M E M O R A N D U M

TO: Jean Dewart (LANL, ESH-17) and Margie Stockton (URS/Radian)

FROM: Bart Eklund (URS/Radian)

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SUBJECT: Results of Ambient Air Monitoring for VOCs at MDA-R

BACKGROUND

Material Disposal Area (MDA) R is located at Los Alamos National Laboratory (LANL), Technical Area (TA)-16. MDA-R is a high explosives burning area dating from the 1940's, that is approximately 600 feet long by 60 feet wide (about 3,300 m^2). Limited characterization of the area has been performed in the past and residues of high explosives, particularly RDX and TNT, were found, along with above-background concentrations of barium, cobalt, lead, silver and zinc.

The landfill began smoldering when the Cerro Grande fire reached the site on May 10 and 11, 2000. It was reported that tree roots, railroad ties, and cabling within the MDA-R were burning. The smoldering materials were extinguished on June 14 after contractors used a remote robotic excavator to scoop up chunks of smoldering debris, move them to a nearby clear area, and douse them with water.

The burning material had the potential to release air emissions, so LANL conducted an ambient air monitoring (AAM) program to address concerns about the impact on human health and the environment from these air emissions. This memorandum addresses the sampling for volatile organic compounds (VOCs) that was performed. Additional air measurements were made by the ESH-17 Air Quality Group and are reported on the LANL air quality web page (http://www.air-quality.lanl.gov/airnet.htm). The monitoring included a particulate matter monitoring station for inhalable particles (PM-10), with the samples analyzed for metals and radionuclides. In addition, two total suspended particulate (TSP) monitors were used to collect samples in conjunction with the VOC samples. The TSP samples will also be analyzed for metals and radionuclides.

SCOPE OF WORK

The work involved several days of monitoring for volatile organic compounds (VOCs) at two locations around the MDA. The samplers were placed at the approximate western and eastern ends of the MDA. These locations were selected based on local winds, availability of power, and the need to remain clear of the earth moving equipment. In addition, one background sample was collected at TA-16, Building 900.

The monitoring was performed on June 2, 5, 6, 8, and 12 by personnel from LANL and from the DOE facility in Carlsbad, NM (WIPP), using equipment provided by WIPP. The schedule of excavation work performed during this time period is given in Table 1. Time-integrated 24-hour VOC samples were collected and the canister samples were submitted to Air Toxics Ltd. laboratory in Folsom, CA for GC/MS analysis for a target analyte list of 60 compounds using EPA Method TO-14. The samples are identified in Table 2.

RESULTS

Meteorological data are continuously collected at several locations at LANL, including TA-6 and TA-49, which are only a few miles from MDA-R. The primary weather data for LANL is collected at TA-6. The meteorological parameter of most importance in interpreting the monitoring results is wind direction. The wind direction data defines which monitoring sites are upwind of the emission source and which monitoring sites are downwind. Wind speed data provides information about the amount of dilution air present during the monitoring period. Rainfall data are meaningful because rainfall can remove ("scrub") pollutants from the atmosphere.

The meteorological conditions during the sampling periods can be found at www.weather.lanl.gov. Ambient temperatures averaged about 80 °F for daily highs, with lows in the 50's. About 0.7 in. of rain fell on June 2 and about 0.15 in. of rain fell on June 9. Typical winds in the area are from the west, making the East sampling location the downwind location under typical conditions and the West sampling location the upwind location.

The complete VOC monitoring results are given in Attachment 1 and are summarized in Table 3. A total of 11 compounds were detected in the sample set, with approximately 5-10 compounds detected in each sample. The compounds include two alcohols (ethanol and isopropyl alcohol); two ketones (acetone and MEK); one furan (tetrahydrofuran), three aromatics (toluene, m/p-xylene, and o-xylene), two chlorinated organics (chloromethane and methylene chloride) and one freon (Freon 12). Five of the 11 compounds contain oxygen (oxygenated compounds are relatively difficult to quantify from an analytical chemistry standpoint). Only two compounds were detected at concentrations above 5 ppbv (acetone and ethanol). The highest measured concentrations were 230 ppbv for ethanol and 26 ppbv for acetone.

DISCUSSION OF RESULTS

In general, there were no data trends of note. The concentrations measured upwind and downwind of the MDA were comparable, indicating that the area was not a net source of air emissions. Furthermore, the concentrations measured at either side of the MDA tended to be equal to or lower than the concentrations measured at the background site. Natural smoke typically contains a number of VOCs, such as ethane, ethene, methyl chloride, benzene, toluene, xylenes, and hexane. The lack of this characteristic "fingerprint" of natural smoke in the samples

collected at the MDA indicates that the smoldering materials did not generate large quantities of smoke. This is consistent with observations made in the field by sampling personnel.

As previously noted, the compounds measured in the highest concentrations were ethanol and acetone. Both acetone and ethanol are commonly measured in ambient air samples. They may be emitted from both biogenic and anthropogenic sources. One likely source is the decomposition of organic matter through natural soil processes. The quantitation of highly polar organic compounds - such as acetone and ethanol - using EPA Method TO-14 has greater uncertainty than the quantitation of non-polar compounds. This is because it is necessary to remove water vapor during the sample preparation and the water management systems tend to affect low molecular-weight polar compounds to a variable extent.

The 11 compounds detected in the samples are summarized in Table 4. As shown in Table 4, all of the VOCs were present at concentrations at least three orders of magnitude (i.e., more than 1,000 times) below the applicable occupational exposure limit, the 8-hr time-weighted average (TWA). Occupational exposure limits are typically adjusted by a factor of 100x to develop screening levels to assess short-term exposure of off-site receptors (Eklund, et al., 1993). The safety factor is used to take into account the differences between occupational and residential exposures. Even with a safety factor applied, none of these compounds exceed the screening level and therefore are not of concern from a human health or risk standpoint.

Table 4 also includes data for each compound on its odor detection threshold; i.e., the lowest concentration of the gas in the air that can be detected by the average, healthy person. None of the compounds were detected at concentrations at or near the odor detection threshold.

The quality control data indicate that the VOC data are reliable and defensible. The laboratory blank samples showed some relatively minor contamination of methylene chloride ($\leq$1.5 ppbv). Sample 3954 was analyzed in duplicate and in both analyses the same two compounds were detected (acetone and ethanol). The results were within ±25% for both compounds, which is considered to be good agreement. The surrogate recoveries also indicate that no analytical problems were present.

CONCLUSIONS

The measurement data provides a point-in-time evaluation of emissions from the smoldering material at the MDA-R under summertime conditions. The VOC monitoring data show that small amounts of VOCs are present in the air around the MDA. The levels upwind of the MDA, however, are comparable to the downwind levels, indicating that the MDA is not the source of most or all of the VOCs present in the air. The VOCs are all far below the applicable occupational exposure limits and are far below the applicable odor detection thresholds. Based on the available data, VOCs at MDA do not contribute to local odors and are not of concern from a human health or risk standpoint.

REFERENCES

Amoore, J.E. and E. Hautala. Odor as an Aid to Chemical Safety: Odor Thresholds Compared with Threshold Limit Values and Volatiles for 214 Industrial Chemicals in Air and Water Dilution. Journal of Applied Toxicology, Vol. 3, No. 6. 1983.

Eklund, B., C. Thompson, and S. Mischler. Estimation of Air Impacts for Solidification and Stabilization Processes Used at Superfund Sites. EPA-451/R-93-006. April 1993.

OSHA. 58 CFR 35338-35351, Part 1910, Subpart Z. June 30, 1993.

Ruth, J.H. Odor Threshold and Irritation Levels of Several Chemical Substances: A Review. Am. Ind. Hyg. Assoc. J., Vol. 47. March 1986.

Table 1. Schedule of Excavation Work at MDA-R

Date	Activity
May 26-30	Fire crews used hoses to apply water/foam to the site.
June 2 -June 3	Contractors began site preparation, including use of non-robotic heavy equipment
June 4 (Sun)	Site preparation performed during morning. Robotic excavation began during afternoon.
June 5 (Mon)	Excavation work continued.
June 6 (Tue)	Excavation work performed during morning.
June 7 (Wed)	Excavation work performed during afternoon.
June 8 (Th)	Excavation work continued. Robotic excavation continued at east end of landfill.
June 9 (Fri)	Robotic excavator was moved back to the west end of landfill. Excavation continued using robotic machine and some hands-on excavation. Smoldering material on east side of MDA-R was completely extinguished.
June 10 (Sat)	Excavation work continued at west end of landfill with robotic operation and hands-on equipment. Another excavator was moved to the site.
June 12 (Mon)	Excavation work continued at west end of landfill.
June 13 (Tue)	Earth moving operations continued with both hands-on equipment and the robotic excavator.
June 14 (Wed)	Robotics operations completed. Use of hands-on equipment continued. Smoldering material on west side of MDAR was completely extinguished
June 15 (Th)	Earth moving operations were performed. Soils and debris found in the landfill were separated into two piles.
June 16 (Fri)	Site stabilization activities were performed. Soil was compiled at one central location. Soil samples were collected from the contaminated pile for analysis.

Table 2. Summary of VOC Monitoring Locations

Location	Sample ID	Sampling Start Date	Total Elapsed Sampling Time (hr)	Comments
MDAR West	3464	June 2	19:50	
MDAR West	3458	June 5	22:30	
MDAR West	3459	June 6	22:35	
MDAR West	10922	June 8	23:27	
MDAR West	3954	June 13	23:41	
MDAR East	3460	June 2	20:55	
MDAR East	3462	June 5	3:00	Lost power to sampler
MDAR East	3457	June 6	12:13	Lost power to sampler
MDAR East	3953	June 8	24:05	
TA-16, Bldg 900	3454	June 5	67:35	Background

Table 3a. Results of VOC Analysis for Air Samples (West Site)

Analyte	Approx. Detection Limit[a] (ppbv)	Measured Concentration (ppbv)					
		June 2	June 5	June 6	June 8	June 13	Background Site[b]
Acetone	2.0 - 8.0	15	11	5.5	10	9.3	16
2-Butanone (MEK)	2.0 - 8.0	ND	ND	ND	ND	ND	2.8
Chloromethane	0.5 - 2.0	1.4	ND	1.6	ND	ND	1.2
Ethanol	2.0 - 8.0	56	20	9.0	7.2	16	190
Freon 12	0.5 - 2.0	ND	ND	ND	ND	ND	0.64
Methylene Chloride	0.5 - 2.0	4.2	ND	3.0	0.83	ND	1.4
2-Propanol	2.0 - 8.0	ND	ND	ND	ND	ND	ND
Tetrahydrofuran	2.0 - 8.0	ND	ND	4.0	ND	ND	ND
Toluene	0.5 - 2.0	ND	ND	ND	ND	ND	0.68
m/p-Xylene	0.5 - 2.0	ND	ND	ND	ND	ND	2.2
o-Xylene	0.5 - 2.0	ND	ND	ND	ND	ND	0.80

ND = Not Detected

a - Detection limits shown are the range over the days analyses were performed. Specific detection limits for each sample may be found in Attachment 1.
b - One background sample was taken during the program.

Table 3b. Results of VOC Analysis for Air Samples (East Site)

Analyte	Approx. Detection Limit[a] (ppbv)	Measured Concentration (ppbv)					
		June 2	June 5	June 6	June 8		Background Site[b]
Acetone	2.0 - 8.0	26	22	18	13		16
2-Butanone (MEK)	2.0 - 8.0	3.6	4.4	3.7	ND		2.8
Chloromethane	0.5 - 2.0	1.2	ND	0.98	ND		1.2
Ethanol	2.0 - 8.0	230	54	19	43		190
Freon 12	0.5 - 2.0	0.73	1.2	ND	0.85		0.64
Methylene Chloride	0.5 - 2.0	2.0	1.2	1.0	ND		1.4
2-Propanol	2.0 - 8.0	2.6	ND	ND	ND		ND
Tetrahydrofuran	2.0 - 8.0	ND	ND	ND	ND		ND
Toluene	0.5 - 2.0	ND	0.55	ND	0.75		0.68
m/p-Xylene	0.5 - 2.0	0.58	ND	ND	ND		2.2
o-Xylene	0.5 - 2.0	ND	ND	ND	ND		0.80

Table 4. Comparison of Measured Values with Odor Threshold and Worker Exposure Levels

Compound	CAS No.	Highest Measured Concentration (ppbv)	Concentration Minus Background Value (ppbv)	Odor Detection Threshold[a] (ppbv)	OSHA TWA (ppbv) (8 hr/day, 40 hr/week)[c]
Acetone	67-64-1	26	10	13,000	1,000,000
2-Butanone (Methy Ethyl Ketone)	78-93-3	4.4	1.6	5,400	200,000
Chloromethane (methyl chloride)	74-87-3	1.6	0.4	10,000[b]	100,000[d]
Ethanol	64-17-5	230	40	84,000	1,000,000
Freon 12	--	1.2	0.6	--	--
Methylene Chloride	75-09-2	4.2	2.8	250,000	25,000
2-Propanol (isopropyl alcohol)	67-63-0	2.6	2.6	22,000	400,000
Tetrahydrofuran	109-99-9	4.0	4.0	2,000	200,000
Toluene	108-88-3	0.75	0.07	2,900	200,000
m/p-Xylene	108-38-3/ 106-42-3	0.58	<0	1,100	100,000
o-Xylene	95-47-6	0	<0	--	100,000

a - Amoore and Hautala, 1983.
b - Ruth, 1986
c - OSHA, 2000 (www.osha-slc.gov).
d - OSHA, 1993.

ATTACHMENT ONE

Report From Analytical Laboratory
(If these data are needed, please contact ESH-17 at 505-665-0239)