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Title: SOIL PORE-GAS SAMPLING BY PHOTOACOUSTIC RADIOMETRY

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Soil Pore-Gas Sampling by Photoacoustic Radiometry

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ABSTRACT

Concentrations of volatile organics in a soil pore-gas plume were measured using a commercially available multigas monitor. The monitor is a photoacoustic radiometer (PAR) controlled by an on-board, programmable microprocessor. The measurements determine the extent and location of the vapor plume in the subsurface. At least twelve wells surrounding the sources are measured quarterly. The sources are located in former liquid chemical waste disposal pits and shafts at Los Alamos National Laboratory. The primary constituents of the plume are 1,1,1 trichloroethane (TCA), trichloroethene (TCE), and tetrachloroethene or perchloroethene (PCE). Four quarters of data are presented for TCA. All were used primarily as solvents and degreasers.

Previously the composition of the vapor plume was determined by Gas Chromatography Mass Spectrometer GCMS methods. Photoacoustic radiometry and gas chromatography are discussed giving the advantages and disadvantages of each method, although in this program they are basically complementary. Gas chromatography is a more qualitative method to determine which analytes are present and the approximate concentration. Photoacoustic radiometry, to function well, requires foreknowledge of constituents and serves best to determine how much is present. Measurements are quicker and more direct with photoacoustic methods. Once the constituents to be measured are known, the cost to monitor is much less using photoacoustics, and the results are available more quickly.

The photoacoustic radiometer uses narrow band filters in the region where trimer or higher molecules have vibrational and rotational resonances, from 2.5 to 15 micrometers (4,000 to 650 reciprocal centimeters). The multigas monitor used is a Model 1302 manufactured by Bruel and Kjaer, a Danish company.

Keywords: photoacoustics, pore-gas, infrared, volatile organics, radiometry, gas monitoring

1. INTRODUCTION AND BACKGROUND

Nonradioactive solvents and various volatile organic compounds were used for years at Los Alamos National Lab. From 1956 to 1985 disposal was by various techniques, from free liquid to drum burial. Most disposal occurred before stringent requirements for record keeping were in effect. Now, pursuant to the Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act (RCRA), as amended (42 U.S. C. 6901 et seq.) and the Hazardous and Solid Waste Amendments of 1984 (HSWA) all disposal is done by permit, and monitoring of the site is part of the requirement for the permit. The permit is issued by the United States Environmental Protection Agency,
Region 6.

The site lies within Los Alamos County in northern New Mexico, and is entirely on Department of Energy property, the reservation of Los Alamos National Laboratory. The disposal site is a narrow finger mesa consisting primarily of dry volcanic tuff. In some places the mesa width is only 500 feet. It extends NW-SE and rises about 120 feet above the canyon floors on either side. A major aquifer is about 900 feet below. The aquifer is capped by a layer of basalt the top of which is around 300 feet below the mesa top.

The disposal shafts and pits were usually shallow, from 10 to 40 feet in depth. The deepest shaft was 85 feet. The known disposal sites are widely dispersed. The maximum extent of the site is 790 acres. In this presentation only the plume associated with the disposal sites in Area L is discussed. The effected area is 18.5 acres. To monitor the plume 27 wells were drilled, some as much as 300 feet deep, with as many as 10 ports, usually at 20 foot intervals. So there were approximately 300 sample ports to characterize the vapor plume.

The ports were sampled using Gas Chromatographic Mass Spectrometer methods from 1985 to 1993. The pore gas was absorbed by activated charcoal and desorbed by carbon disulfide to start the analysis. Up to 13 analytes could be detected and their concentrations estimated in this way. The list of analytes is given in Figure 1. Solvent desorption GCMS is an allowed EPA SW-846 method.

In order to plan an extraction program concentration data were required. The existing voluminous body of data were carefully analyzed.[1,2,3,4,5] The large variations in the data were difficult to understand from physical principles. It was apparent that better data were required. The sampling method was improved and the single solvent desorption SDGCMS analysis method was replaced with two new methods, a thermal desorption TDGCMS technique, which is sensitive to 50 analytes (list of analytes given in Figure 1) and a nondispersive infrared method, which employs photoacoustic radiometry PAR. These techniques are complementary. By using both a great savings is realized.

From previous measurements the constituents in the plume were known. This allowed the PAR to be configured to measure only the 3 primary compounds. Hence the plume's temporal and spatial behavior can be monitored with the PAR which gives real-time results, and about 90% fewer GCMS samples need be taken. It is still important to do some GCMS analysis to monitor the suite of analytes and protect against surprises. For example an old buried container of some new chemical may rust thru releasing a previously unsuspected compound. The remainder of this paper will deal only with the PAR results.

2. PHOTOACOUSTIC RADIOMETRY

2. 1 Background and principle of operation

Thomas Edison discovered in 1880 that various airborne constituents will absorb energy from sunlight. The absorbed energy can manifest as an increase in pressure. To make the signal more noticeable the sunlight can be chopped at an audible frequency. The Bruel and Kjaer Model 1302 Multigas Analyzer is a sophisticated embodiment of this principle.

In order to be more selective and specific in detection of particular gases, narrow band infrared filters are chosen to allow light of only specific frequencies to pass thru the sample cell. Water must always be measured and compensation must be made for its absorption anywhere in the spectrum. In addition to the filter for water five other filters may be chosen. In principle each filter may be calibrated for up to 5 different gases, for a total of 25 compounds, plus water. In practice, in the field, at most 5 gases are measured, one per filter.

The concentration range for the instrument is impressive. It will read over 10,000 times the limit of quantization. A measurement of 5 gases plus water typically takes a little over 2 minutes. Limits of quantification are typically from 0.1 ppm to 10 ppm depending upon the compound and the other constituents. Calibration of the instrument is required. Pure samples of the analytes are prepared. Five liter tedlar bags are filled with sample gases of known concentration in a background gas of dry nitrogen. The response of the instrument is noted for each gas thru each filter. For example, in the equation below the response measured thru filter i is r_i . It is comprised of the coefficient of response a_{ij} times s_j the concentration of the jth substance summed over the number of substances.

$$\begin{array}{c} r_1 \\ r_2 \\ r_3 \\ r_4 \\ r_5 \end{array} = \begin{array}{ccccc} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} \\ a_{21} & a_{22} & a_{23} & a_{24} & a_{25} \\ a_{31} & a_{32} & a_{33} & a_{34} & a_{35} \\ a_{41} & a_{42} & a_{43} & a_{44} & a_{45} \\ a_{51} & a_{52} & a_{53} & a_{54} & a_{55} \end{array} \quad \begin{array}{c} s_1 \\ s_2 \\ s_3 \\ s_4 \\ s_5 \end{array}$$

Thus by determining the response for individual gases the response matrix a_{ij} is determined. To measure concentrations in the field the inverse of a_{ij} is required.

In a favorable situation where it is known that there are only 3 dominant analytes the coefficient of response matrix will only be a 3x3. In addition to TCA, TCE and PCE we monitor for vinyl chloride and carbon dioxide. We are concerned about vinyl chloride because it is the most dangerous compound since it is a proven carcinogen. Carbon dioxide is a product of biodegradation, hence we monitor for that also. In the third quarter of '94 an oxygen sensor was installed to determine whether there is simultaneous oxygen depletion when elevated carbon dioxide is found. This would be corroborating evidence that biodegradation is occurring.

2.2 Development of a sampling method

Uncertainty in the measurement arises from uncertainties in both sampling and analysis. We feel that much of the previous variability was due to the sampling. Hence we spent considerable time developing a sampling technique. To determine how much gas needed to be pumped out before a valid sample was taken several ports were monitored using the PAR for extended periods, as much as six hours. During that time about 40 liters of pore gas were extracted. Not all ports exhibit the same behavior, but frequently they are more or less asymptotic following a relation of the form

$$c = co\ \{1 - \exp(-v/vo)\},$$

where c is the concentration, co is the final value of the concentration, and vo is approximately the volume of the headspace.

As a rule of thumb we pump 5x the head space plus 2.5x the dust filter volume. The head space is the volume of the tube from the top of the well casing to the port, plus the volume of the measuring apparatus, the values and tubing in the manifold and pressure gauges, but does not include the rather large volume of the dust filter. The most important thing to establish before sampling is that the port is not blocked and can furnish gas to sample from the proper depth. A pair of pressure gauges was added to the sampling manifold to allow measurement of the port back pressure. Experience has shown that a dust filter is required. An oxygen sensor was added in the 3rd quarter.

2.3 Advantages and disadvantages

Previously used SDGCMS methods required less time in the field than PAR methods, which may be considered an advantage. However the number of samples taken was enormous and the analysis time was typically 6 to 9 months. Not so much because the analysis intrinsically takes that long but because the GCMS apparatus is very expensive ($100,000) its use must be coordinated with other programs. The GC is in use essentially full time. The cost to the program to analyze each GC sample is also quite high, about $300. With GC methods, because of the scheduling requirement, there is an inevitable amount of paperwork. There is an official "chain-of-custody" for the samples that must be maintained. And there are complications which arise with holding the sample at a sufficiently low temperature (preferably less than -20 degrees Fahrenheit) so that it will not out gas before processing. And one must be careful not to wait too long (40 days) before performing the GCMS analysis. And of course there are the peripatetic issues of sorption efficiency and recovery or desorption efficiency . Of course expendables are required. They must be stocked and accounted for. Before a sampling session the thermal desorption tubes must be baked and prepared.

Increased time in the field for the PAR method may be considered a disadvantage. However the increased field time, from 2 weeks with GCMS only, to 4 weeks with GCMS and PAR is a small price to pay for immediate quantitative results on the dominant analytes. Also, by reducing the number of GCMS samples required by 90% the cost of monitoring is reduced by as much as $288,000 per year. The cost of the GCMS equipment is about $100,000, whereas a PAR like the Bruel and Kjaer Model 1302 Multigas Analyzer is about $25,000. There are no expendables required with PAR analysis.

3. RESULTS

3.1 Quality of the data

The data for a single compound measured as part of the calibration procedure are often within 1% of the value given for the calibration gas, and the instrument will repeat to 0.5%. However we have noticed a systematic drift in both of the units we have used of -12% per hour in TCA, for continuous monitoring. To put this in perspective, good GCMS data is in the 20% range.

When unknown compounds provide interferences the PAR will give erroneously high concentrations. In the first field test comparison of TDGCMS and PAR, the PAR readings were 4 to 5 times those of the TDGCMS for TCA.[6] For other analytes the interference effects were not so severe. For PCE the ratio was more nearly 1 to 2. Some of that may be due to recovery problems, which were being resolved at that time with the TDGCMS, and some of it was probably due to interferences in the PAR data.

For example, on one well when we first started to measure for vinyl chloride the PAR indicated concentrations of more than 500 ppm. The action level is 1 ppm. Immediately we took sorption samples for TDGCMS analysis and combed thru previous measurements for that well for confirmation of the presence of vinyl chloride. Vinyl chloride was not present. However, we noticed a lot of chlorofluorocarbons, freons. In an experiment using only freon 113, trichlorotrifluoroethane, a significant false positive came thru on the vinyl chloride channel and the others, TCA, TCE, and PCE as well. So, a word of caution is in order. When the mix of chemicals in the plume changes significantly from the calibration conditions the numbers are likely to be inaccurate.

However, even if the composition of the plume is different from place to place the PAR can be useful for monitoring for changes in time. That is, unless something dynamic is happening with the source, the readings will reflect the same amount of false positives from quarter to quarter, so the readings will at least be consistent, and comparable.

As an example consider the following as indications of the limit of quantification for various analytes. These are typical measurements of clean air. Carbon dioxide is high because we calibrate at the high end, 10,000 ppm. In clean air CO2 should be more nearly 350 ppm. The value for water has units of mg/m3, all the other measurements are in ppm.

TCA	PCE	TCE	VC	CO2	Water
0.0232	0.0415	-0.129	0.418	595	5,490

As a measure of repeatability in the field consider this set of duplicate readings from the same port. These are sampled from well #32 at 100' depth.

TCA	PCE	TCE	VC	CO2	Water
16.4	1.34	1.11	0.0334	11,800	17,700
17.0	1.58	1.21	-0.278	11,900	15,500

3.2 Results for Area L

Measurements made using photoacoustic techniques for TCA by well and quarter are shown in Figure 2. The maximum value for the concentration in ppm is listed, with the depth in parenthesis. Photoacoustic measurements are frequently high relative to the gas chromatography due to interferences. Figure 3 is a map showing the maximum concentrations of TCA and the depth of occurrence for the last quarter of '93 and the first quarter of '94. Figure 4 is a map showing the maximum concentrations of TCA and the depth of occurrence for the first quarter of '94 and the second quarter of '94. It is displayed like this so that changes are easily noticed.

Note, the PAR was configured slightly differently in the 4th quarter of '93 (Dec. '93) and the 1st quarter of '94 (March '94) compared to the final two quarters. In the first two quarters we sensed TCA, TCE, PCE, SF6, and "total" organics referenced to methane. There is no SF6 in the plume except what we insert as a tracer. "Total" organics referenced to methane is an artificial measurement. Often the "total" concentration was less than the concentration measured for a single constituent. Hence those channels were put to better use. We decided to measure vinyl chloride and carbon dioxide instead. We chose vinyl chloride, both because it is a dangerous compound, a proven carcinogen, and it is an end product of anaerobic bacterial metabolism of some chlorocarbons. Carbon dioxide is of interest because it is a metabolic end product of aerobic bacteria eating some chlorocarbons. In the 3rd quarter of '94 (Sept. '94) we added the capability to monitor for oxygen as well. Hence if we see both an increase in carbon dioxide and a decrease in oxygen we have evidence that natural bioremediation is taking place.

4.CONCLUSION

Photoacoustic radiometry offers an option for monitoring pore gas in vapor plumes that is cost effective and offers many advantages over more conventional methods, such as gas chromatography. It is best used in conjunction with GCMS to determine the main constituents. For monitoring it offers speed and accuracy, and cost savings. Still GCMS is required for analysis.

List of Figures

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BIOGRAPHY

Dr. Sollid has more than 50 archival papers and presentations in optical science and engineering. Jon is a Fellow of SPIE. As a pioneer in holographic interferometry he introduced the concept of the Sensitivity Vector. Besides environmental optics his interests include laser fusion, free-electron lasers, diamond turning, optical metrology and manufacturing.

Figure 1 A list of analytes measurable by both GCMS techniques.

Solvent Desorb Gas Chromatography Mass Spectrometry

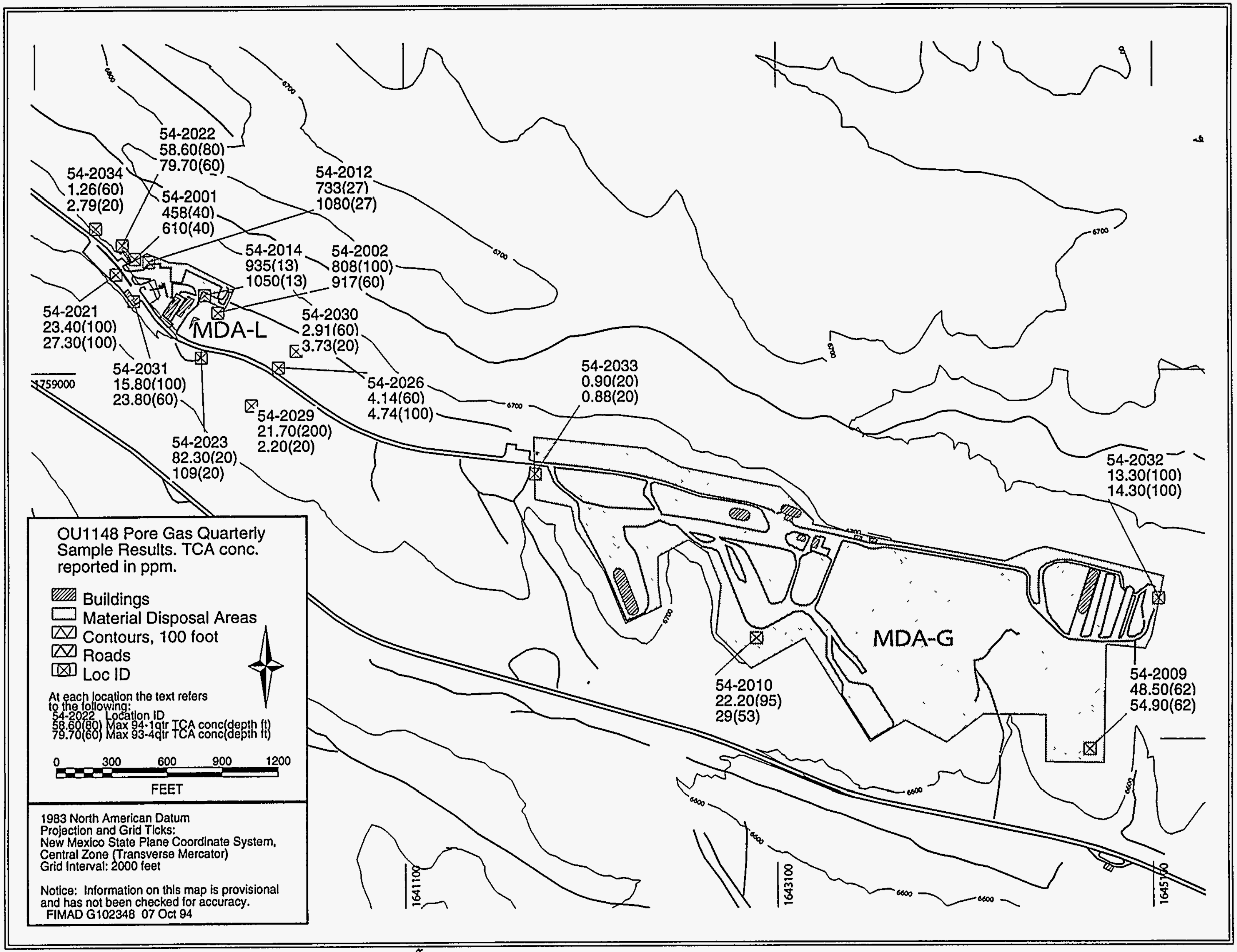
ethylbenzene
bromobenzene
toluene
benzene
chlorobenzene
o-xylene
1,2,4,-trimethylbenzene
carbon tetrachloride
chloroform
tetrachloroethene
mix-xylenes
1,1,1-tricholorethane
trichloroethene

Thermal Desorb Gas Chromatography Mass Spectrometry

Dichlorodifluoromethane
Bromomethane
1,1-Dichloroehtene
Carbon Disulfide
1,1-Dichloroethane
Bromomchloromethane
1,1-Dichloropropene
Benzene
Trichloroethene
4-Methyl-2-pentanone
1,1,2-Trichloroethane
Chlorodibromomethane
Ethylbenzene
Bromoform
n-Propylbenzene
1,3-Dichlorobenzene
Chloromethane
Chloroethane
Acetone
Methylene Chloride
2-Butanone
Chloroform
Carbon Tetrachloride
1,2-Dichloropropane
Dibromomethane
Toluene
2-Hexanone
Chlorobenzene
o,m,p-Xylene (mixed)
1,1,2,2-Tetrachloroethane
1,3,5-Trimethylbenzene
1,4-Dichlorobenzene
Vinyl Chloride
Trichlorofluoromethane
Trichlorotrifluoroethane
t-1,2-dichloroethene
c-1,2-Dichloroethene
1,1,1-Trichloroethane
1,2-Dichloroethane
c-1,3-Dichloropropene
Bromodichloromethane
t-1,3-Dichloropropene
Tetrachloroethene
1,1,1,2-Tetrachloroethane
Styrene
Bromobenzene
1,2,4-Trimethylbenzene
1,2-Dichlorobenzene

Figure 2. PAR measurements by well and quarter of max conc TCA

	Max concentration of 1,1,1 Trichloroethane (TCA) in ppm (depth in ft)				
Well No.	3rd Q '93	4th Q '93	1st Q '94	2nd Q '94	3rd Q '94
2	1330	917(60)	808(100)	909(100)	779(100)
9	78	55(62)	48.5(62)	67.5(62)	61.0(62)
10	44	29(53)	21.3(95)	29.4(95)	26.9(95)
12	1590	1080(27)	733(27)	1120(27)	1400(27)
21	36	27(100)	22.6(60)	38.5(100)	37.5(100)
22	95	80(60)	58.6(80)	88.0(80)	94.8(100)
23	41	109(20)	82.3(20)	35.5(80)	27.5(140)
26	7	4.7(100)	4.14(60)	5.35(100)	11.9(20)
29	10	2(200)	21.7(200)	9.25(200)	3.82(200)
30	3	4(20)	2.91(60)	2.84(60)	7.83(243)
31	23	24(60)	15.7(100)	21.6(100)	24.6(60)
32	21	14.3(100)	13.3(100)	18.8(100)	17.0(100)
33	1	0.8(20)	0.65(20)	.794(277)	
34	8	2.8(20)	1.26(60)	3.04(20)	
1	712	594(40)	458(40)	550(40)	493(40)
14	1130	1050(13)	935(13)	1190(13)	1100(13)
15				1340(82)	1300(82)
16				1100(82)	1050(82)
25				337(100)	330(100)
27				66.2(160)	66.1(250)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79.70(60)
54-2034
1.26(60)
2.79(20)
54-2001
458(40)
610(40)
54-2012
733(27)
1080(27)
54-2014
935(13)
1050(13)
54-2002
808(100)
917(60)
54-2030
2.91(60)
3.73(20)
54-2021
23.40(100)
27.30(100)
MDA-L
54-2031
15.80(100)
23.80(60)
54-2026
4.14(60)
4.74(100)
54-2033
0.90(20)
0.88(20)
54-2029
21.70(200)
2.20(20)
54-2023
82.30(20)
109(20)
54-2032
13.30(100)
14.30(100)
MDA-G
54-2009
48.50(62)
54.90(62)
54-2010
22.20(95)
29(53)
1759000
1641100
1643100
1645100
6700
6600
OU1148 Pore Gas Quarterly Sample Results. TCA conc. reported in ppm.
Buildings
Material Disposal Areas
Contours, 100 foot
Roads
Loc ID
At each location the text refers to the following:
54-2022 Location ID
58.60(80) Max 94-1qtr TCA conc(depth ft)
79.70(60) Max 93-4qtr TCA conc(depth ft)
0
300
600
900
1200
FEET
1983 North American Datum
Projection and Grid Ticks:
New Mexico State Plane Coordinate System, Central Zone (Transverse Mercator)
Grid Interval: 2000 feet
Notice: Information on this map is provisional and has not been checked for accuracy.
FIMAD G102348 07 Oct 94

Figure 3

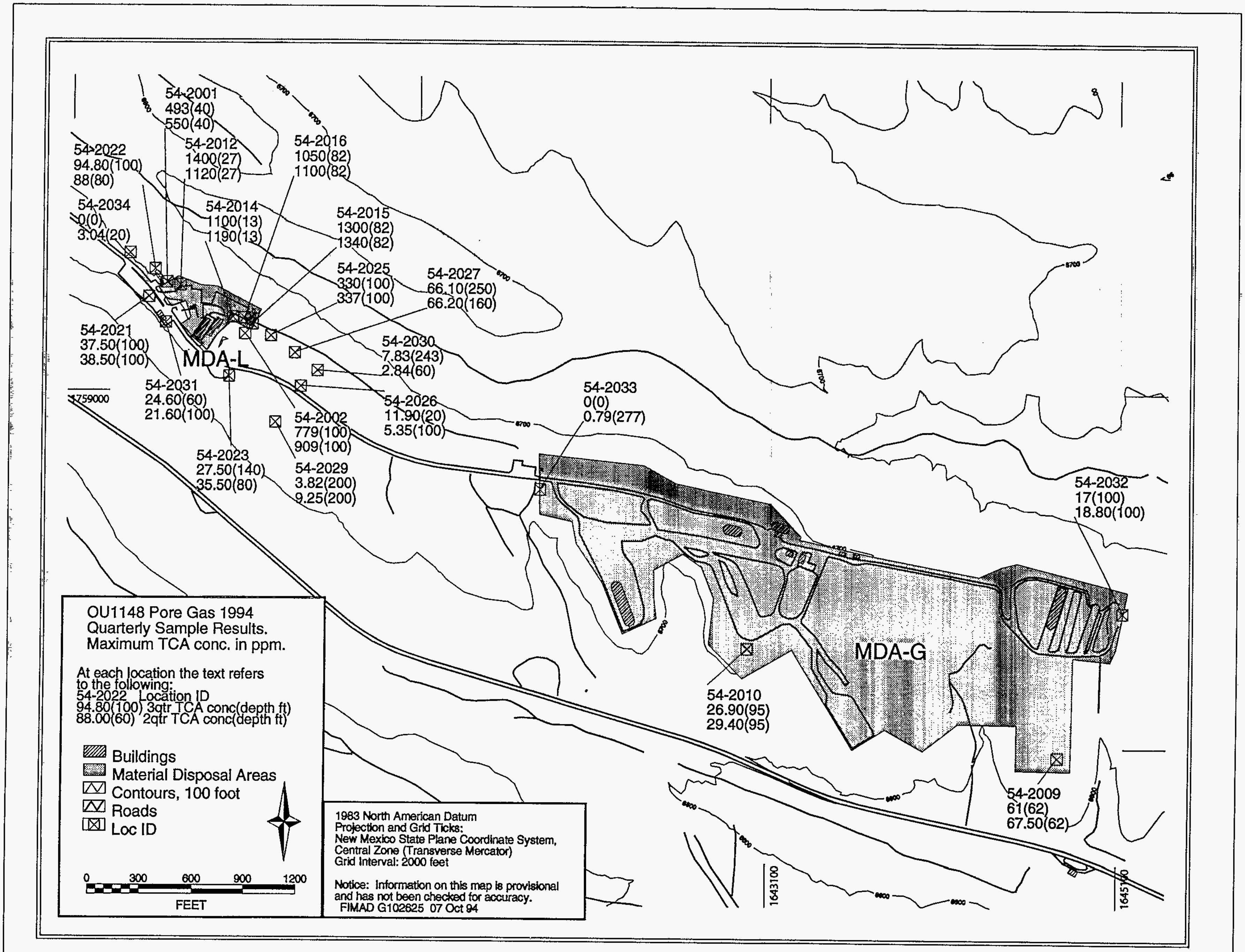

Figure 4

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