Supporting Information

Evaluation and Testing of Analytical Methods for Cyanide Species in Municipal and Industrial Contaminated Waters

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SI-1. Acquisition and Pretreatment of Contaminated Water Samples

Samples of municipal wastewater and contaminated groundwater from two industrial sites representing a range of matrix types were collected at each of five locations shown in Table 2 of the manuscript. For each water matrix, ten-gallon (approximately 37-liter) samples were acquired. From the 37 liters, two liters were taken for characterization analyses and 30 liters were adjusted to pH=12.5 with NaOH and then distributed into one-liter brown plastic bottles. The large sample was kept cool and in the dark after acquisition, and was preserved and subdivided into the brown plastic bottles as soon as possible. Groups of five one-liter samples were packed in coolers and shipped to each of the six participant labs for next day delivery.

A general protocol for sample acquisition and pretreatment is presented in Section SI-1.1. This general protocol was slightly revised in the sampling events for contaminated groundwater (CW1) and chlorinated POTW secondary effluent (CW3), as shown in Sections SI-1.2 and SI-1.3.

SI-1.1 General Sampling Protocol

- (1) Collect 10 gallons of water in two 5-gallon containers.
- (2) Prepare the bottles for the characterization analyses, i.e, two one-liter bottles unpreserved/unfiltered for pH, ORP, ALK, Residual Cl_2 , Cl^- , NO_2^- , NO_3^- , pH, SO_4^{2-} , S^{2-} and BOD, one 500 mL bottle (pre-preserved with base for CN^-), two 100 mL bottles (one pre-preserved with acid for metals and the other with base for SCN^-), and one 50 mL glass bottle (pre-baked) for TOC. The metal analyses include the following: Ag, Al, Cd, Ca, Co, Cu, Fe, K, Hg, Mg, Mn, Ni, Pb, Na, and Zn.
- (3) Ship the characterization samples to the characterization laboratory.
- (4) Test for Sulfide: Moisten the lead-acetate paper with acetate acid buffer at pH 4. With the help of a dropper, apply few drops of the water from the carboys on the moistened test paper. If the paper darkens, which indicates the presence of sulfide, add lead acetate, or if S^{2-} -concentration is too high (indicated by significant darkening of the test paper), add powdered PbCO_3 to prevent significant reduction in pH. Add a little bit of PbCO_3 and

check it again. This test is repeated until a drop of treated sample no longer darkens the acidified lead acetate test paper. The pH is monitored during PbCO_3 addition to make sure that the pH does not drop. If the test indicates presence of sulfide, oxidizing compounds such as residual chlorine would not be expected and the following test is not necessary.

- (5) Test for Residual Chlorine: Moisten the potassium iodide (KI) starch paper with acetate acid buffer at pH 4. With the help of a dropper, apply few drops of the water from the carboys on the moistened test paper. If the test paper turns blue, then pre-treat with sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$). Add a little bit of $\text{Na}_2\text{S}_2\text{O}_3$ and check it again. Don't add more than 0.1 gram $\text{Na}_2\text{S}_2\text{O}_3$ per liter.
- (6) In case of thiosulfate and lead carbonate addition, filter the treated water immediately into two other 5-gallon containers.
- (7) Add NaOH (pellets or liquid) to raise the pH to exactly 12.5. Distribute that water into 30 one liter brown plastic bottles.
- (8) Ship the samples to the five participating laboratories (5 one liter bottles to each lab).

SI-1.2 Specific Sampling Procedure for CW1 – Contaminated Groundwater

This was the first contaminated water sample collected, and the amount of water collected for was less than in subsequent sampling events.

- (1) Use a sampling pump and low-flow sampling procedures.
- (2) Fill up two one-liter bottles, one 500 mL bottle (preserved with base), two 100 mL bottles (one preserved with acid and the other with base), and one 50 mL glass bottle (pre-baked) directly with the water for characterization analysis.
- (3) Ship the characterization samples to the characterization laboratory.
- (4) Pump 7 gallons of water into two 5 gallon or one 8 gallon carboy with lid.
- (5) Test for Residual Chlorine: Moisten the KI starch paper with acetate acid buffer at pH 4. With the help of a dropper, apply few drops of the water from the carboys on the moistened test paper. If the test paper turns blue, then pre-treat with $\text{Na}_2\text{S}_2\text{O}_3$. Add a little bit of $\text{Na}_2\text{S}_2\text{O}_3$ and check it again. Don't add more than 0.1 gm $\text{Na}_2\text{S}_2\text{O}_3$ per liter.
- (6) Test for Sulfide: Moisten the Lead-Acetate paper with acetate buffer. With the help of a dropper, apply few drops of the water from the carboys on the moistened test paper. If the paper darkens, add lead acetate, or if S^{2-} concentration is too high, add powdered PbCO_3 to

prevent significant reduction in pH. Add a little bit of PbCO_3 and check it again. Monitor the pH during PbCO_3 addition to make sure that the pH does not drop.

- (7) In case of thiosulfate and lead carbonate addition, filter the treated water into another 8 gallon carboy. Add NaOH pellets (app. 1.264 gm/L) to raise the pH to exactly 12.5. Distribute that water into 24 one liter amber bottles.
- (8) Ship the samples to the five participating laboratories (4 one liter bottles to each lab):

SI-1.3 Specific Sampling Procedure for CW3 – Chlorinated POTW Secondary Effluent

Since it was necessary to implement dechlorination treatment for the chlorinated POTW secondary effluent sample, the step (5) of the general sampling protocol for testing residual chlorine was revised as follows:

- (5) To test the residual chlorine and dechlorinate the sample, the sample was sent back to the laboratory. The chlorine residual was analyzed with a titrator, then the minimum amount (approximately stoichiometric amount) of thiosulfate was added.

SI-2. Characterization of Contaminated Water Samples

Subsamples of each contaminated water sample were collected for characterization analyses and preserved appropriately. Characterization included analysis of major ions, metals, alkalinity, organic content (BOD, TOC), and total cyanide and thiocyanate. Table SI-1 lists the results of complete sample characterization. Characterization analyses were performed by the organizations that collected the samples or their designated laboratories. A list of specific sample preservation techniques and analytical methods used is available in Zheng (PhD Thesis, Carnegie Mellon University, 2001).

Table SI-1 – Characterization Data for Contaminated Waters ^a

Analyte	Contaminated Water					Units
	CW1	CW2	CW3	CW4	CW5	
Alkalinity	547	202	161	166	NA ^b	mg/L as CaCO ₃
BOD ₅	24.8	< 2	4	102	NA	mg/L
CBOD ₅	NA	< 2	3	NA	NA	mg/L
Chloride	14	124	114	688	6.6	mg/L
Chlorine - Residual	0.01	0.0	0.7	<0.030	NA	mg/L
Chlorine / Oxidants - Test Strip	NA	Neg ^c	Neg	NA	NA	
Cyanide - Total, Manual Dist	0.182	0.002	0.004	<0.010	0.0295	mg/L
Cyanide - WAD	NA	0.0002	0.0033	NA	NA	mg/L
Hardness	NA	NA	280	NA	NA	mg/L
Nitrogen - Ammonia (NH ₃ -N)	NA	0.10	0.00	25.40	<0.293	mg/L
Nitrogen - Nitrate (NO ₃ -N)	<0.1	7.21	10.98	<0.005	0.26	mg/L
Nitrogen - Nitrite (NO ₂ -N)	<0.1	0.00	0.10	<0.005	<0.1	mg/L
Nitrogen - Total Kjeldahl (TKN)	NA	0.70	1.54	NA	NA	mg/L
ORP	215	360	406	-190	NA	mV
Oxygen, Dissolved	NA	7.1	7.3	NA	NA	mg/L
pH	7.41	7.0	7.3	6.8	NA	pH Units
Phenol - Automated Dist	NA	NA	9	NA	NA	ug/L
Phenol - Manual Dist	NA	< 2	< 2	NA	NA	ug/L
Phosphorous - Total	NA	1.90	3.00	NA	NA	mg/L
Solids - Suspended	NA	< 2	< 2	NA	NA	mg/L
Solids - Total	NA	650	536	NA	NA	mg/L
Sulfate (SO ₄ ²⁻)	6.04	66.24	66	83.3	18.9	mg/L
Sulfide (S ²⁻)	<0.02	0.07	0.03	4.09	<0.02	mg/L
Sulfide - Test Strip	NA	Neg	Neg	NA	NA	
Thiocyanate	<0.005	0.10	NA	0.0468	0.005	mg/L
Total Arsenic (As)	NA	0.00	0.00	NA	NA	mg/L
Total Aluminum (Al)	0.0137	NA	NA	0.353	NA	mg/L
Total Barium (Ba)	NA	0.034	0.026	NA	NA	mg/L
Total Cadmium (Cd)	<0.0003	0.000	0.001	<0.002	NA	mg/L
Total Calcium (Ca)	159.0	NA	NA	29.0	78.7	mg/L
Total Chromium (Cr)	NA	0.000	0.005	NA	NA	mg/L
Total Cobalt (Co)	1.60	NA	NA	<4.00	NA	ug/L
Total Copper (Cu)	<0.001	0.012	0.036	0.0456	NA	mg/L
Total Iron (Fe)	12.8	0.09	0.13	1.32	NA	mg/L
Total Lead (Pb)	<0.0003	0.000	0.006	<0.015	NA	mg/L
Total Magnesium (Mg)	14.71	NA	NA	38.3	7.29	mg/L
Total Manganese (Mn)	1.71	0.03	0.011	0.132	NA	mg/L
Total Mercury (Hg)	<0.2	NA	0.06	0.0657	NA	ug/L
Total Molybdenum (Mo)	NA	0.00	0.01	NA	NA	mg/L

Analyte	Contaminated Water					Units
	CW1	CW2	CW3	CW4	CW5	
Total Nickel (Ni)	0.00428	0.000	0.007	<0.003	NA	mg/L
Total Potassium (K)	12.77	NA	NA	22.7	3.78	mg/L
Total Selenium (Se)	NA	0.00	0.00	NA	NA	mg/L
Total Silver (Ag)	<0.0003	0.002	0.001	0.00315	NA	mg/L
Total Sodium (Na)	867	NA	NA	383	45.6	mg/L
Total Zinc (Zn)	0.00146	0.065	0.069	0.0637	NA	mg/L
Total Organic Carbon (TOC)	9.45	9	11	89.3	4.15	mg/L

^a Analyses for pH, ORP, ALK, Residual Cl_2 , Cl^- , NO_2^- , NO_3^- , pH, SO_4^{2-} , S^{2-} and BOD were performed on unpreserved/unfiltered samples. Analyses for CN^- and SCN^- were performed on base-preserved samples. Analyses for metals were conducted on acid-preserved samples. TOC sample was stored on pre-baked bottles.

^b NA = Not Analyzed

^c Neg = Negative.

SI-3. Procedure for Method Detection Limit (MDL) Study in Reagent Water Matrix

To perform the MDL study, we generally followed USEPA's definition and procedures codified in 40 CFR 136, Appendix B, i.e., the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The determinative procedures involve spiking seven replicate aliquots of reagent water or sample matrix with the analytes of interest at a concentration within one to five times the estimated MDL. The seven aliquots are then carried through the entire analytical process, and standard deviation of the seven replicate determinations is calculated. The standard deviation is multiplied by the one-tailed t-statistic factor of 3.143 to give MDL. This definition with the associated determinative procedures is required by many regulatory agencies, and is an industry standard in commercial and academic environmental chemistry laboratories in the United States.

Each laboratory determined the MDLs of its assigned test method(s) using reagent water spiked with each of three cyanide species (NaCN , $\text{K}_2\text{Ni}(\text{CN})_4$, $\text{K}_4\text{Fe}(\text{CN})_6$). Separate spiking experiments were conducted for each species. The general procedure for conducting an MDL test is as follows:

- (a) Prepare reagent water based on Type II Specification in ASTM D 1193-91 and demonstrated to be as free of cyanide as possible.
- (b) Prepare a laboratory standard sample (one cyanide species spiked in reagent water) at a concentration that is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated MDL). Detailed guidance for spiking into aqueous samples is presented in Section SI-4.
- (c) Take seven aliquots of the sample and process each subsample through the entire analytical method.
- (d) Calculate the variance (S^2) and the standard deviation (S) of the replicate measurements.
- (e) Compute the MDL as follows: $\text{MDL} = 3.143 * S$.

SI-4. Spiking Procedure

Each of the three cyanide species was spiked separately into the water matrix being evaluated by each laboratory following the procedures listed below. Doses of sodium cyanide, nickel cyanide, and ferrocyanide were added separately to yield concentrations at the following levels: 5-20 ppb, 30-50 ppb, and 100-150 ppb. The order of compound spiking tests was the same with every new water sample tested, in an attempt to make the holding time approximately equal for each cyanide species from sample to sample.

- (a) Determine the volume of the portion of sample to be spiked, depending on such factors as the sample volume required by specific analytical method to be used, convenience of dilution factors, and amount of sample for replicate analysis.
- (b) Prepare a spiking solution of suitable concentration. Where solubilities permit, stock spiking solutions may be prepared 25 to 100 times as concentrated as the working spike solution and diluted volumetrically to produce the working spike solution at the time of use.
- (c) Determine the appropriate amount of spike and spiking solution to be added to the reagent water. The spiking solution will generally constitute less than 2% of the total volume of the sample, so the matrix is not altered appreciably and the carrier solvent does not interfere in the test method.
- (d) Add the desired volume or mass of spiking solution or spike to the reagent water. Cap the sample and mix well.

SI-5. Procedure for Method Detection Limit Study in Contaminated Water Matrices

Each laboratory determined matrix-dependent MDLs for its assigned cyanide analytical test methods and the various cyanide-bearing contaminated water samples. The general procedure for conducting an MDL test in reagent water was followed, as described in Section SI-3.

If the concentration of cyanide species in a contaminated water sample was less than the detection limit obtained from the reagent water matrix tests, each of three cyanide species was added to bring the level of analyte to between one and five times the estimated detection limit. If the measured level of analyte was greater than five times the estimated detection limit, it was

impossible to determine a matrix-based MDL for the sample. If the measured analyte level was in the range of one to five times the estimated MDL, then no spiking was needed for MDL determination.