Soil & Sediment Contamination, 15:497–510, 2006
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ISSN: 1532-0383 print / 1549-7887 online
DOI: 10.1080/15320380600847864

Free Cyanide Sorption on Freshwater Sediment and Model Components

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The sorption of free cyanide (HCN) on mineral components of sediment, activated carbon, and a freshwater sediment was studied via batch experiments in synthetic freshwater at pH 6.4–7.6. It was found that free cyanide did not sorb to any significant extent on sediment mineral components, but did sorb strongly to activated carbon and moderately to a freshwater sediment. Results of experiments with 100 and 150 μg/L free cyanide spike amounts resulted in no observed sorption to kaolin clay, Ottawa sand, or alumina in the synthetic freshwater. Extensive removal of free cyanide from the aqueous phase was observed in the partitioning experiments with the powdered activated carbon. Results with whole sediment indicated up to 46% removal of free cyanide from the aqueous phase in experiments with 20 and 50 μg/L free cyanide. The organic-carbon-normalized distribution coefficient K_{oc} ($= C_s/C_w f_{oc}$) for free cyanide sorption on the activated carbon ($f_{oc} = 1.0$), 4.2 L/g_s, was similar to the K_{oc} value for free cyanide sorption on the freshwater sediment ($f_{oc} = 0.0031$), approximately 12.9 L/g_s. The results indicate that free cyanide can sorb to sediments with organic carbon content under freshwater conditions, primarily through interaction of HCN with organic carbon in the sediment.

Keywords Activated carbon, sediment, cyanide, sorption, distribution coefficient

Introduction

While free cyanide (HCN, CN^-) is readily biodegradable under both aerobic and anaerobic conditions in water (Ebbs *et al.*, 2006) and thus is generally not persistent in aquatic sediments (Nakles *et al.*, 2006), its sustained presence in sediments can pose risks to benthic organisms. Free cyanide present on a continuing basis in water overlying sediment will contaminate sediment through diffusion into sediment porewater and, depending on the solids present, by sorption on sediment particles. No regulatory sediment quality criteria have yet been established for cyanide compounds in the U.S. or elsewhere, but sediment quality guidelines for free cyanide near or equal to 0.1 μg/g in sediments have been developed for particular applications (SAIC, 1991; Persaud *et al.*, 1993; Nakles *et al.*, 2006).

The USEPA Equilibrium Partitioning (EqP) model for sediment (USEPA, 2003) provides a means for estimating bulk sediment concentrations of free cyanide that are protective of benthic organisms (Gensemer *et al.*, 2006). This approach assumes that the sediment porewater concentration of the bioavailable form of a toxic substance mediates toxicity to benthic organisms. If free cyanide is assumed to exist in the water column at a concentration

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equal to the water quality criterion (i.e., level below which aquatic life is protected), the corresponding bulk sediment concentration can be estimated using the EqP approach. This is done by assuming the porewater is in diffusive equilibrium with the overlying water (i.e., overlying water and porewater constituent concentrations are the same) and then estimating the additional contribution of sorption on sediment particles to the bulk sediment concentration. Hence, knowledge or estimation of free cyanide sorption on sediment particles is needed to develop a sediment quality guideline.

There are no available data for free cyanide sorption to sediment, and very little data available for free cyanide sorption to individual sediment components like iron oxides (Theis and West, 1986) or clays (Schenck and Wilke, 1984). Limited data are available for free cyanide sorption to whole soils (Alesii, 1976).

Free cyanide showed no sorption to goethite, a common form of iron oxide in soils and sediments, for pH 3–10, ionic strength (I) ranging from 0.01 to 0.1 M KNO_3 and free cyanide of 10^{-4} to 10^{-3} M (Theis and West, 1986). In flow-through column studies with various soils and potassium cyanide (KCN) solutions in deionized water, Alesii (1976) found that the mass of cyanide sorbed correlated strongly (0.94) with percent iron oxide. The extent of cyanide sorption also had a fair correlation (0.68) to the percent clay in the soil. There was no correlation (<0.25) to CEC (cation exchange capacity), pH, or surface area. The column studies of Alesii (1976) were, however, conducted with biologically active soils, and it is likely that most of the observed free cyanide removals were due to biodegradation.

Chatwin *et al.* (1988) determined that the magnitude of free cyanide sorption on soils correlated strongly with soil organic carbon content. Further, it was proposed that sorption of free cyanide to soil was followed by oxidation to cyanate. The mechanism of interaction of HCN with organic carbon has not been established but likely involves weak site–specific binding involving C—C or C—H interactions.

Additional support for the role of organic carbon as a sorbent for free cyanide in soils is provided by the well-demonstrated ability of activated carbon to remove free cyanide from water. For example, Guo *et al.* (1993) demonstrated that free cyanide at a concentration of 1 ppm sorbs significantly to granular activated carbon (GAC) across the pH range 4 to 9. Generally, uptake was independent of pH except for a slight increase at pH 8–9. Guo *et al.* (1993) also observed that dissolved humic acid, Ca(II), Mg(II), Al(III), and Fe(III) reduced cyanide uptake by 30–50%, probably through competitive sorption and complexation of cyanide in solution.

The objective of this research was to develop some initial data for free cyanide sorption onto a freshwater sediment, and also onto model sediment components to assess their relative contributions to overall sorption. Free cyanide solid-water partitioning experiments were conducted with models of some common freshwater sediment components (aluminum oxide, sand, clay, organic carbon) to gather information about the capacities of these materials to sorb free cyanide in the neutral pH range (6–8) where HCN is the predominant form of free cyanide ($pK_a = 9.24$ at 25°C). Powdered activated carbon (PAC) was used as a model organic carbon component, though it is recognized to be far different from sediment natural organic carbon. PAC was used to investigate the affinity of pure organic carbon for HCN in the same experimental system used for the sediment and the various pure phase mineral sorbents investigated. Equilibrium sediment-water partitioning experiments were also run with free-cyanide-spiked suspensions of a whole sediment collected from Lake Pymatuning, a freshwater lake in northwestern Pennsylvania. Results were used to determine solid-water distribution coefficients for free cyanide interaction with the whole sediment and sediment components.

Table 1
Physical characteristics of solid sorbents investigated

Solid tested	Bulk density (g/cm^3)	Particle size	Molecular formula	Supplier
Alumina (C30)	2.42	0.086–0.152 mm (100-200 mesh)	$Al(OH)_3 \cdot 3H_2O$	Alcoa, Inc.
Kaolin	1.8-2.6	NA[1]	$H_2Al_2Si_2O_8 \cdot H_2O$	Fisher Sci.
Ottawa Sand	2.65	0.541–0.686 mm (20-30 mesh)	SiO_2	Fisher Sci.
PAC (WPH)	NA[1]	95% < 0.043 mm (325 mesh)	NA[1]	Calgon Carbon, Inc.

[1] NA indicates this information was not available.

Materials and Sediment Characterization

The physical and chemical properties of the model sediment components and the whole sediment used in batch sorption experiments were characterized. Additionally, for the freshwater sediment used, the overlying water obtained from the sampling location was analyzed. This information was used to define the experimental conditions, as well as to interpret the free cyanide removal observed in the sorption experiments.

Characteristics and Preparation of Model Sorbents

The following solid materials were used in batch equilibrium sorption tests to determine the degree of free cyanide sorption to sediment components: hydrated alumina ($Al(OH)_3 \cdot 3H_2O$, Alcoa, Inc., Port Allen, LA), kaolin clay (Fisher Scientific, Pittsburgh, PA), Ottawa sand (Fisher Scientific, Pittsburgh, PA), and powdered activated carbon (Calgon Carbon, Pittsburgh, PA). Physical characteristics, including particle size ranges, can be found in Table 1. All solids were autoclaved prior to use to ensure abiotic conditions in the sorption experiments. The powdered activated carbon (PAC) was Calgon Carbon type WPH, a virgin activated carbon manufactured for treatment of potable water. Both the hydrated alumina and Ottawa sand were pre-washed with deionized (DI) water before autoclaving. The solids were placed in a large, acid-washed evaporating dish and washed at least three times with DI water. The evaporating dish was then placed in a 99°C oven for at least an hour to remove excess water. Kaolin clay and PAC were not washed due to the fineness of the particles.

Sediment Collection and Characterization

A freshwater lake sediment was collected from Lake Pymatuning in northwestern Pennsylvania on July 27, 2003. Two grab samples were collected 0.6–1.8 m from shore in 0.6 m of water near Tuttle Point at Lake Pymatuning. The samples were placed in 3.8 L polyethylene containers that were then sealed, placed in a cooler, and transported to the Hauck Environmental Engineering Laboratories at Carnegie Mellon the same day. The sediment samples were stored in a refrigerator at 4°C. Prior to any work with the sediment, excess water was poured from the sediment samples, they were mixed thoroughly and homogenized, and then replaced in the storage containers. Unless indicated otherwise, a sample of whole sediment was analyzed, with only large gravel pieces removed.

Table 2
Lake Pymatuning sediment characteristics

Characteristic	Value	Method	Reference
D_{60}	1.5 mm	ASTM D 421-85	ASTM, 1988
D_{10}	0.3 mm	ASTM D 421-85	ASTM, 1988
Water Content	16–23% by wt.	ASTM D 2216-98	ASTM, 2001
pH	6.21 in DI water 5.84 in 0.01 M $CaCl_2$	ASTM D 4972-01	ASTM, 2001
Organic Carbon Content	0.20% (dry wt.)—whole sed. 0.31% (dry wt.)—sed. fraction <0.500 mm	ASTM D 3178-89	ASTM, 2002
Acid Volatile Sulfide	Not detectable (det. limit = 0.74 μmol/g)	EPA AVS	USEPA, 1991
Fe, total	12,000 mg/kg dry sediment	ICP	USEPA, 1996
Al, total	4,700 mg/kg dry sediment	ICP	USEPA, 1996
Mg, total	1,200 mg/kg dry sediment	ICP	USEPA, 1996
Ca, total	630 mg/kg dry sediment	ICP	USEPA, 1996
K, total	500 mg/kg dry sediment	ICP	USEPA, 1996
Mn, total	340 mg/kg dry sediment	ICP	USEPA, 1996
Si, total	330 mg/kg dry sediment	ICP	USEPA, 1996
P, total	160 mg/kg dry sediment	ICP	USEPA, 1996
Ba, total	26 mg/kg dry sediment	ICP	USEPA, 1996
Zn, total	26 mg/kg dry sediment	ICP	USEPA, 1996
Cu, total	8.9 mg/kg dry sediment	ICP	USEPA, 1996
Ni, total	8.5 mg/kg dry sediment	ICP	USEPA, 1996
Pb, total	7.9 mg/kg dry sediment	ICP	USEPA, 1996
Sr, total	4.5 mg/kg dry sediment	ICP	USEPA, 1996

The sediment was analyzed to obtain the following physical and chemical characteristics: particle size distribution, water content, pH, organic carbon content, total metals, mineral composition (by X-ray diffraction), and Acid Volatile Sulfide/Simulatenously Extracted Metals (AVS/SEM). Selected results are given in Table 2; additional data are provided in Higgins (2004). The sediment was not analyzed for background free cyanide as the lake is in a park and not subject to industrial inputs.

Particle size distribution was determined via ASTM Method D421-85 (ASTM, 1988). The dried sediment was sieved and the particle size distribution showed the sediment to be predominantly sand with less than 0.8% silt. Sixty percent of the particles were finer than 1.5 mm diameter while 10% were finer than 0.3 mm (see Table 2).

Data for water content, pH, and organic carbon content are listed in Table 2. The sediment had a water content of 12–23% by weight. The dried sediment was acidic (pH = 6.21 in DI water, 5.84 in 0.01 M $CaCl_2$), and the whole sediment had a low organic carbon content of 0.20% by weight. The organic carbon content of an autoclaved fraction that passed a 0.500 mm sieve was 0.31%, a slightly higher organic carbon content than the whole sediment. Both analyses were done using a modified procedure for measuring carbon in coal and coke, ASTM Method D3178-89 (ASTM, 2002).

Total metals were measured on acid digest solutions via inductively-coupled-plasma emission spectroscopy (ICP) by Severn Trent Laboratories, Pittsburgh, PA (USEPA, 1996). Results of selected (highest) total metals measurements are listed in Table 2. Approximately 2.5 g of oven-dried sediment were digested with concentrated nitric acid, followed by dilution with hydrochloric acid. This sample was then nebulized and combusted in a plasma torch. Emissions were analyzed with atomic emission spectroscopy. Iron was the most abundant element in the sediment, followed by aluminum.

Dried sediment, <0.500 millimeter size, was also analyzed with X-ray diffraction to identify mineral components. The minerals detected included muscovite ($H_2Al_3(SiO_4)_3$), albite ($NaAlSi_3O_8$), quartz (SiO_2), and manganese sulfide (MnS). These results are consistent with the particle size distribution analysis, which indicated that the sediment consisted of primarily sand and clay. The fraction retained on a 0.500 millimeter sieve was also scanned and there was no difference between this fraction and the fraction that passed through the sieve. Thus, analyses of the <0.500 millimeter size were assumed to be valid for the whole sediment.

Measurement of AVS/SEM was made according to established EPA methods (USEPA, 1991) by Severn Trent Laboratories, Pittsburgh, PA. AVS was not detected in the sample (Table 2), indicating that the MnS detected via X-ray diffraction was present only at low levels. Nondetectable AVS is not unusual for a surface sediment after a rainy period: rainfall can result in AVS removal (Ankley *et al.*, 1996) and it rained for several days prior to sampling and on the day of sampling.

Overlying Water Characterization

Concomitant with the sediment sample collection from Lake Pymatuning at Tuttle Point, samples of overlying water were obtained. Two 3.8 L polyethylene terephthalate containers were filled, rinsed with lake water, and then filled to capacity and sealed. The containers were placed in a cooler and transported to the Hauck Environmental Engineering Laboratories at Carnegie Mellon the same day. The water samples were stored in a refrigerator at 4°C.

The lake water samples were analyzed for pH, specific conductivity, total organic carbon (TOC), total inorganic carbon (TIC), and alkalinity. Results indicated that the Lake Pymatuning water overlying the sediment was a relatively soft water with moderate alkalinity. The water had pH = 7.4, with an alkalinity of 50.2 mg/L as $CaCO_3$. Additionally, the specific conductance was 341 μS/cm, TIC was 7.75 mg/L as C, and the TOC was 6.00 mg/L as C. Based on these data, it was decided to use a synthetic freshwater with characteristics of a relatively soft water in the batch partitioning experiments. A recipe for a synthetic, soft freshwater developed by EPA for use in toxicity testing was selected for use (USEPA, 1993). This recipe is given in Table 3.

Sorption Test Methods

Batch equilibrium partitioning tests were conducted with free cyanide and several solids (freshwater sediment, alumina, kaolin clay, Ottawa sand, and PAC) in separate sets of experiments. An identical procedure was used for all solids tested. All experiments were conducted at room temperature (21 ± 2°C).

A spiked solution of potassium cyanide was prepared using de-aerated synthetic freshwater. For each solid studied, 50 mL polycarbonate centrifuge tubes were used as batch reactors. Each tube was covered with aluminum foil during the experiment, to prevent photolysis of any metal-cyanide complexes formed. For each solid sorbent, initial kinetics

Table 3
Synthetic freshwater recipe[1]

Ingredient	Units	Soft freshwater
$NaHCO_3$	mg/L	48
$CaSO_4 \cdot 2H_2O$	mg/L	30
$MgSO_4$	mg/L	30
KCl	mg/L	2
pH	—	7.2–7.6
Hardness	mg/L as $CaCO_3$	40

[1] Source: US EPA, 1993.

experiments, varying in length from 24 to 117 hours, were run to ascertain if sorption occurred and when equilibrium was reached. For all experiments, an initial aliquot of the cyanide-spiked freshwater solution was added to the centrifuge tube. Pre-measured dry solid masses were then added, and spiked solution added to top off the tube. At least two reactors (replicates) were prepared for each experimental condition studied. After addition of solids to the spiked synthetic freshwater solution, the resulting pH was in the range of 6.2–8.0, depending on the solid added. The tubes were then capped and placed on a rotator with a speed of 18 rpm. At time intervals or after a pre-determined equilibration time (24–72 hours depending on experimental conditions), centrifuge tubes were removed from the rotator and centrifuged, with the supernatant liquid removed for analysis. Controls were run for all experiments to quantify losses of HCN (primarily by volatilization), for which data were corrected. Additional spiking experiments with larger volumes (140 mL) of cyanide and freshwater sediment were also performed to determine the extent of metal-cyanide complexation, if any, that occurred during the batch sorption experiments.

For the routine small-volume experiments, only free cyanide measurements were made. Free cyanide concentrations were measured using the Free Cyanide by Microdiffusion Method, ASTM D4282-02 (ASTM, 2001). Total and free cyanide measurements were made on large-volume samples for the experiments with the whole sediment in which complexation of cyanide by metals released from the sediment was a possibility. Total cyanide was measured by acid distillation using *Standard Methods* Method 4500 CN^- C (APHA, 1998).

Finally, results of the batch equilibrium partitioning (aqueous phase cyanide concentrations, C_w, and solid phase cyanide concentrations, C_s) were used to determine equilibrium distribution coefficients ($K_d = C_s/C_w$). The cyanide sorbed to the solid was determined by a mass balance calculation, using the measured supernatant concentrations and the known initial mass added.

Results

Kinetic experiments were conducted with the model sorbents to determine sorption equilibration times. The results of kinetic experiments with model sorbents are shown in Figure 1. The results indicated that there was little to no sorption ($<10\%$) of free cyanide to alumina, kaolin clay, or Ottawa sand in the synthetic freshwater system. Given that free cyanide is known to not sorb to iron oxide (Theis and West, 1986), clays (Schenk and Wilke, 1984), or sand (Ghosh *et al.*, 1999, who studied sorption of weak-acid dissociable cyanide) and

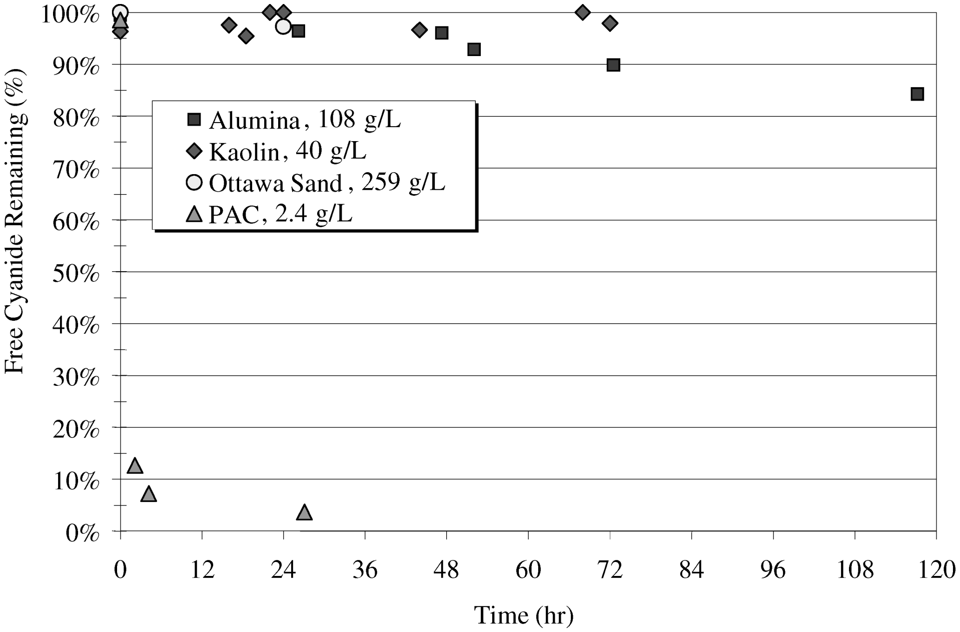

Figure 1. Kinetics data for sorption of free cyanide to model sorbents in synthetic freshwater. Nominal free CN spike conc. = 150 μg/L, Final pH = 8.1–8.4 for Alumina, 6.8–7.7 for Ottawa Sand, and 7.5–8.4 for PAC. No pH measurements were taken for Kaolin.

the fact that $<$10% of the free cyanide sorbed after 24 hours, the systems with the mineral sorbents were determined to have reached equilibrium within 24 hours. In contrast, nearly complete uptake of free cyanide by PAC was observed in less than 36 hours. Thus, additional batch sorption experiments were only conducted with the PAC.

To develop an isotherm for HCN sorption on PAC in freshwater, additional batch partitioning studies were conducted with varying amounts of PAC (25, 50, 75, and 100 mg of PAC) and three cyanide concentrations (50, 100, and 150 μg/L). An equilibration period of 24–36 hours was used, depending on experimental conditions. The final pH in the batch reactors varied from 7.4 to 8.0. Significant sorption of free cyanide on PAC was observed. Only the experiments with the 100 and 150 μg/L nominal spikes yielded sufficient free cyanide in solution to determine extent of sorption. An isotherm plot of C_s versus C_w for all the PAC batch sorption data combined is given in Figure 2. Tabulated experimental data and ancillary details are given in Table 4. The K_d values from the PAC batch sorption experiments ranged from 2.7–9.8 L/g_s. The slope of the isotherm plot, determined using a least-squares fit of the data with the fit forced through the origin, gave a best-fit K_d value of 4.2 L/g_s ($R^2 = 0.4$), which is lower than the arithmetic average of the K_d values. Normalizing with an f_{oc} value of 1.0, the best fit K_{oc} value thus was 4.2 L/g_s. The scatter in Figure 2 is attributable to variable losses of volatile HCN during the experiment (identical correction for HCN loss was applied to all data in each set based on control results) and perhaps by the variation in pH as well.

Initial sorption kinetics experiments were also run with the Lake Pymatuning sediment to determine the equilibriation time to be used in subsequent batch testing. Results from the kinetics experiment with dried and autoclaved Lake Pymatuning sediment, given in Figure 3, showed that equilibrium was reached in approximately three days for the sorbate/sorbent ratios tested. Thus, a 72-hour equilibration period was used in the subsequent batch testing.

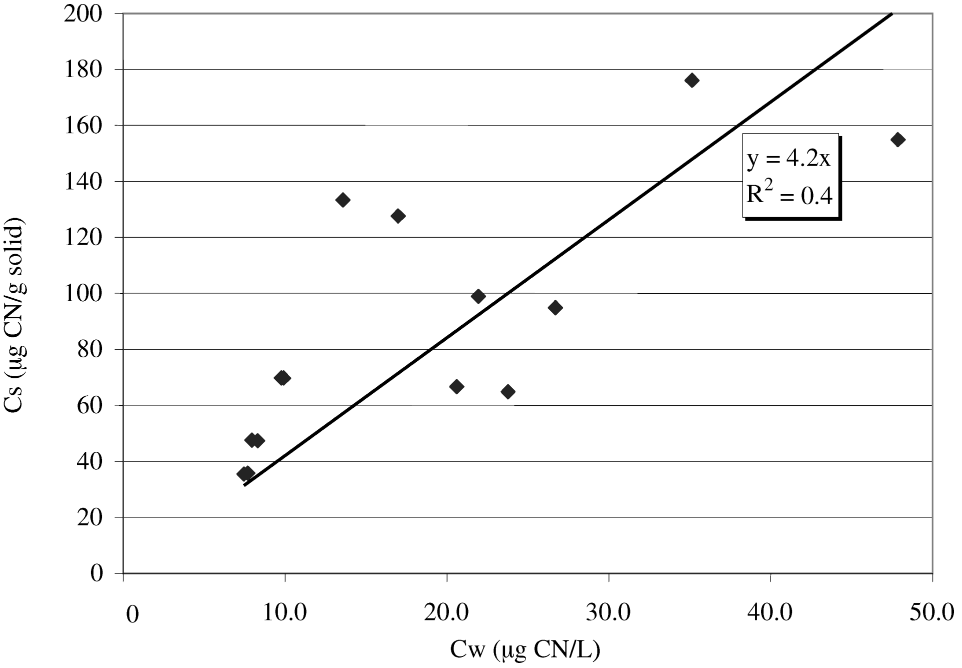

Figure 2. C_s versus C_w for PAC batch sorption experiments with HCN in synthetic freshwater. Solid conc. = 0.6–2.4 g/L, Nominal free cyanide spike conc. = 100–150 μg/L, Final pH = 7.4–8.0.

The batch sorption studies conducted with Lake Pymatuning sediment involved varying amounts of solid (0.15–1.5 g dried sediment) and four cyanide spike concentrations (20, 50, 100, and 150 μg/L), though only the lower two spike concentrations did not exceed the limited sorption capacity of the sediment. Equilibrations were performed in 50 mL polycarbonate reactors with subsequent analysis of free cyanide in the supernatant. Some larger volume (140 mL) experiments were conducted for selected conditions, so that both total and free cyanide measurements could be made. No significant differences were observed between total cyanide and free cyanide measurements, indicating complexation of free cyanide by metals released from the sediment did not occur (Higgins, 2004). Thus, decrease in the free cyanide concentration of the supernatant was attributed to sorption.

Results from batch equilibrium partitioning testing with Lake Pymatuning sediment were plotted on an isotherm graph, C_s versus C_w, as shown in Figure 4. Tabulated experimental data with ancillary details are given in Table 5, which includes information about the losses observed in the controls. Given that the controls were also autoclaved and did not have losses much larger than 6%, the autoclaving minimized or eliminated biological activity and losses via that pathway. The final pH in the batch reactors varied from 6.4 to 7.6. The data in Figure 4 include only those experiments in which the free cyanide in the spiked solution decreased by more than 10%, and two outliers are omitted. The measured K_d values for individual data points ranged from 0.024 to 0.108 L/g_s. A best-fit line of the data forced through the origin yielded a slope of 0.04 L/g_s, which corresponds to the best-estimate sediment experimental K_d value. If all sorption of HCN is attributed to organic carbon, then

$$K_{oc} = K_d/f_{oc} = K_d/0.0031$$

Table 4
Results of batch sorption testing with free CN and PAC in synthetic freshwater

Sample	PAC (mg)[1]	V_f, Spike volume (mL)	Solid dose (g/L)[1]	C_{spike}, CN^- spike (μg/L)[2]	Final CN^- (μg/L)[2,3]	Corrected $CN^- = C_w$ (μg/L)[4]	% Free CN Remaining[5]	C_s (μg/g)[6]	K_d (L/g)[7]
				100 μg/L nominal spike					
Control	NA	37	NA	93.9	87.6	93.9	100	NA	NA
1	25	41.5	0.60	93.9	10.8	17.0	18	127.6	7.5
2	25	41.5	0.60	93.9	7.3	13.6	14	133.3	9.8
3	50	41.5	1.2	93.9	3.7	9.9	11	69.7	7.0
4	50	41.5	1.2	93.9	3.5	9.8	10	69.8	7.2
5	75	41.5	1.8	93.9	1.7	7.9	8	47.6	6.0
6	75	41.5	1.8	93.9	2.1	8.3	9	47.3	5.7
7	100	41.5	2.4	93.9	1.5	7.7	8	35.8	4.6
8	101	41.5	2.4	93.9	1.2	7.5	8	35.5	4.8
				150 μg/L nominal spike					
Control	NA	37	NA	141	123	141	100	NA	NA
1	25	41.5	0.6	141	29.8	47.9	34	154.9	3.2
2	25	41.5	0.6	141	17.1	35.1	25	176.0	5.0
3	50	41.5	1.2	141	3.9	21.9	16	99.0	4.5
4	50	41.5	1.2	141	8.7	26.7	19	94.8	3.6
5	75	41.5	1.8	141	2.6	20.6	15	66.6	3.2
6	75	41.5	1.8	141	5.7	23.8	17	64.8	2.7
7	100	41.5	2.4	141	ND	ND	ND	50.4	ND
8	100	41.5	2.4	141	ND	ND	ND	50.5	ND

[1] NA indicates not applicable—no solid was added to Control experiments so listing of solid amounts or subsequent calculations using a solid dose were not applicable.

[2] ND indicates non-detect (below MDL of 1.0 μg/L) and further calculations using ND data was also indicated as "ND".

[3] Average of at least two replicate measurements of cyanide concentration.

[4] Corrected [CN^-] calculated by taking difference between final measured control cyanide concentration and initial spike amount; this amount was the cyanide lost during the course of the experiment, probably due to volatilization. It was assumed this loss was the same for all trials within a batch, so the same amount was added to the final cyanide concentration to yield the corrected cyanide concentration.

[5] The "corrected" cyanide concentration divided by the initial spike concentration.

[6] The concentration of cyanide sorbed to the solid, calculated by taking the difference between the spike concentration and final C_w concentration, normalizing for volume, and dividing by the mass of solid present:

$$C_s = (C_{spike} - C_w) \times V_f/PAC(g)$$

[7] $K_d = C_s/C_w$

and the K_{oc} of the test sediment was 12.9 L/g_s. This is about three times the K_{oc} value determined for PAC, $K_{oc} = 4.2$ L/g_s. As the calculated K_{oc} value is directly dependent on the f_{oc} value, which was very low for the sediment studied here (and determined for only one sample of the homogenized sediment), the K_{oc} values are reasonably comparable in that they are well within an order of magnitude of each other.

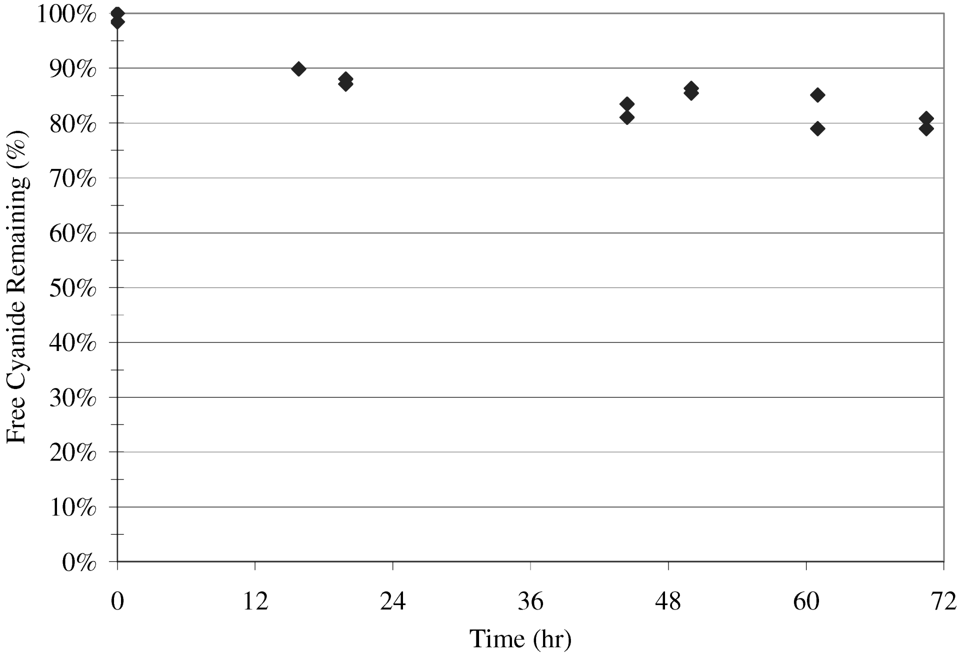

Figure 3. Kinetics data for sorption of free cyanide to Lake Pymatuning sediment in synthetic freshwater. Nominal free CN spike conc. = 150 μg/L. Sediment conc. = 36.7 g/L, Final pH= 6.4–7.1.

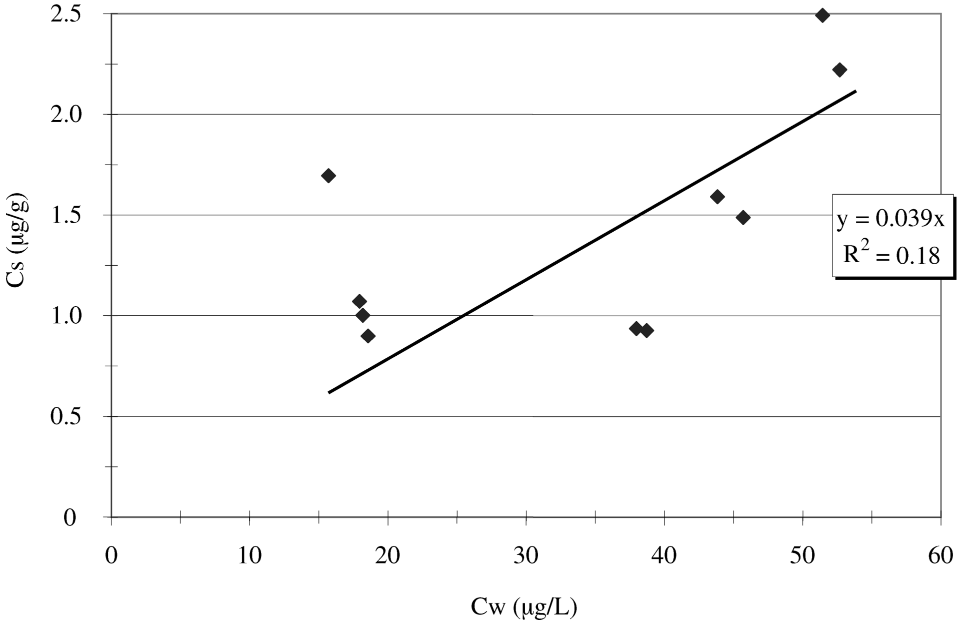

Figure 4. C_s versus C_w for Lake Pymatuning sediment batch sorption experiments with HCN in synthetic freshwater. Sediment conc. = 3.6–36.7 g/L, Nominal free CN spike conc. = 20–50 μg/L, Final pH = 6.4–7.6.

Table 5

Results of batch sorption testing with free CN and Lake Pymatuning sediment in synthetic freshwater

Sample	Sediment(g)	V_f, Spike Vol (mL)	Solid Dose (g/L)[1]	Initial pH	Final pH	C_{spike}, CN^- spike (μg/L)[2]	Final CN^- (μg/L)[2]	Corrected $CN^- = C_w$ (μg/L)[3]	% Free CN Remain[4]	C_s(μg/g)[5]	K_d (L/g)[6]	K_{oc} (L/g)[7]
20 μg/L Nominal Spike												
Control	NA	42	NA	8.665	8.325	21.8	17.1	21.8	100	NA	NA	NA
1	0.1514	42	3.6	8.78	7.52	21.8	13.8	18.6	85	0.90	0.048	15.6
2	0.1515	42	3.6	8.77	7.58	21.8	13.2	17.9	82	1.07	0.060	19.4
3	0.1513	42	3.6	8.76	7.61	21.8	11.0	15.7	72	1.70	0.108	34.8
4	0.1515	42	3.6	8.71	7.60	21.8	13.5	18.2	83	1.00	0.055	17.7
50 μg/L Nominal Spike												
Control	NA	43	NA	6.92	6.845	72.3	65.7	72.3	100	NA	NA	NA
1	0.1513	42	3.6	7.08	6.84	72.3	47.3	53.8	74	5.12	0.095	30.7
2	0.1517	42	3.6	6.98	6.75	72.3	47.0	53.6	74	5.19	0.097	31.3
3	0.3516	42	8.4	6.96	6.73	72.3	44.9	51.4	71	2.49	0.048	15.6
4	0.3708	42	8.8	6.95	6.71	72.3	46.1	52.7	73	2.22	0.042	13.5
5	0.7505	42	17.9	6.95	6.49	72.3	39.1	45.7	63	1.49	0.033	10.6
6	0.7512	42	17.9	6.99	6.54	72.3	37.3	43.8	61	1.59	0.036	11.6
7	1.504	41	36.7	6.94	6.38	72.3	31.4	38.0	53	0.94	0.025	8.1
8	1.504	42	36.2	6.91	6.38	72.3	32.2	38.7	54	0.93	0.024	7.7

[1] NA indicates not applicable – no solid was added to Control experiments so listing of solid amounts or subsequent calculations using a solid dose were not applicable.

[2] Average of at least two replicate measurements of cyanide concentration.

[3] Corrected [CN^-] calculated by taking difference between final measured control cyanide concentration and initial spike amount; this amount was the cyanide lost during the course of the experiment, probably due to volatilization. It was assumed this loss was the same for all trials within a batch, so the same amount was added to the final cyanide concentration to yield the corrected cyanide concentration.

[4] The "corrected" cyanide concentration divided by the initial spike concentration.

[5] The concentration of cyanide sorbed to the solid, calculated by taking the difference between the spike concentration and final Cw concentration, normalizing for volume, and dividing by the mass of solid present:

$$C_s = (\text{Cspike-}C_w) \times V_f/\text{sediment(g)}$$

[6] $K_d = C_s/C_w$

[7] $K_{oc} = K_d/f_{oc} = K_d/0.0031$

Discussion

Results of the batch sorption tests with model sorbents agree with literature findings. Theis and West (1986) found no measurable sorption of free cyanide on iron oxide across a range of pH values. Schenk and Wilke (1984) observed that free cyanide was not sorbed by sesquioxides or clay minerals, but was sorbed by humic acid. Alesii (1976) observed a correlation of free cyanide and the percent clay in soils, which is not consistent with the results of Schenk and Wilke (1984) or those obtained with kaolin clay in the work presented here. However, Alesii worked with biologically active soils, in a flow-through system, and biodegradation of free cyanide likely contributed to cyanide loss in the experiments. Chatwin *et al.* (1988) determined that free cyanide sorbs to soil organic carbon, and Guo *et al.* (1993) observed significant adsorption of free cyanide to granular activated carbon. These findings are consistent with the PAC sorption experiments conducted here.

The K_{oc} value determined for free cyanide (HCN) sorption to PAC (4.2 L/g_s) differs by about a factor of three from that determined for HCN sorption to Lake Pymatuning sediment (12.9 L/g_s). It should be noted that the C_s values determined in the PAC sorption experiments were an order of magnitude larger than those measured in the experiments with Lake Pymatuning sediment. If C_s is normalized to organic carbon content, the organic-carbon-normalized solid phase solid concentrations observed in the sediment experiments were an order of magnitude larger than those observed in the PAC experiments. Differences in the values are likely due to the different types of organic carbon present in each solid.

Thus, a first approximation of HCN sorption on a whole sediment in a freshwater system can be obtained via the expression

$$C_s = (12.9\mathrm{L}/g_s)C_w f_{oc}$$

where f_{oc} is the measured organic carbon content of the sediment and C_w is in μg/L. It is emphasized that the experiments conducted in this study were conducted in freshwater with pH in the range 6.4–7.6, so the K_{oc} value is only valid for these conditions. However, Guo *et al.* (1993) indicate that free cyanide sorption to activated carbon is relatively constant for the pH range 5–9, with slightly greater sorption at pH 8–9. This observation, coupled with consideration that the pK_a for HCN dissociation is 9.24, suggests that the K_{oc} value of 12.9 L/g_s might provide reasonable predictions at pH values as low as 5 and up to about 8.2 in freshwater systems considering that HCN is the dominant form of free cyanide throughout this pH range and sorption appears to be on organic carbon exclusively.

Conclusions

In model freshwater systems at pH 6.4–7.6, free cyanide (HCN) did not sorb to a significant extent on mineral components of sediments (alumina, kaolin clay, sand), but free cyanide did sorb strongly to activated carbon and moderately to a freshwater sediment. The freshwater sediment tested was predominantly sand and clay, with a small organic carbon content (0.31% by weight). Given experimental data showing no sorption of free cyanide to representative inorganic components of the sediment, it appeared that free cyanide sorbed to the organic carbon fraction of the sediment.

The organic-carbon normalized distribution coefficient K_{oc} ($= C_s/C_w f_{oc}$) for free cyanide sorption on the activated carbon, 4.2 L/g_s, was similar to the K_{oc} value for free cyanide sorption on the Lake Pymatuning sediment ($f_{oc} = 0.0031$), approximately 12.9 L/g_s. Overall, these results indicate that free cyanide can sorb to sediment under freshwater conditions, primarily through interaction of HCN with organic carbon in the sediment. For the low free cyanide concentrations investigated in this study and generally of interest in water quality assessments (5–150 μg/L), HCN sorption can be estimated for freshwater systems through measurement of the organic carbon content of the sediment and use of the simple linear partitioning expression $C_s = 12.9\ L/g_s\ C_w\ f_{oc}$ where C_w is in μg/L. This work indicates the potential for free cyanide to sorb to sediments with organic carbon content in a freshwater system. It also provides a means for obtaining a quantitative estimate for free cyanide sorption on freshwater sediment, and thereby to make a first-order assessment of the potential for impact of free cyanide in the water column on benthic organisms.

Acknowledgements

This study was funded by the Water Environment Research Foundation (WERF), Alexandria, VA, under Project No. 01-ECO-1 with Parametrix, Inc., Carnegie Mellon University, and HydroQual, Inc. The authors thank Robert Gensemer and Rick Cardwell of Parametrix, Inc., Robert Santore and Paul Paquin of HydroQual, Inc., and Walter Berry of the U.S. EPA for helpful suggestions and insights in the planning of the study.

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