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June 12, 2013

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Re: Letter of Transmittal – Onondaga Lake Repository Addition

The below document has been approved by the New York State Department of Environmental Conservation (NYSDEC) and is enclosed for your document holdings:

- Odor Characterization Sampling and Analysis Plan – February 2013 (Onondaga Lake Remediation)

Sincerely,

John P. McAuliffe by ccc

John P. McAuliffe, P.E.
Program Director, Syracuse

Enc.

cc: Tim Larson - NYSDEC

ODOR CHARACTERIZATION SAMPLING AND ANALYSIS PLAN
FEBRUARY 2013
ONONDAGA LAKE REMEDIATION

This work plan describes the sample collection and analyses of compounds in the headspace above Geotube effluent process water and sediment slurry associated with the Onondaga Lake remediation program. The purpose of the sampling is to analyze compounds that are believed to be contributing to odors from the process water and sediment slurry. Compound concentrations will be measured and compared to their respective odor thresholds to rank the top odorants.

It should be noted that compound concentrations that will be created in the headspace of a small container will not represent actual emission or ambient air concentrations. These concentrations will be created only to compare one compound to the other in an effort to rank the primary odorants.

This work is a continuation of studies conducted as pre-design investigations to this program and of work conducted in November 2012 that followed a similar work plan to analyze air emission compounds from the surface of a freshly filled Geotube.

SAMPLING OVERVIEW

Samples will be collected from headspace of the following:

- Process water – One sample of process water collected on November 16, 2012 from an actively dewatering Geotube containing Remediation Area D (ILWD) dredge material.
- Sediment slurry – Two samples of sediment slurry (~10% solids) collected from different locations in Remediation Area D on November 15, 2012. The headspace will be created primarily from volatilization of compounds in the overlying water rather than in the solids.

Headspace samples will be analyzed for the following parameters and sampling methods:

Parameter	Sampling Methods		
	Collection	Sample	Analysis
VOC*	6-L Canister	4 L	EPA TO-15 (GC/MS)
SVOC*	Tenax Sorption Tube	0.1 & 1 L[c]	EPA TO-17 (GC/MS)
Sulfides/Mercaptans	1-L Tedlar Bag	0.5 L	ASTM D5504-08 (GC/Chemilum.)
Amines	Treated Alumina Sorption Tube	0.1	GC/NPD
Odorography[a]	[d]	[d]	Odor Evaluator
Odor Evaluation[b]	10-L Tedlar Bag	5 L	ASTM E679-04, E544-99

* Includes the analytical method's standard compound list plus tentatively identified compounds (TICs).
[a] Odor intensity and character for each compound as it elutes from the gas chromatograph will be evaluated by a trained odor evaluator.
[b] Odor detection and recognition thresholds, intensity, characterization, persistence, hedonic tone.
[c] Two tubes will be collected for each sample using different sample volumes that will facilitate lower reporting limits if necessary.
[d] The SVOC sample will also be analyzed for this analysis. The Tenax sorption tube will collect both VOC and SVOC.

These methods do not include inorganic compounds, aldehydes, and organic acids.

A total of five samples (one per collection method) will be collected from each headspace. All five samples will be collected simultaneously. A total of 10.7 L of headspace are planned to be withdrawn over a 2 hour period. There will be three sample sets, one for the process water and two for the sediment slurry. Duplicate or blank samples will not be collected. Blank samples are not warranted because background (indoor air) concentrations of the previously identified primary odorants are expected to be at least 3 orders of magnitude above typical indoor air

levels. However, if the indoor air at the sampling location exhibits an odor, a sample of indoor air may be collected and analyzed for background odor levels.

O'Brien & Gere will collect the samples. Columbia Analytical Services in Simi Valley, CA will conduct all headspace sample analyses except for the odor evaluation. The standard compounds for the VOC, SVOC, sulfides/mercaptans, and amines methods and their anticipated reporting limits are provided in Attachment A. An example report for the odorography is also provided in Attachment A. St. Croix Sensory, Inc. in Stillwater, MN will conduct the odor evaluations. Columbia Analytical Services in Rochester, NY will analyze the water samples.

Headspace over the process water and slurry samples will be created by placing one-gallon of the process water or sediment slurry in a 5-gallon never-used plastic container and allowing it to come to room temperature. This will create ~4 gallon (17 L) headspace per water/slurry sample. The water/slurry will be stirred and the headspace concentration will be measured for total VOC with a PID to identify when the headspace concentrations have reached equilibrium. A minimum total VOC concentration of 10 ppm in the headspace is targeted for sampling, as it is expected to contain VOC and SVOC concentrations well above the analytical reporting limits for the primary odorants.[1] Once the headspace is equilibrated (and the minimum total VOC concentration is reached or exceeded), air samples will be collected from sampling ports' in the side of the container. Fresh air will enter the container at the top. Headspace samples will be removed during a 2-hour period, at a rate of ~5.5 liters per hours. The total VOC headspace levels will be checked at regular intervals during the 2-hour sample collection to ensure that they do not drop below the 10 ppm minimum. The stirring rate will be increased and/or more (fresh) water or slurry will be added, if necessary.

Samples of the water (process and slurry) will also be collected and analyzed for VOC and SVOC following EPA Method SW-846. One sample of each water (one process water and two slurry water) will be collected at the beginning and again at the end of the headspace sample collection. Therefore, there will be a total of six water samples collected and analyzed. Water samples will be collected in 40-ml VOA bottles and kept cold after collection and during shipment to the laboratory.

The VOC method (TO-15) is able to detect some SVOCs as well, but less accurately due to lower removal efficiencies of higher boiling point compounds. Similarly, the SVOC method (TO-17) is able to detect most VOCs, but less accurately due to the lower adsorption efficiencies of lower boiling point compounds. Therefore, when a compound is detected in both methods, the higher analytical result will be used for odor ranking evaluation.

REPORTING

The laboratories' analysis reports will be submitted to NYSDEC. The data will not undergo an independent data validation. Analytical results will be used to derive the odor level (in units of odor units) using published odor detection thresholds, and the odor levels will be used to identify primary odorants. A summary table of odor levels and ranking will be submitted to NYSDEC.

SCHEDULE

Sampling is anticipated to occur the week of February 4, 2013, provided that NYSDEC approval of this sampling plan is received by January 31. Prior to sampling, NYSDEC will be notified of the scheduled sample collection date.

Attachments: A – Method Standard Compounds and Reporting Limits

[1] Based on measurements from the Geotube air emissions characterization sampling conducted in November 2012.

Method Standard Compounds and Reporting Limits

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RESULTS OF ANALYSIS

Client:
Client Sample ID: Method Blank
Client Project ID:

Project ID: P120XXXX
Sample ID: P121019-MB

20 Reduced Sulfur Example Report

Test Code: ASTM D 5504-08
Instrument ID: HP5890 II/GC5/SCD
Analyst:
Sampling Media: Tedlar Bag
Test Notes:

Date Collected: NA
Time Collected: NA
Date Received: NA
Date Analyzed: ########
Time Analyzed (PDT): 07:48
Volume(s) Analyzed: 1.00 ml(s)

CAS #	Compound	Result µg/m³	MRL µg/m³	Result ppbV	MRL ppbV	Data Qualifier
7783-06-4	Hydrogen Sulfide	ND	7.0	ND	5.0	
463-58-1	Carbonyl Sulfide	ND	12	ND	5.0	
74-93-1	Methyl Mercaptan	ND	9.8	ND	5.0	
75-08-1	Ethyl Mercaptan	ND	13	ND	5.0	
75-18-3	Dimethyl Sulfide	ND	13	ND	5.0	
75-15-0	Carbon Disulfide	ND	7.8	ND	2.5	
75-33-2	Isopropyl Mercaptan	ND	16	ND	5.0	
75-66-1	tert-Butyl Mercaptan	ND	18	ND	5.0	
107-03-9	n-Propyl Mercaptan	ND	16	ND	5.0	
624-89-5	Ethyl Methyl Sulfide	ND	16	ND	5.0	
110-02-1	Thiophene	ND	17	ND	5.0	
513-44-0	Isobutyl Mercaptan	ND	18	ND	5.0	
352-93-2	Diethyl Sulfide	ND	18	ND	5.0	
109-79-5	n-Butyl Mercaptan	ND	18	ND	5.0	
624-92-0	Dimethyl Disulfide	ND	9.6	ND	2.5	
616-44-4	3-Methylthiophene	ND	20	ND	5.0	
110-01-0	Tetrahydrothiophene	ND	18	ND	5.0	
638-02-8	2,5-Dimethylthiophene	ND	23	ND	5.0	
872-55-9	2-Ethylthiophene	ND	23	ND	5.0	
110-81-6	Diethyl Disulfide	ND	12	ND	2.5	

ND = Compound was analyzed for, but not detected above the laboratory detection limit.
MRL = Method Reporting Limit - The minimum quantity of a target analyte that can be confidently determined by the referenced method.

ALS Environmental

RESULTS OF ANALYSIS

Amines Example Report

Client:
Client Sample ID:
Client Project ID:

Project ID: P080XXXX
Sample ID: P080XXXX-001

Test Code: GC/NPD
Instrument ID: Agilent 6890N/GC14/NPD
Analyst:
Sampling Media: Treated Alumina Tube
Test Notes: **BC, DE**

Date Collected: 5/21/08
Date Received: 5/22/08
Date Analyzed: 5/28/08
Desorption Volume: 2.0 ml
Volume Sampled: 100 Liter(s)

CAS #	Compound	Result µg/Tube	Result µg/m³	MRL µg/m³	Result ppbV	MRL ppbV	Data Qualifier
124-40-3	Dimethylamine	< 0.52	ND	5.2	ND	2.8	
75-04-7	Ethylamine	< 0.58	ND	5.8	ND	3.2	
75-50-3	Trimethylamine	< 0.46	ND	4.6	ND	1.9	
75-31-0	Isopropylamine	< 0.49	ND	4.9	ND	2.0	
75-64-9	t-Butylamine	< 0.48	ND	4.8	ND	1.6	
107-10-8	Propylamine	< 0.72	ND	7.2	ND	3.0	
109-89-7	Diethylamine	< 0.51	ND	5.1	ND	1.7	
13952-84-6	s-Butylamine	< 0.50	ND	5.0	ND	1.7	
78-81-9	Isobutylamine	< 0.51	ND	5.1	ND	1.7	
109-73-9	Butylamine	< 0.50	ND	5.0	ND	1.7	
108-18-9	Diisopropylamine	< 0.48	ND	4.8	ND	1.2	
121-44-8	Triethylamine	< 0.50	ND	5.0	ND	1.2	
142-84-7	Dipropylamine	< 0.47	ND	4.7	ND	1.1	

ND = Compound was analyzed for, but not detected above the laboratory reporting limit.
MRL = Method Reporting Limit - The minimum quantity of a target analyte that can be confidently determined by the referenced method.
BC = Results reported are not blank corrected.
DE = Results reported are corrected for desorption efficiency.

ALS Environmental Air Quality Laboratory
Volatile Organic Compounds (VOCs)
Standard EPA Method TO-15 75 Compound List

Method Reporting Limits (MRLs) assume a 1 L sample analysis volume (from 6L canister).

Actual reporting limits will be higher depending on the canister pressurization dilution factor and/or sample matrix effects. Typical canister pressurization dilution factors for 6L cans are between 1.5-2.0.

	CAS #	Compound	ug/m3	ppbv
			MRL	MRL
1	115-07-1	Propene	0.50	0.29
2	75-71-8	Dichlorodifluoromethane (CFC 12)	0.50	0.10
3	74-87-3	Chloromethane	0.50	0.24
4	76-14-2	1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC 114)	0.50	0.072
5	75-01-4	Vinyl Chloride	0.50	0.20
6	106-99-0	1,3-Butadiene	0.50	0.23
7	74-83-9	Bromomethane	0.50	0.13
8	75-00-3	Chloroethane	0.50	0.19
9	64-17-5	Ethanol	5.0	2.7
10	75-05-8	Acetonitrile	0.50	0.30
11	107-02-8	Acrolein	2.0	0.87
12	67-64-1	Acetone	5.0	2.1
13	75-69-4	Trichlorofluoromethane (CFC 11)	0.50	0.089
14	67-63-0	2-Propanol (Isopropyl Alcohol)	5.0	2.0
15	107-13-1	Acrylonitrile	0.50	0.23
16	75-35-4	1,1-Dichloroethene	0.50	0.13
17	75-09-2	Methylene Chloride	0.50	0.14
18	107-05-1	3-Chloro-1-propene (Allyl Chloride)	0.50	0.16
19	76-13-1	Trichlorotrifluoroethane (CFC 113)	0.50	0.065
20	75-15-0	Carbon Disulfide	5.0	1.6
21	156-60-5	trans-1,2-Dichloroethene	0.50	0.13
22	75-34-3	1,1-Dichloroethane	0.50	0.12
23	1634-04-4	Methyl tert-Butyl Ether	0.50	0.14
24	108-05-4	Vinyl Acetate	5.0	1.4
25	78-93-3	2-Butanone (MEK)	5.0	1.7
26	156-59-2	cis-1,2-Dichloroethene	0.50	0.13
27	141-78-6	Ethyl Acetate	1.0	0.14
28	110-54-3	n-Hexane	0.50	0.14
29	67-66-3	Chloroform	0.50	0.10
30	109-99-9	Tetrahydrofuran (THF)	0.50	0.17
31	107-06-2	1,2-Dichloroethane	0.50	0.12
32	71-55-6	1,1,1-Trichloroethane	0.50	0.092
33	71-43-2	Benzene	0.50	0.16
34	56-23-5	Carbon Tetrachloride	0.50	0.080
35	110-82-7	Cyclohexane	1.0	0.15
36	78-87-5	1,2-Dichloropropane	0.50	0.11
37	75-27-4	Bromodichloromethane	0.50	0.075
38	79-01-6	Trichloroethene	0.50	0.093
39	123-91-1	1,4-Dioxane	0.50	0.14
40	80-62-6	Methyl Methacrylate	1.0	0.12
41	142-82-5	n-Heptane	0.50	0.12
42	10061-01-5	cis-1,3-Dichloropropene	0.50	0.11
43	108-10-1	4-Methyl-2-pentanone	0.50	0.12
44	10061-02-6	trans-1,3-Dichloropropene	0.50	0.11
45	79-00-5	1,1,2-Trichloroethane	0.50	0.092
46	108-88-3	Toluene	0.50	0.13

ALS Environmental Air Quality Laboratory
Volatile Organic Compounds (VOCs)
Standard EPA Method TO-15 75 Compound List

Method Reporting Limits (MRLs) assume a 1 L sample analysis volume (from 6L canister).

Actual reporting limits will be higher depending on the canister pressurization dilution factor and/or sample matrix effects. Typical canister pressurization dilution factors for 6L cans are between 1.5-2.0.

	CAS #	Compound	ug/m3	ppbv
			MRL	MRL
47	591-78-6	2-Hexanone	0.50	0.12
48	124-48-1	Dibromochloromethane	0.50	0.059
49	106-93-4	1,2-Dibromoethane	0.50	0.065
50	123-86-4	n-Butyl Acetate	0.50	0.11
51	111-65-9	n-Octane	0.50	0.11
52	127-18-4	Tetrachloroethene	0.50	0.074
53	108-90-7	Chlorobenzene	0.50	0.11
54	100-41-4	Ethylbenzene	0.50	0.12
55	179601-23-1	m,p-Xylenes	1.0	0.23
56	75-25-2	Bromoform	0.50	0.048
57	100-42-5	Styrene	0.50	0.12
58	95-47-6	o-Xylene	0.50	0.12
59	111-84-2	n-Nonane	0.50	0.095
60	79-34-5	1,1,2,2-Tetrachloroethane	0.50	0.073
61	98-82-8	Cumene	0.50	0.10
62	80-56-8	alpha-Pinene	0.50	0.090
63	103-65-1	n-Propylbenzene	0.50	0.10
64	622-96-8	4-Ethyltoluene	0.50	0.10
65	108-67-8	1,3,5-Trimethylbenzene	0.50	0.10
66	95-63-6	1,2,4-Trimethylbenzene	0.50	0.10
67	100-44-7	Benzyl Chloride	0.50	0.097
68	541-73-1	1,3-Dichlorobenzene	0.50	0.083
69	106-46-7	1,4-Dichlorobenzene	0.50	0.083
70	95-50-1	1,2-Dichlorobenzene	0.50	0.083
71	5989-27-5	d-Limonene	0.50	0.090
72	96-12-8	1,2-Dibromo-3-chloropropane	0.50	0.052
73	120-82-1	1,2,4-Trichlorobenzene	0.50	0.067
74	91-20-3	Naphthalene	0.50	0.095
75	87-68-3	Hexachlorobutadiene	0.50	0.047

ALS Environmental Air Quality Laboratory
Volatile Organic Compounds (VOCs)
EPA Method TO-17 Standard Compound List

Sampling Tube: Tenax TA

Sample Volumes: Please reference appropriate sampling guide (must use lower volumes for high humidity samples)

	CAS #	Compound	ng/tube MRL
1	75-69-4	Trichlorofluoromethane	1.0
2	67-63-0	2-Propanol (Isopropyl Alcohol)	2.0
3	75-35-4	1,1-Dichloroethene	0.5
4	75-09-2	Methylene Chloride	5.0
5	75-15-0	Carbon Disulfide	5.0
6	156-60-5	trans-1,2-Dichloroethene	0.5
7	75-34-3	1,1-Dichloroethane	0.5
8	1634-04-4	Methyl tert-Butyl Ether	0.5
9	78-93-3	2-Butanone (MEK)	1.0
10	156-59-2	cis-1,2-Dichloroethene	0.5
11	110-54-3	n-Hexane	0.5
12	67-66-3	Chloroform	0.5
13	109-99-9	Tetrahydrofuran (THF)	1.0
14	107-06-2	1,2-Dichloroethane	0.5
15	71-55-6	1,1,1-Trichloroethane	0.5
16	71-43-2	Benzene	2.0
17	56-23-5	Carbon Tetrachloride	0.5
18	110-82-7	Cyclohexane	1.0
19	78-87-5	1,2-Dichloropropane	0.5
20	75-27-4	Bromodichloromethane	0.5
21	79-01-6	Trichloroethene	0.5
22	123-91-1	1,4-Dioxane	1.0
23	540-84-1	2,2,4-Trimethylpentane (Isooctane)	0.5
24	142-82-5	n-Heptane	0.5
25	10061-01-5	cis-1,3-Dichloropropene	5.0
26	108-10-1	4-Methyl-2-pentanone	2.0
27	10061-02-6	trans-1,3-Dichloropropene	5.0
28	79-00-5	1,1,2-Trichloroethane	0.5
29	108-88-3	Toluene	0.5
30	591-78-6	2-Hexanone	1.0
31	124-48-1	Dibromochloromethane	0.5
32	106-93-4	1,2-Dibromoethane	0.5
33	111-65-9	n-Octane	1.0
34	127-18-4	Tetrachloroethene	0.5
35	108-90-7	Chlorobenzene	0.5
36	100-41-4	Ethylbenzene	0.5
37	179601-23-1	m,p-Xylenes	1.0
38	75-25-2	Bromoform	1.0
39	100-42-5	Styrene	0.5
40	95-47-6	o-Xylene	0.5
41	79-34-5	1,1,2,2-Tetrachloroethane	0.5
42	98-82-8	Cumene	0.5
43	108-67-8	1,3,5-Trimethylbenzene	0.5
44	95-63-6	1,2,4-Trimethylbenzene	0.5
45	541-73-1	1,3-Dichlorobenzene	0.5
46	106-46-7	1,4-Dichlorobenzene	0.5
47	95-50-1	1,2-Dichlorobenzene	0.5
48	96-12-8	1,2-Dibromo-3-chloropropane	2.0
49	120-82-1	1,2,4-Trichlorobenzene	5.0
50	91-20-3	Naphthalene	2.0
51	87-68-3	Hexachlorobutadiene	2.0

ALS Environmental

Odorography Example Report

CASE NARRATIVE

Gas Chromatography/Mass Spectrometry/Olfactometry (GC/MS/O) &Tentatively Identified Compounds (TICs) Analysis

A portion of each of the samples was weighed and transferred into a glass purge vessel specially cleaned prior to use for the TO-17 methodology. The vessel was then purged with ultra-pure dry air and sealed, then allowed to equilibrate at 60^{o}C, for 24 hours. A clean vessel was also set up as a control and run as a Chamber Blank, which was under the same set of conditions as the samples.

An aliquot of the headspace from each vessel was flushed onto a thermal desorption tube and analyzed simultaneously for odor-active compounds by GC/MS/O and for tentatively identified compounds (TICs) in accordance with the methodology outlined in EPA Method TO-17. The analyses were performed by thermal desorption/gas chromatography/mass spectrometry.

The olfactometry was performed using a Gerstel ODP-3 olfactory detection port. The effluent from the GC column was split 2:1 (ODP:MS). The ODP uses a heated transfer line and sniff port to prevent condensation of the eluting compounds. The analyst recorded time and intensity of each detected compound and a brief descriptor characterizing the perceived odor.

Odor-Active Compounds Detected by Olfactometry

In general, the majority of odors perceived in the samples were of a low intensity and of a neutral or pleasant hedonic tone. There were many barely perceptible odors throughout the chromatograms that were not recorded. There are several odors for which no peak could be detected or identified by the mass spectrometer due to the greater sensitivity of the human nose for certain chemicals.

There were two compounds identified in every sample that were distinctly stronger than the rest. These were Diacetyl (2,3-butanedione) and 1-Hexen-3-one. Diacetyl is one of the compounds that give butter its distinctive odor. It has a neutral to slightly unpleasant hedonic tone at higher concentrations. It has a very low odor threshold (less than 10 ppb has been cited). The compound 1-Hexen-3-one was perceived as a rubber-like odor and had an unpleasant tone. No value for the odor threshold was found in the literature but it must be very low because it was difficult to get an identifiable peak in many of the samples even though the odor was strong.

MES Fines Lot# 2010 (P120xxxx-001)

RT, minutes	Odor Descriptor	Intensity (1-4)	MS Identification
4.08	Butter	2	Diacetyl
4.19	Grassy	1	n-Butanal + 2-Butanone
6.07	Rubber	1	2-Pentanone
8.60	Rubber	2	1-Hexen-3-one
9.45	Grassy	1	n-Hexanal
11.59	Plastic	1	1-Hepten-2-one
13.57	Cucumber	1	Unidentified
14.48	Pine	1	Eucalyptol
14.95	Soap	1	Dihydromyrcenol
18.64	Banana	1	Tricyclodecenyl Acetate
19.00	Indole	1	2-Methoxynaphthalene
19.50	Fruity	1	Unidentified