Characterization and Monitoring of Fugitive Emissions at the DuPont FUSRAP Site

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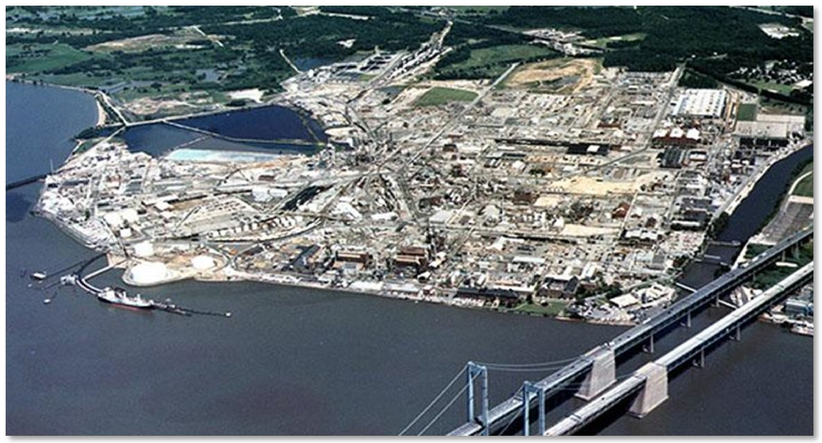

1942 DuPont Chambers Works Site (DCWS), begins support to the Manhattan Engineering District Project (MED).

1942-47 DCWS was under contract to the USACE MED to process uranium compounds and uranium scrap to produce uranium tetrafluoride, uranium hexafluoride, and uranium metal.

1949 USACE and AEC Assess Radioactive Contamination at site. Some equipment buried in building at Niagara Falls Storage Site. Rest of site declared clean for unrestricted use. DuPont begins using MED contaminated soil and building material as fill across site.

1998 U.S. Army Corps of Engineers begins cleanup at DuPont

Issues:

1. Significant chemical contamination unrelated to FUSRAP program
2. Excavation and stockpiling can release volatile chemical compounds into the atmosphere and undesirable odors.

The USACE is partnering with PNNL to better understand chemical emissions and odors and identify previously unidentified compounds for concerns of health and safety.

- PNNL collaborated with USACE to evaluate direct-read odor detection instruments and demonstrate their potential to provide greater insights into odor sources.
- In addition, PNNL developed a vapor-sampling method and refined methodologies for field-portable instruments.

Direct Read and Sampling Equipment

Shinyea Odor Meters

- Semiconductor sensor array
- Handheld size
- Internal air pump

Sensigent MSEM 160

- Chemical sensor array
- Photoionization detector
- Size: ≈ 12" x 12" x 8"
- Internal air pump

Hapsite ER

- Portable gas chromatograph and mass spectrometer
- Mass Spectral Libraries: NIST, NIOSH, AMDIS
- Size: ≈ 18" x 17" x 7"
- Internal air pump

Vacuum sampling case by St. Croix Sensory

- Battery powered pump creates negative pressure inside the case and the sample bag fills directly from the source (no pump contamination)
- Viewing window allows sample collection control from outside the case

Shinyei Handheld Instruments

- Shinyei handheld instruments were utilized to help identify odor hot spots (odor plume locations and centroids).
- The Shinyei instrument OMX-ADM offers immediate insight into the chemical source of the odors.

Sample #	Sample Identification	OMX-ADM	
		Odor Strength	Odor Intensity
24-1	Air Sample - Cell D3 Excavation North	1-31	2.5
24-3	Air Sample - Cell D3 Excavation In the Hole	14	2.5
24-4	Air Sample - 100' North of Location 24-1	0	2.5
24-6	Air Sample - 194' North of Location 24-1	0	2.5
25-1	Air Sample - Cell D3 Excavation Southwest	695	3.5
25-2	Air Sample – Same location as 25-1	99	2.5
25-3	Air Sample - Cell D3 Excavation In the Hole	NM	2.5

Sensigent MSEM 160

Sample #	Sample Identification	SO_2 (ppm)	H_2S (ppm)	SH (ppm)
25-0	Background Measurement: Tedlar® Bag Filled with UHP N_2	0.21	0.00	0.00
24-1	Air Sample - Cell D3 Excavation North	0.20	0.46	0.04
24-3	Air Sample - Cell D3 Excavation In the Hole	0.19	0.33	0.01
24-4	Air Sample - 100' North of Location 24-1	0.20	0.47	0.02
24-5	Headspace Sample - From Location 24-3	0.19	0.37	0.04
24-6	Air Sample - 194' North of Location 24-1	0.19	0.48	0.09
25-1	Air Sample - Cell D3 Excavation Southwest	0.17	0.75	0.70
25-2	Air Sample – Same location as 2-1	0.16	0.60	0.43
25-3	Air Sample - Cell D3 Excavation In the Hole	0.18	0.41	0.07

- The two highest mercaptan and H_2S readings (25-1 and 25-2) were concurrent with the highest Shinyei ADM readings (695 and 99 respectively).
- One complicating factor is that the mercaptan electrochemical sensor is known to have a significant (160%) cross sensitivity with H_2S, meaning that some or all of the measured mercaptan concentration may have been due to H_2S.
- A proton transfer reaction mass spectrometer (PTR-MS) measurement was performed to speciate H_2S and organosulfur compounds to help resolve mercaptans

VOC Analysis via Hapsite GC-MS

Analyte Name	Trailer Background (ppb)	24-5 Headspace Sample (ppb)	25-4 Headspace Sample (ppb)	24-3 Air Sample Excavation (ppb)	25-3 Air Sample Excavation (ppb)	24-1 Air Sample Location 1 (ppb)	24-4 Air Sample Location 2 (ppb)	24-6 Air Sample Location 3 (ppb)	Maximum Air Sample (ppb)	Occupational Exposure Limit (ppb)	Maximum Air Sample % OEL	Odor Detection Threshold (ppb)	Maximum Air Sample % ODT
Benzene	<DL	935.5	1701.9	28.4	22.8	3.1	0.7	0.8	28.4	20	142%	2690	1%
Cyclohexane	<DL	747.8	1086.2	2.8				1.6	2.8	100000	0%	2470	0%
Propane, 1,2-dichloro-	<DL					0.5			0.5	10000	0%	8660	0%
Trichloroethylene	<DL			0.4					0.4	10000	0%	110000	0%
Heptane	<DL	229.0		0.8	1.1				1.1	400000	0%	410	0%
Toluene	<DL	653.5	544.0	6.4	9.9	22.9	0.4	1.0	22.9	20000	0%	350	7%
Benzene, chloro-	<DL	1620.6	1573.8	49.1	73.9	6.0	1.1	5.1	73.9	10000	1%	980	8%
Ethylbenzene	<DL	350.3	421.5	6.3	8.7	2.4	0.4	0.8	8.7	20000	0%	170	5%
p-Xylene	<DL	752.7	545.5	2.5	15.9	1.0	0.1	0.3	15.9	20000	0%	324	5%
Styrene	<DL			0.4		0.9	0.6	0.9	0.9	10000	0%	100	1%
Nonane	<DL	293.7	138.1	2.9	3.8	1.0	0.3	2.0	3.8	200000	0%		
Benzene, (1-methylethyl)-	<DL	49.6	33.7	1.9	3.2	0.5	0.2	0.4	3.2				
Benzene, 1-ethyl-4-methyl-*	NM			1.9									
2-Chlorotoluene	<DL	406.1	123.3	2.6	2.9			2.5	2.9	50000	0%		
Benzene, propyl-	<DL			1.5	2.8	0.6	0.1		2.8				
Benzene, 1,3,5-trimethyl-	<DL	42.5	24.8	9.3	15.5	2.2	0.3	1.2	15.5	10000	0%	2400	1%
Benzene, 1,2,3-trimethyl-*	NM			8.6									
Benzene, 1,2,4-trimethyl-	<DL	9.4	7.4	5.8	13.2	1.9	0.4	0.4	13.2	10000	0%	2400	1%
Benzene, 1,3-dichloro-	<DL	7.8	2.6	2.9	1.9	1.1	0.5	2.7	2.9				
Benzene, 1,4-dichloro-*	NM			4.1									
Benzene, 1,2-dichloro-	<DL	211.1	68.5	3.3	45.1	1.4	0.8	4.2	45.1	25000	0%	700	6%
Carbon disulfide	<DL	38.4	51.9										
Ethene, 1,1-dichloro-	<DL	5.2											
Ethene, 1,2-dichloro-, (E)-	<DL	3.1											
Ethene, 1,2-dichloro-, (Z)-	<DL	2.8											
Total Organics by Hapsite		6309.5	6271.6	141.8	220.7	45.6	5.9	24.0					34%

* Additional analytes measured with 40°F Method

- Headspace and air samples largely consist of BTEX (benzene, toluene, ethylbenzene, and xylene)
- Headspace concentrations: 2–3 orders of magnitude higher than ambient air near excavation
- Benzene reached 142% of ACGIH TWA
- Benzene elevation warrants monitoring and controls

Conclusions

PNNL developed and validated a vapor sampling method to support reliable detection and quantification of airborne contaminants. We also demonstrated and refined methodologies for field-portable analytical instruments, confirming their capability to provide actionable real-time data in operational environments. The Hapsite ER can be used to perform to an EPA TO-15 type method similar to commercial laboratories but can also be used in a portable mode to directly sample breathing air. Results from direct-read instruments were compared with off-site laboratory methods (GC-MS and PTR-MS) to build confidence and interpretive guidance for field data.

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