.7 V.

Previous pseudopolarographic studies were unable to completely recover all dissolved Zn (22), Cu (25), and Pb (27) in natural samples. This was attributed to electrochemically inert complexes that were organic (25, 27, 34) and/or inorganic in nature. The latter was postulated to involve highly stable multinuclear metal sulfide clusters and/or nanoparticles (27, 35–38). These species have been observed in oxic estuarine (39, 40) and fresh (37) waters for Fe, Cu, and Zn. The low reactivity of metal sulfide clusters has been attributed to their extended structures that exhibit covalent bonding (35, 37, 38); which allow them to persist in oxic waters.

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**FIGURE 1.** Potomac watershed showing USGS gauge stations, the filled circles (●) denote sampling sites.

Pseudopolarography has been used to study  $\text{Cd}^{2+}$  complexation with inorganic (9, 15, 19) and organic (15, 19, 29) ligands as well as natural humic (41) and fulvic (8, 16, 41) acids. Most of these studies were performed in acidic model electrolyte solutions; some were also performed in high ionic strength. The application of pseudopolarography for determination of  $\text{Cd}^{2+}$  complexation in unaltered natural freshwater is scarce or nonexistent.

The objectives of this study were to employ pseudopolarography to detect  $\text{Cd}^{2+}$  complexes in unaltered samples collected along the Potomac River and estimate their  $K_{\text{THERM}}$ . The latter was achieved by generating a  $\text{Cd}^{2+}$  chelate scale using model organic ligands. The possibility of Cd-sulfide complexes contributing to Cd speciation in the Potomac River was assessed by measuring the acid volatile sulfide (AVS) content of samples. The formation, stoichiometry, and stability of some Cd-sulfide species were determined from titrations involving  $\text{Cd}^{2+}$  and sulfide.

## 2. Experimental Section

Chemicals used in this study were of analytical grade. All solutions were prepared in deionized water (18.4 MΩ cm). All plasticware was acid washed with 10% HCl, rinsed thoroughly with deionized water, dried, and triple bagged to ensure trace metal clean conditions.

On 12 June and 16 September, 2004, water samples were collected at four sites along the Potomac River: Cumberland, MD; Hancock, MD; Point of Rocks, MD; and Chain Bridge, D.C. (Figure 1). A Teflon bailer attached to nonmetallic line was used to collect 2 L of surface water at each site. Samples were vacuum filtered through an acid washed 47 mm diameter 0.4 μm Isopore polycarbonate membrane (Millipore) loaded into a Nalgene filter stack. Filtration was performed on site in a glovebag to avoid contamination and dissolution of particles during storage. The filtrate was transferred to acid washed 50 mL polypropylene tubes (Falcon), quick-frozen by dry ice, and stored for metal speciation analysis by pseudopolarography.

Pseudopolarography was performed with 10 mL of sample, in an acid washed Teflon polarographic cell, which was deaerated with Ar (ultra high purity) prior to analysis. Electrochemical measurements were performed with an EG&G Princeton Applied Research model 303A static drop-

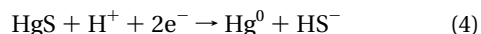
ping mercury electrode, in hanging mercury drop mode, coupled to an Analytical Instrumentation Systems, Inc. model DLK-100A voltammetric analyzer. The cell stand was modified to use a saturated calomel electrode (SCE). Square wave anodic stripping voltammetry (SWASV) was used for all analyses (scan rate of 100 mVs<sup>-1</sup>; potential range -1.3 to 0 V; 20 mV pulse height). Pseudopolarographic determination of  $\text{Cd}^{2+}$  complexes involved decreasing the  $E_{\text{dep}}$  from -0.50 to -1.70 V by 0.05 V increments.  $\text{Cd}^{2+}$  was reduced and deposited on the mercury drop for 10 min at each  $E_{\text{dep}}$ . In each voltammogram, the concentration of  $\text{Cd}^{2+}$  was determined by the anodic current produced at -0.62 V - the specific stripping peak potential for  $\text{Cd}^{2+}$ .

Total dissolved  $\text{Cd}^{2+}$  at each site was determined from samples that were UV-irradiated for 5 h and analyzed by SWASV with  $E_{\text{dep}}$  -1.5 V.  $\text{Cd}^{2+}$  was quantified by a standard curve generated by standard additions into the sample matrix. Standard solutions were prepared by dissolving  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Fisher) in 0.1 M  $\text{HNO}_3$ .

Determination of AVS was performed according to a previously reported method (42). Samples were acidified with 3 M HCl in a sealed system at room temperature. The released AVS was swept via Argon into a trap of 1 M NaOH and quantified by square wave voltammetry (SWV).

Two titration experiments were conducted to determine the stoichiometries and stability constants of Cd-sulfide complexes; the method was adapted from previous work involving other metal-sulfide complexes (35, 43). A 1 mM  $\text{Cd}^{2+}$  stock solution was prepared in 0.1 M  $\text{HNO}_3$ . Sulfide stock solutions were prepared daily by dissolving  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  (Fisher) in deaerated, deionized water to yield 2-3 mM. Sulfide was added in increments of about 1-2 μM to a solution that contained 10 μM  $\text{Cd}(\text{NO}_3)_2$ , 0.3 M KCl, and 5 mM HEPES (buffered at pH 7.5). The model solution was deaerated with Ar prior to the sulfide titration. After each sulfide addition, SWV was used to measure  $\text{Cd}^{2+}$ ; which entailed a 2 s conditioning step at -0.1 V followed by scanning from -0.1 to -1.5 V at a rate of 200 mVs<sup>-1</sup> with a 50 mV pulse height. The peak potential for the reduction of  $\text{Cd}^{2+}$  to the amalgam was observed at -0.70 V in the voltammogram due to chloride complexation.

$\text{Cd}^{2+}$  was also incrementally added to a model solution containing about 10 μM  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , 0.1 M  $\text{NaNO}_3$  and 1 mM HEPES buffer (pH 7.6). Free sulfide was also measured by SWV, using the same parameters as the first titration. The reduction of HgS (eq 4) yields free sulfide, which was identified by a peak centered near -0.64 V in the voltammogram. The

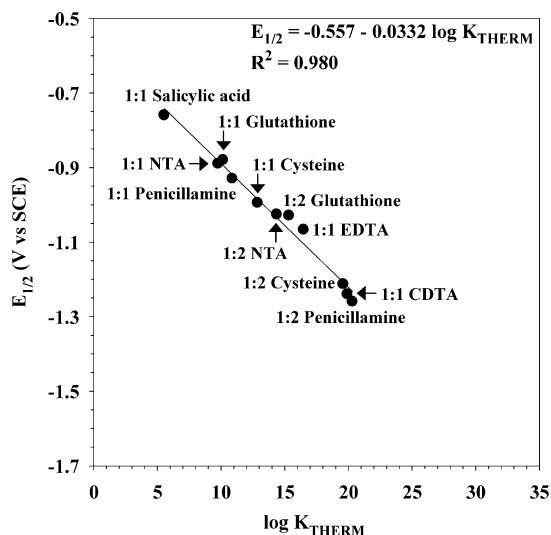


above Cd-sulfide solutions were also titrated with acid to pH 1 and monitored for sulfide using SWV. A sulfide signal was detected only at pH ≤ 3; indicating Cd-sulfide species were deprotonated above pH 3.

To determine whether Cd-sulfide complexes were electroactive, additional experiments were conducted using SWASV to measure any  $\text{Cd}^{2+}$  in model solutions containing 0.1 to 10 μM Cd-sulfide (Cd:S ratios were 1:1). SWASV parameters were: scan rate of 200 mVs<sup>-1</sup>; potential range of -1.5 to -0.1 V; 50 mV pulse height. Deposition times ranged from 0.5 to 5 min at  $E_{\text{dep}}$  -1.5 V. No  $\text{Cd}^{2+}$  was detected.

## 3. Results and Discussion

**3.1. Chelate Scale.** A  $\text{Cd}^{2+}$  chelate scale was developed to ascertain the stability of the unknown  $\text{Cd}^{2+}$  complexes detected in Potomac River samples using pseudopolarography. Seven model ligands (Table S1 in the Supporting Information), with a variety of functional groups, were allowed to react with  $\text{Cd}^{2+}$  to form eleven complexes with metal:ligand ratios of 1:1 and 1:2 that had a range of



**FIGURE 2.** Chelate scale for the complexation of  $\text{Cd}^{2+}$  with selected model organic ligands in UV-irradiated Sargasso seawater.

thermodynamic stabilities. Pseudopolarography was performed on all  $\text{Cd}^{2+}$  complexes; the resulting  $E_{1/2}$  was plotted against the corresponding literature (44–48)  $\log K_{\text{THERM}}$  for each complex to construct the  $\text{Cd}^{2+}$  chelate scale (Figure 2).  $K_{\text{THERM}}$  data account for the  $\text{Cd}^{2+}$  and ligand side reactions and are pH independent. Hence the  $\text{Cd}^{2+}$  chelate scale is applicable to freshwater samples even though it was developed in UV-irradiated Sargasso seawater. This is supported by the work of Branica and co-workers (19, 49, 50) in which an  $E_{1/2} = -0.9$  V was reported for the irreversible reduction of  $\text{Cd}^{2+}$ –NTA in 0.1 M electrolyte solutions. This value closely agrees with the  $E_{1/2} = -0.89$  V determined for  $\text{Cd}^{2+}$ –NTA reduction in seawater (Table S1 in the Supporting Information). Moreover,  $\Delta E_{1/2} = 60$  mV was observed for  $\text{Cd}^{2+}$  complexation in seawater. This shift was also reported for  $\text{Cd}^{2+}$  complexation in 0.1 M KCl (30).

The linearity of the  $\text{Cd}^{2+}$  chelate scale (Figure 2) indicates  $E_{1/2}$  values identified in pseudopolarograms can be used to determine  $K_{\text{THERM}}$  of unknown  $\text{Cd}^{2+}$  complexes present in natural water samples. The observed slope of 0.0332 for the  $\text{Cd}^{2+}$  chelate scale is comparable to a two electron-transfer value of 0.0295; indicating near Nernstian behavior. This supports the use of pseudopolarography to provide reliable empirical estimations of stability data for  $\text{Cd}^{2+}$  complexation as previously found for Zn (22), Cu (25), and Pb (27).

Although  $\text{Cd}^{2+}$  complexes with a maximum of  $\log K_{\text{THERM}} = 20.33$  were used to generate the  $\text{Cd}^{2+}$  chelate scale (Figure 2), the linear correlation between  $E_{1/2}$  and  $\log K_{\text{THERM}}$  is expected beyond this point. Taylor et al. (51) observed linearity up to  $\log K_{\text{THERM}} = 49$  for  $\text{Fe}^{3+}$ –organic complexes. Using the  $\text{Cd}^{2+}$  chelate scale (Figure 2),  $\text{Cd}^{2+}$  complexes with  $\log K_{\text{THERM}} \leq 34.4$  should be observed using pseudopolarography – before  $\text{Na}^+$  reduction begins to interfere at  $E_{\text{dep}}$  more negative than  $-1.7$  V. The  $[\text{Na}^+]$  of Potomac River samples ranged from 0.2 to 0.6 mM (Table 1).

Table 1 shows pseudopolarography detected  $\text{Cd}^{2+}$  complexes in Potomac River samples that had estimated  $\log K_{\text{THERM}}$  greater than 1:2  $\text{Cd}^{2+}$ –penicillamine; the strongest complex used to develop the chelate scale (Figure 2). Similar observations were made by Croot et al. (25) for  $\text{Cu}^{2+}$  complexation by algal and cyanobacterial exudates. Complexation by specialized biological chelators may also be responsible for strong  $\text{Cd}^{2+}$  complexes as discussed below.

**3.2. Potomac River Samples.** Metal speciation is influenced by site-specific seasonal and spatial variations (52). Thus, samples were collected at four sites along the Potomac River on 12 June and 16 September, 2004. The matrices of the June and September samples were similar (Table S2 in the Supporting Information). However, dissolved organic carbon (DOC) and chlorophyll *a* were higher in June (Table 1; Table S2 in the Supporting Information), indicating greater primary productivity in summer. The total dissolved  $\text{Cd}^{2+}$  in the samples ranged from 2.55 to 4.62 nM (Table 1), which were comparable to previous Potomac River studies (53, 54).

Pseudopolarography was used to investigate  $\text{Cd}^{2+}$  complexation. Weak inorganic  $\text{Cd}^{2+}$  complexes, involving ligands such as chloride, hydroxide, and sulfate, were not detected in any samples as there were no sigmoid shaped polarographic waves at  $-0.62$  V (Figures 3 and 4), which is the  $E_{1/2}$  for free  $\text{Cd}^{2+}$ . The presence of sigmoid curves at  $E_{\text{dep}}$  values more negative of  $-0.62$  V indicated stronger  $\text{Cd}^{2+}$  complexes; possibly involving humic substances and other organic ligands owing to the presence of DOC (Table 1).

Lam et al. (16) also reported the absence of inorganic  $\text{Cd}^{2+}$  in Rideau River but detected a  $\text{Cd}^{2+}$ –organic complex ( $\log K_{\text{THERM}} = \sim 15$ ) by pseudopolarography. Xue and Sigg (17, 18) used competitive ligand exchange to study Cd speciation in lakes. Most complexes detected had conditional constants around log 10, which were more stable than Cd bound to fulvic and humic acids indicating other highly specific ligands were present (18).

**TABLE 1.** Data for Unknown  $\text{Cd}^{2+}$  Complexes Detected in Surface Potomac River Water Collected on 12 June and 16 September, 2004<sup>a</sup>

sample	date	$[\text{Na}^+]_{\text{total}}$ (mM)	[DOC] (mM)	$[\text{SO}_4^{2-}]$ (mM)	[AVS] (nM)	$[\text{Cd}^{2+}]_{\text{total}}$ (nM) <sup>b</sup>	$E_{1/2}$ (V)	$\log K_{\text{THERM}}$	$[\text{Cd}^{2+}]_{\text{compound}}$ (nM) <sup>c</sup>	% $\text{Cd}_{\text{detected}}$ <sup>d</sup>
Cumberland (upstream)	12/6/04	0.37	1.14	1.21	88	3.95	–1.41	25.8	0.51	1.7 <sup>e</sup>
	16/9/04	0.61	0.31	1.26	16	3.49	–1.62	32.0	0.52	29.5
Hancock	12/6/04	0.35	4.39	0.45	184	2.95	–1.53	29.3	0.24	10.4
	16/9/04	0.24	0.35	0.42	47	3.64	–1.45	27.0	1.68	77.2
							< –1.70	> 34.4	N/A	N/A
Point of Rocks	12/6/04	0.33	1.23	0.30	70	3.60				10.3 <sup>e</sup>
	16/9/04	0.22	0.26	0.24	18	2.55	–1.45	27.0	2.00	84.6
Chain Bridge (downstream)	12/6/04	0.31	2.63	0.21	50	2.57	–1.27	21.5	0.33	40.7
							–1.56	30.2	0.68	
	16/9/04	0.20	0.33	0.21	6	4.62	–1.34	23.7	0.26	50.9
							–1.46	27.3	1.92	

<sup>a</sup> N/A = Not applicable. <sup>b</sup>  $[\text{Cd}^{2+}]_{\text{total}}$  = total concentration of dissolved  $\text{Cd}^{2+}$  detected by ASV after UV-irradiation. <sup>c</sup>  $[\text{Cd}^{2+}]_{\text{compound}}$  = concentration of  $\text{Cd}^{2+}$  bound in compounds detected by pseudopolarography. <sup>d</sup> %  $\text{Cd}_{\text{detected}}$  = % of total dissolved  $\text{Cd}^{2+}$  detected by pseudopolarography = (maximum  $\text{Cd}^{2+}$  anodic current detected by pseudopolarography/total  $\text{Cd}^{2+}$  anodic current detected by ASV after UV-irradiation). <sup>e</sup> No sigmoid curves were observed in the pseudopolarogram, but Cd current was detected at the end of these pseudopolarography experiments.



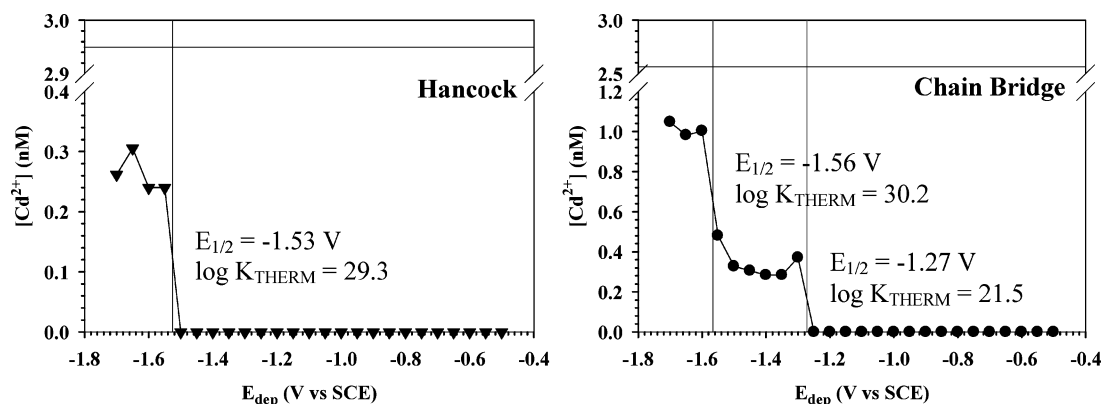


FIGURE 3. Cadmium pseudopolarograms for surface Potomac River water collected on 12 June 2004 (The horizontal lines represent total  $\text{Cd}^{2+}$ ).

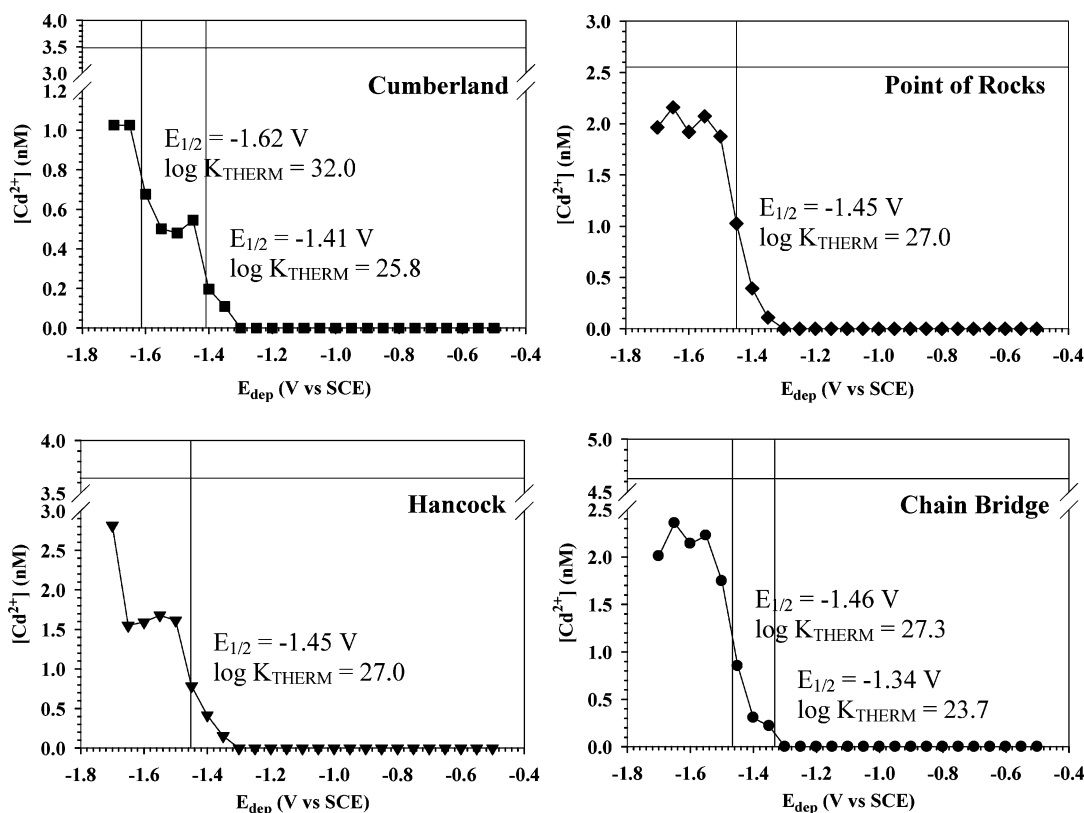


FIGURE 4. Cadmium pseudopolarograms for surface Potomac River water collected on 16 September 2004 (The horizontal lines represent total  $\text{Cd}^{2+}$ ).

In June, no  $\text{Cd}^{2+}$  complexes were detected in samples collected at Cumberland and Point of Rocks. However, a complex with  $E_{1/2} = -1.53$  V ( $\log K_{\text{THERM}} = 29.3$ ) was present at Hancock (Figure 3); which was comparable to a complex observed at Chain Bridge ( $E_{1/2} = -1.56$  V,  $\log K_{\text{THERM}} = 30.2$ ). These two complexes were considered the same within experimental error ( $\pm 20$  mV). Another  $\text{Cd}^{2+}$  complex with  $E_{1/2} = -1.27$  V ( $\log K_{\text{THERM}} = 21.5$ ) was also present at Chain Bridge (Figure 3). The  $E_{1/2}$  of this complex was similar to a 1:2  $\text{Cd}^{2+}$ –penicillamine complex ( $E_{1/2} = -1.26$  V, Figure 2). Hence  $\text{Cd}^{2+}$  complexation in the Potomac River may involve multidentate ligands.

Two  $\text{Cd}^{2+}$  complexes were also detected at Chain Bridge in September; however, these were different from the complexes observed in June as determined by their  $E_{1/2}$ , which were  $-1.34$  and  $-1.46$  V (Figure 4). The strongest complex identified at Chain Bridge ( $E_{1/2} = -1.46$  V,  $\log K_{\text{THERM}} = 27.3$ ) may have also occurred at Hancock and Point of Rocks where compounds with  $E_{1/2} = -1.45$  V ( $\log K_{\text{THERM}} = 27.0$ ) were

observed (Figure 4). Moreover, a similar complex with  $E_{1/2} = -1.41$  V ( $\log K_{\text{THERM}} = 25.8$ ) was detected at Cumberland.

A second stronger  $\text{Cd}^{2+}$  compound ( $E_{1/2} = -1.62$  V;  $\log K_{\text{THERM}} = 32.0$ ) was detected at Cumberland in September (Figure 4). The increase in  $[\text{Cd}^{2+}]$  at the end of the pseudopolarogram for the Hancock sample also indicated the presence of a second  $\text{Cd}^{2+}$  complex (Figure 4); its  $E_{1/2}$  was beyond the detection window of  $\text{Cd}^{2+}$  pseudopolarography ( $E_{1/2} < -1.7$  V, Table 1). The concentration of this unresolved species is at least equivalent to the weaker  $\text{Cd}^{2+}$  complex (1.68 nM, Table 1).

$\text{Cd}^{2+}$  was equally distributed between the two complexes observed in the September Cumberland sample ( $\sim 0.5$  nM, Table 1). However, irrespective of sampling time, this was not the case for  $\text{Cd}^{2+}$  complexation at Chain Bridge; where  $\text{Cd}^{2+}$  predominantly existed in the more stable complex (Table 1).

The results of pseudopolarography indicated  $\text{Cd}^{2+}$  complexes with the same  $E_{1/2}$  values (within experimental error  $\pm 20$  mV) existed at different spatial locations along the Potomac River on 12 June and 16 September, 2004 (Table 1). This may be attributed to river transport. We cannot indicate if this was the same  $\text{Cd}^{2+}$  complex or a different species with the same  $E_{1/2}$ . Localized ligand production at each site may yield complexes with the same  $E_{1/2}$ . Although complexes with the same  $E_{1/2}$  were observed in June and September, no complexes were common in both samplings.

Irrespective of location and collection date, Figures 3 and 4 showed incomplete recovery of  $\text{Cd}^{2+}$  by pseudopolarography. The percentage of total  $\text{Cd}^{2+}$  detected by pseudopolarography (%  $\text{Cd}_{\text{detected}}$ ) at Cumberland, Hancock, Point of Rocks and Chain Bridge were 1.7, 10.4, 10.3, and 40.7%, respectively, in June (Table 1). The remainder of the  $\text{Cd}^{2+}$  at each site existed in very stable complexes ( $\log K_{\text{THERM}} > 34.4$ ) that were beyond the detection window of pseudopolarography.  $\text{Cd}^{2+}$  occluded in colloids may also not be electroactive and would contribute to the undetectable  $\text{Cd}^{2+}$ .

The trend of %  $\text{Cd}_{\text{detected}}$  values for the June samples indicated that highly stable  $\text{Cd}^{2+}$  complexes with  $\log K_{\text{THERM}} > 34.4$  generally decreased downstream. This is true for the September samples collected at Cumberland, Hancock and Point of Rocks where the %  $\text{Cd}_{\text{detected}}$  values were 29.5, 77.2, and 84.6, respectively. The only exception to the observed trend was the 50.9%  $\text{Cd}_{\text{detected}}$  for Chain Bridge in September (Table 1). However, the %  $\text{Cd}_{\text{detected}}$  at Chain Bridge was comparable in June and September; which was not the case for the other three sites. Therefore, environmental conditions at Chain Bridge may have a greater influence on  $\text{Cd}^{2+}$  speciation than seasonal effects.

Previous pseudopolarographic studies (22, 25, 27) also reported incomplete metal recovery. Croot et al. (25) showed cyanobacterial exudates formed highly stable complexes with  $\text{Cu}^{2+}$  ( $\log K_{\text{THERM}} = 36$ ), some were electrochemically inert to pseudopolarography. Coordination of  $\text{Cd}^{2+}$  by specialized biomolecules may also contribute to the undetectable Cd. The stabilities of these  $\text{Cd}^{2+}$  complexes are expected to be less than those with  $\text{Cu}^{2+}$  according to the Irving–Williams series. This is demonstrated by complexation with hydroxamate siderophores, such as desferrioxamine B and E, which decrease in stability in the order  $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$  (45). However, biomolecules with chelating moieties containing sulfur may form more stable complexes with  $\text{Cd}^{2+}$ . This can be observed by the greater stability of  $\text{Cd}^{2+}$ -penicillamine compared to  $\text{Cd}^{2+}$ -NTA complexes (Table S1 in the Supporting Information). It is conceivable that specialized biological chelators with multiple sulfur ligating atoms would yield more stable  $\text{Cd}^{2+}$  complexes such as those observed in Figures 3 and 4, as well as those undetectable by pseudopolarography. An increase in ligating atoms per ligand molecule was shown to increase  $\Delta E_{1/2}$  and stability of Zn complexes (22). However, at present,  $\log K_{\text{THERM}}$  data for  $\text{Cd}^{2+}$  complexation by ligands with multiple sulfur ligating atoms is scarce or nonexistent.

In addition to organic complexation, metal sulfide clusters may contribute to metals unrecovered by pseudopolarography (27). Rozan et al. (37) reported high concentrations of total dissolved sulfide, including metal sulfides, in the Potomac River. According to Hard–Soft Acid–Base theory, a soft donor such as sulfide is expected to form stable complexes with soft  $\text{Cd}^{2+}$ . Hence the fraction of Cd not recovered by pseudopolarography may include Cd-sulfide species.

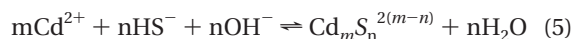
All samples contained AVS (Table 1), which supports the presence of Cd-sulfide species. For each site, [AVS] varied inversely to the %  $\text{Cd}_{\text{detected}}$  (Figure S1 in the Supporting Information); which qualitatively indicated inorganic Cd-sulfide species contributed to the highly stable  $\text{Cd}^{2+}$  com-

pounds that were beyond the detection window of pseudopolarography. Rozan et al. (37, 55) reported Zn-sulfide and Cu-sulfide complexes are thermodynamically and kinetically stable. This can also be expected for Cd-sulfide species. The lower %  $\text{Cd}_{\text{detected}}$  in June may also be a result of the greater primary productivity in summer;  $\text{Cd}^{2+}$  would be strongly bound by biomolecules containing sulfur ligating atoms. Xue and Sigg (18) also reported the occurrence of strong ligands linked to biological productivity.

Samples collected at Cumberland contained the greatest  $[\text{SO}_4^{2-}]$  (Table 1), which may reflect the effects of coal mining in the area.  $[\text{SO}_4^{2-}]$  was similar at each site in June and September. However, [AVS] was higher in the June samples (Figure S1 in the Supporting Information) indicating greater bacterial sulfate reduction in summer as observed by Koretsky et al. (56). Irrespective of sampling time, [AVS] decreased downstream from Hancock. This trend was also observed for  $[\text{SO}_4^{2-}]$  and supports sulfate reduction as a source of the sulfide. However, Cumberland, which had the highest  $[\text{SO}_4^{2-}]$  of all the samples, contained less [AVS] than Hancock, the adjacent downstream sample site (Figure S1 in the Supporting Information). This was observed on both sampling occasions and indicated precipitation or oxidation reactions at Cumberland lowered [AVS].

Higher [AVS] at each site in summer appeared to lower %  $\text{Cd}_{\text{detected}}$  (Figure S1 in the Supporting Information). This may have ecotoxicological importance. Di Toro and co-workers (57, 58) demonstrated that AVS reduced the concentration of  $\text{Cd}^{2+}$  in sediment porewater, and hence, was not toxic to amphipods. All complexes identified in Potomac River samples had  $\log K_{\text{THERM}} \geq 21.5$ . The high stability of these complexes suggests Cd present in the Potomac River may not be readily bioavailable. Moreover, Point of Rocks (September) sample contained excess ligands (Figure S2 in the Supporting Information) that can decrease the concentration of free  $\text{Cd}^{2+}$  and, therefore, its toxicity. Pseudopolarography confirmed excess ligands as the same sample equilibrated with a 20 nM  $\text{Cd}^{2+}$  spike showed an increase in concentration of the original  $\text{Cd}^{2+}$  compound ( $E_{1/2} = -1.45$  V,  $\log K_{\text{THERM}} = 27.0$ , Figure S3 in the Supporting Information). A new but weaker  $\text{Cd}^{2+}$  complex ( $\log K_{\text{THERM}} = 5.2$ ) was observed at  $E_{1/2} = -0.73$  V.

**3.3. Cadmium Sulfide.** AVS data suggested Cd-sulfide species contributed to the fraction of Cd not recovered by pseudopolarography and thus had  $\log K_{\text{THERM}} > 34.4$ . To verify this, the stability of Cd-sulfide complexes were determined by the mole ratio method (35, 36, 59). Titration experiments indicated  $\text{Cd}^{2+}$  and sulfide formed complexes with Cd:S ratios of 1:1 and 1:2 (Figure S4 in the Supporting Information); which were deprotonated ( $\text{Cd}_m\text{S}_n^{2(m-n)}$ ) at pH > 3. The  $K_{\text{THERM}}$  of Cd-sulfide species formed by reaction 5 were calculated with eq 6. With the exception of CdS, all Cd-sulfide complexes



$$K_{\text{THERM}} = \frac{[\text{Cd}_m\text{S}_n^{2(m-n)}]}{[\text{Cd}^{2+}]^m [\text{HS}^-]^n [\text{OH}^-]^n} \quad (6)$$

identified by the mole ratio method had  $\log K_{\text{THERM}} \geq 43.4$  (Table 2); which exceeded the detection window of  $\text{Cd}^{2+}$  pseudopolarography ( $\log K_{\text{THERM}} \leq 34.4$ ). Moreover, analysis of model Cd-sulfide solutions by SWASV showed Cd-sulfide complexes were not detectable. These experiments were performed at  $E_{\text{dep}} = -1.5$  V and indicated Cd-sulfide complexes that were present had  $\log K_{\text{THERM}} > 28.4$ . Hence CdS ( $\log K_{\text{THERM}} = 23.4$ , Table 2) was not a significant species. These results indicated that  $\text{CdS}_2$ , higher order unprotonated multinuclear sulfide clusters and/or nanoparticles may

**TABLE 2. Stability Constants of Cadmium Sulfide Complexes Determined by the Mole Ratio Method**

Cd:S ratio	m	n	$\log K_{\text{THERM}}^a (\text{Cd}_m\text{S}_n^{2(m-n)})$	
			average	SD
1:1	1	1	23.4	0.3
	2	2	51.8	0.5
	3	3	80.3	0.7
	4	4	108.8	0.9
1:2	1	2	43.4	0.4
	2	4	91.6	0.8
	3	6	140.1	1.2

<sup>a</sup> Cd-sulfide species were stable at pH > 3.

contribute to the pool of  $\text{Cd}^{2+}$  that was not detected by pseudopolarography.

Conditional stability constants for CdS and  $\text{CdS}_2$  were also calculated. These values were comparable to previously reported values (Table S3 in the Supporting Information). Hence,  $\log K_{\text{THERM}}$  values for Cd-sulfide species determined by the mole ratio method are reliable. This technique was also used to identify multinuclear sulfide clusters for Ag (43), Cu (38), Pb (27), and Zn (36).

The existence of these higher order unprotonated species for Cu, Pb, and Zn are supported by Fourier transform mass spectrometric evidence (27, 37). Rozan et al. (37) reported  $\text{Fe}_2\text{S}_4\text{OH}_5$ ,  $\text{Cu}_3\text{S}_3$ ,  $\text{Cu}_4\text{S}_6$ ,  $\text{Zn}_3\text{S}_3$ , and  $\text{Zn}_3\text{S}_4$  in river water samples that included the Potomac River. Hence it is plausible that multinuclear Cd-sulfide clusters and/or nanoparticles were present in the Potomac River at the time of sampling; particularly since sulfide forms more stable complexes with  $\text{Cd}^{2+}$  (Table 2) than  $\text{Zn}^{2+}$  (43). Moreover, competition experiments confirmed that  $\text{Cd}^{2+}$  displaced  $\text{Zn}^{2+}$  in sulfide species (Figure S5 in the Supporting Information).

Weak inorganic  $\text{Cd}^{2+}$  species were not present in Potomac River samples but pseudopolarography detected one or two stable ( $\log K_{\text{THERM}} \geq 21.5$ ), soluble  $\text{Cd}^{2+}$  compounds at each site. Multidentate organic ligands are likely responsible for these data and indicate Cd in the Potomac River may not be bioavailable.  $E_{1/2}$  data showed certain complexes were common at different locations during each sampling. However, similar complexes were not observed in June and September. Pseudopolarography could not account for all the  $\text{Cd}^{2+}$  present in the samples. The presence of AVS indicated that the undetectable  $\text{Cd}^{2+}$  occurred as highly stable inorganic sulfide species, which may be stabilized by organic matter.

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## Supporting Information Available

Additional theory, Figures and Tables include typical water chemistry of samples, complexation capacity, Cd-sulfide titrations, conditional stability constants, and exchange reactions involving  $\text{Cd}^{2+}$  and ZnS. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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