Adapting sampling, cleaning, and analytical methods for low-level detection of Volatile Organic Compounds at the Waste Isolation Pilot Plant

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- Disclaimer: The views and opinions expressed in this presentation are those of the author and do not necessarily reflect those of the DOE or WIPP operators.

Waste Isolation Pilot Plant

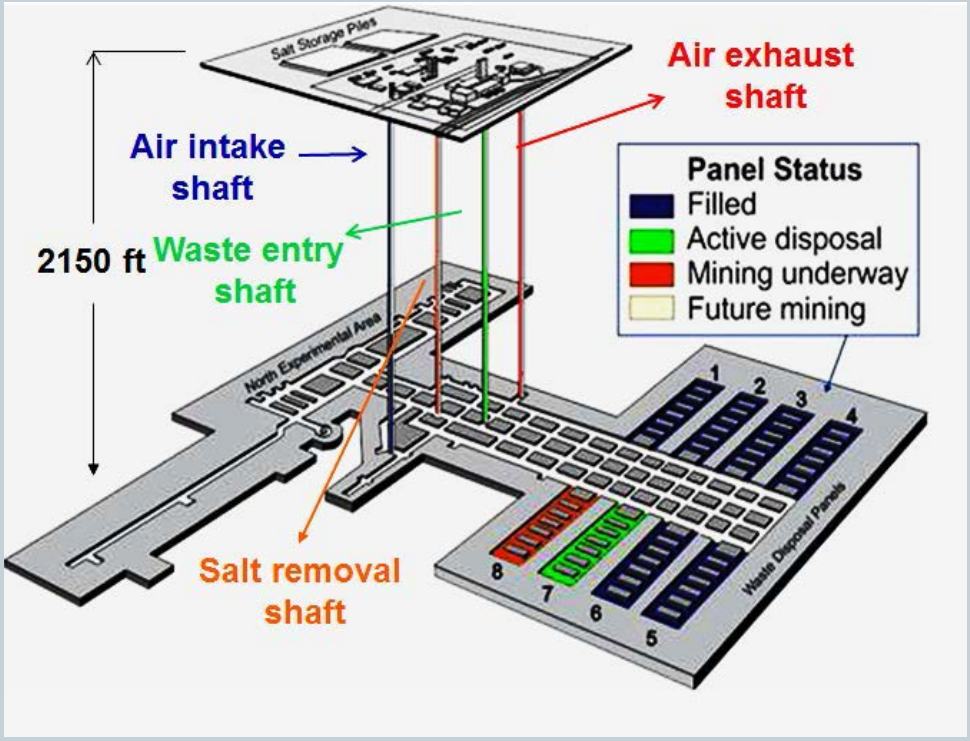
- WIPP is a permanent disposal facility for transuranic (TRU) waste near Carlsbad, New Mexico
- Operated ~17 years by U. S. Department of Energy (DOE)
- To safely dispose of defense-related transuranic (TRU) waste.
- Began disposal operations in 26 March 1999.
- WIPP was established due to deep geologic disposal of nuclear waste is safe and cost-effective.
- The Salado salt formation can accept as much nuclear waste as the world can generate in the next 10,000 yrs.

WIPP Operations

- TRU waste was generated during the production of nuclear weapons at DOE facilities across the country
- After 1970, transuranic waste was put into containers such as 55-gallon drums and stored in above-ground and shallow-burial facilities for eventual retrieval and disposal
- TRU Waste : Personal protective equipment, tools, rags, debris, residues, process sludges and other items, contaminated with man-made radioactive elements that are heavier than uranium
- Two types of TRU waste : Contact-handled (Dose <200 mrem/h); Remote-handled (Dose >200 mrem/h & < 1000 mrem/h)

WIPP Snapshot

- 17+ years of operation.
- 86,000 cubic meters of TRU waste disposed.
- 165,000 containers disposed in the underground.
- 17 storage sites cleaned of legacy TRU waste.
- 11,112 shipments received.
- ~ 8 waste panels mined
- 6 Panels filled and closed.



Carlsbad Environmental Monitoring & Research Center

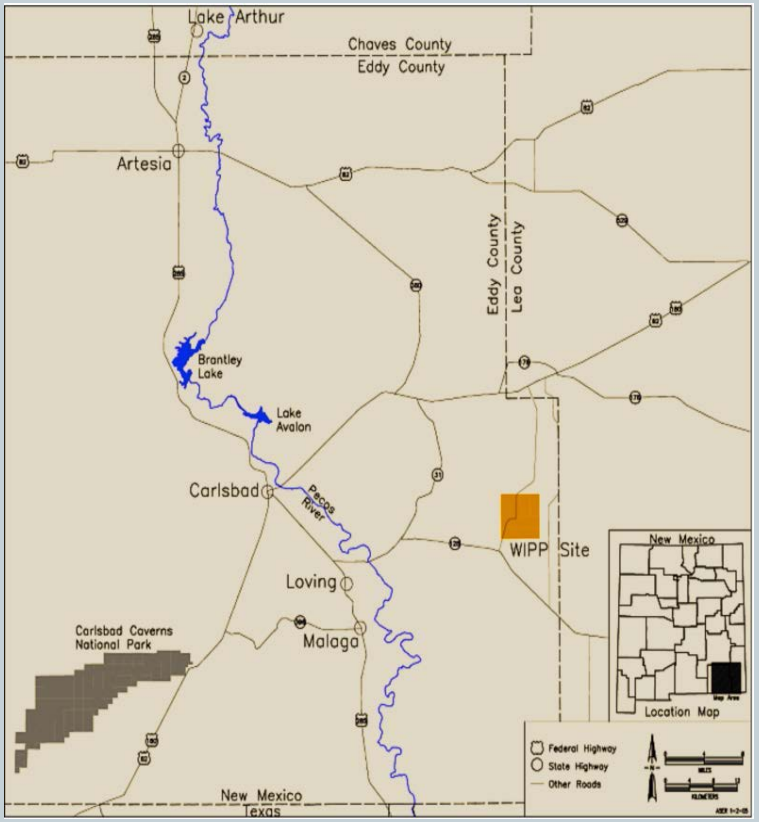
- CEMRC is an independent environmental monitoring organization, a part of New Mexico State University
- CEMRC performs independent health and environmental monitoring in the vicinity of the Waste Isolation Pilot Plant (WIPP)

CEMRC's mission includes:

- Detecting releases
- Evaluating potential sources of detected releases
- CEMRC responsive to public concerns (citizens within 100 miles of WIPP)
- Surveys in the 1990's showed public concerned about: air, whole body, drinking and surface water, soil, and sediment
- CEMRC was born out of regional community demand for independent monitoring

CEMRC Routine Analyses

- Radiological, Inorganic, Organic, and Whole Body



VOC Generation from WIPP

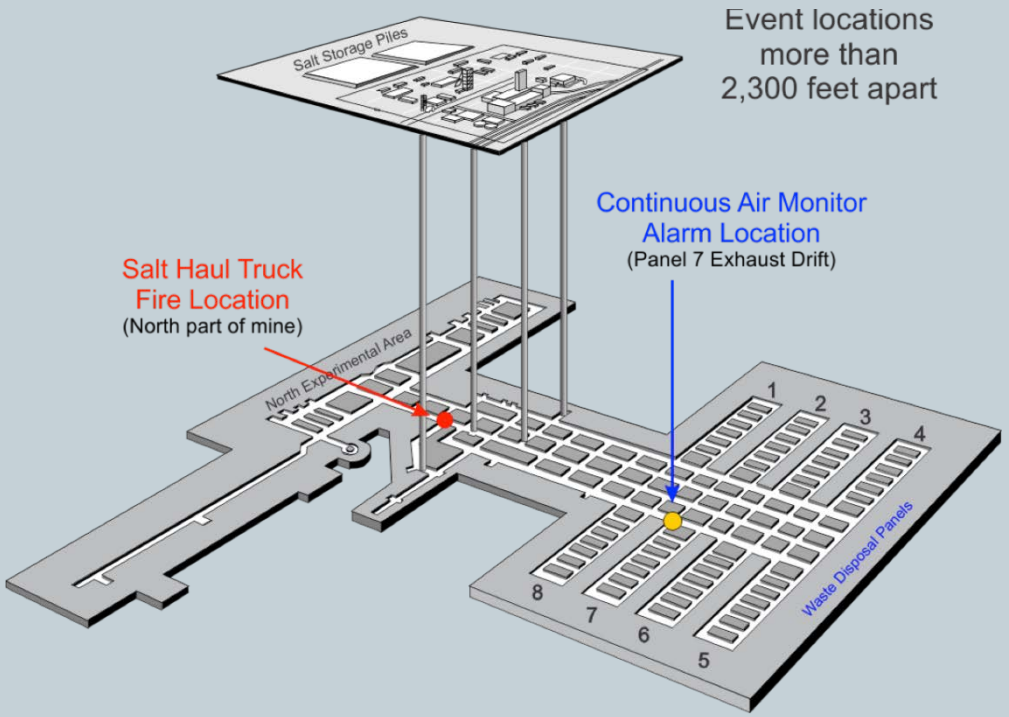
- Waste package in steel drums which have a high density polyethylene liner.
- TRU waste payload containers contain more than 100 nCi/g of alpha-emitting TRU isotopes with half-lives greater than 20 years.
- 95% CH waste, 5% RH waste
- Drum contents: Cellulosics, plastics, rubbers, inorganics, metals, asphalt
- VOC generation processes: Bacterial, Thermal, Radiolysis, Alpha Decay, Corrosion

Volatile Organic Compound Monitoring Program

- Developed as part of DOE no-migration variance petition to EPA
- Program designed to demonstrate that there will be no migration of hazardous chemicals past the unit boundary in concentrations which exceed health based standards.
- Current WIPP target VOCs are carbon tetrachloride, chlorobenzene, chloroform, 1,2-dichloroethane, 1,1-dichloroethylene, methylene chloride, 1,1,2,2-tetrachloroethane, toluene, 1,1,1-trichloroethane, and trichloroethylene.
- Any additional VOCs be targeted for routine quantification if the avg. concentration at the point of sampling is one ppm or more during any four month period and the compound is detected in at least 10% of the samples.

WIPP Incidents

- **Feb 5th, 2014 – Salt Haul Truck Fire**
- **Feb 14th, 2014, – Waste Drum Burst**



Sampling pre-events vs post-events

- Pre-event – underground sampling , sampling from exhaust air and rooms where waste is being emplaced.
- Upon the possibility of VOC migration to the surface, and since underground sampling is not possible, surface monitoring was started.
- Safety and Health of non-waste surface workers – revised risk factors
- Mine ventilation is the only possible migration pathway.
- VOC concentrations might be affected by ventilation changes in the repository throughout the day.
- Samplers vs PASK's

Analysis pre-events vs post-events

- Pre-event – GC/MS full scan : 1- 100 ppbv
- Post-event – GC/MS full scan : 0.2 – 10 ppbv, GC/MS SIM : 0.05 – 10 ppbv.
- Synchronous SIM/scan
- Post-event - background in carrier and dilution gases, internal standard contamination, carry over due to age of instruments
- All target compounds must pass blank criteria < 50 pptv (SIM), and no TICs or unknown compounds above 0.2 ppbv (full scan).

Cleaning of Canisters and PASKs

Canisters –

- Initial evacuation to < 50 mtorr;
- 8 cycles – pressurize to 30 psia, evacuation to 1000 mtorr; 80-100 deg C.
- Final evacuation < 50 mtorr, and pressurize to ~ 43 psia for 24 hr leak check.

PASKs –

- Flushed with UHP nitrogen for 4-6 hrs at < 80 deg C.
- Fill mini-canisters through PASKs after cleaning for certification.

Certify each and every canister and PASK

- All target compounds < 50 pptv
- No TICs or unknown compound above 0.2 ppbv

Canister Pressure vs VOC Stability

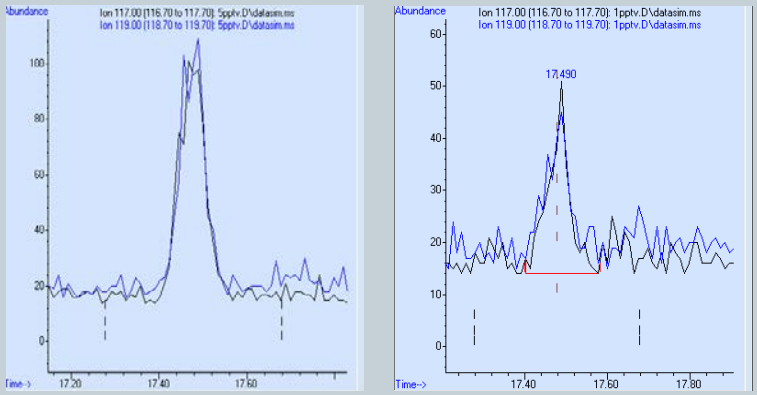
	Canister Pressure			
	30psia	20psia	15psia	~13psia
Target VOCs	(pptv)	Stability (%)		
Chloroform	977.66	3.40	4.23	4.79
1,1-Dichloroethylene	969.92	10.09	7.17	4.61
1,2-Dichloroethane	960.49	0.38	2.65	4.06
Methylene Chloride	998.62	1.03	0.82	1.46
Carbon Tetrachloride	989.68	11.97	8.73	10.58
1,1,1-Trichloroethane	975.99	9.95	8.21	8.49
Trichloroethylene	986.21	2.55	4.21	3.34
Chlorobenzene	908.01	9.81	11.12	8.60
1,1,2,2-Tetrachloroethane	922.74	0.75	1.05	0.10
Toluene	985.32	8.50	5.16	5.07

Canister Pressure vs VOC Stability

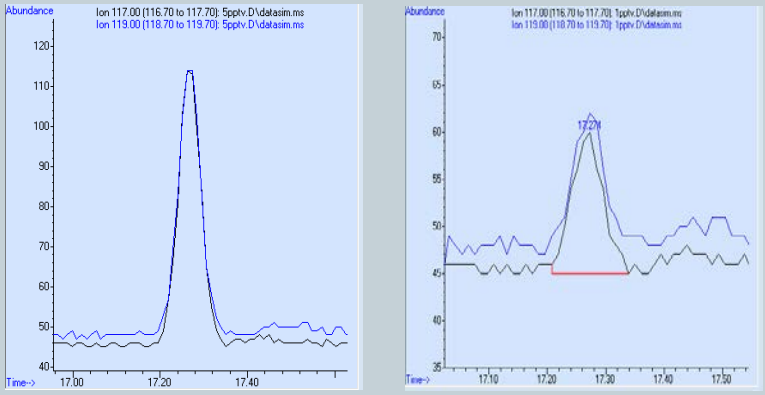
	Canister Pressure			
	30psia	20psia	15psia	~13psia
Target VOCs	(pptv)	Stability (%)		
Chloroform	120.69	1.89	1.18	3.14
1,1-Dichloroethylene	105.11	5.37	2.05	1.16
1,2-Dichloroethane	120.87	1.06	0.41	0.22
Methylene Chloride	124.89	1.83	3.08	3.07
Carbon Tetrachloride	118.12	7.23	5.47	6.20
1,1,1-Trichloroethane	116.85	6.38	5.38	7.22
Trichloroethylene	108.28	0.21	4.25	3.65
Chlorobenzene	125.59	8.46	13.68	10.90
1,1,2,2-Tetrachloroethane	122.91	2.19	6.73	5.11
Toluene	103.94	8.35	9.55	10.40

Future work

- Reduce the lower calibration level as needed based on risk factors.
- Decrease carry-over
- Does lab-air affect cleaning and measurements?
- Old vs New Instrumentation



Agilent GC/MS 6890/5975
with Entech 7100A/7016CA



Agilent GC/MS 7820/5977E
with Entech 7200/7016D

Thank You