UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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SUBJECT: Analysis of Llangollen Landfill Samples

DATE: May 9, 1977

FROM: T. O. Munson, Ph.D.
Chief, Organic Analysis Unit

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TO: Orterio Villa, Jr.
Director, AFO

This memo contains a description of the work performed related to the Llangollen Landfill problem from the initial preparations for sample collection through a discussion of the analytical results. At this time, the results have not yet been received from the University of Illinois group (Dr. Ed Chian).

I. Introduction

We were requested to collect and analyze for trace organics by GC/MS samples from monitoring, recovery, and drinking water wells specified by the Water Supply and Enforcement Branches. The data were to be used to determine whether organic chemicals from the Llangollen Landfill were present in water supply wells as far from the landfill as Well #2 of the Artesian Water Company and Well PW-3 of the Amoco Chemical Corporation (see attached sketch).

We recognized that this request would be straining our analytical capabilities in two areas:

1. Detection limit -- the toxic limits for many chemicals in drinking water are below the limits of detection by our GC/MS system; and,
2. Volatile organics -- many of the chemicals of interest would probably be volatile organics because of their mobility in aquatic systems, and our capabilities and experience for volatile organics analysis by GC/MS are quite limited.

As will be described in the next section, efforts were made to strengthen the analysis program in these areas.

II. Sample Collection

Although personnel at AFO planned and prepared for the sample collection trip over a period of several months, things got a bit hectic when we were informed a few days prior to the sampling date that samples were to be collected for Dr. Ed Chian of the University of Illinois as well.

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Table 19

Overall Ratings of Organic Contaminants in Groundwater Samples from Llangollon Landfill

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Sample	Location	Number of Peaks 1 ppb VOA	ACID	BASE	Overall Ratings*
No. 8	Artisian Well #2	11	1	3	A
No. 2	Monitoring Well #42	20	7	7	B
No. 7	Amoco Well PW3	24	4	12	C
No. 6	Recovery Well #3	28	5	9	D
No. 4	Recovery Well #27	27	22	40	E
No. 3	Recovery Well #29	29	41	42	F

*A refers to the cleanest and F the most contaminated.

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At the sample site, another difficulty was encountered. Due to the soggy soil and roughness of the terrain, neither Well 49 nor alternate choice Well 24 could be sampled. Samples were obtained from six wells --Monitoring Wells, 42, 27, and 29; Recovery Well 3; Artesian Water Company Well 2; and Amoco Chemical Corporation Well PW-3.

1. AFO Samples. The primary samples were 1-gallon grab samples to be analyzed for extractable organics. We took 1-liter samples for volatile organics analysis by the hexadecane extraction procedure which is used routinely by EPA, Region II. Although our experience using this procedure for GC/MS was quite limited, the method had been well documented by Region II. We attempted to improve our detection limit for extractable organics by passing larger volumes of water through XAD-2 resin columns to concentrate the organic materials. Although our experience with this method was also quite limited, a preliminary field test at several of the Llangollen wells on 2/1/77 by Jim Barron produced apparently acceptable samples.

2. Dr. Ed Chian's Samples. At the time of sampling, we thought we had collected nearly exactly the samples which had been requested by Dr. Chian -- a volatile organics sample in a 40 ml bottle with a teflon-faced septum, and a 1-gal. sample for extractable organics in a glass bottle with a teflon-lined screw-cap. He asked that the 1-gal. bottle be baked in a muffle furnace which we could not do, but under ordinary circumstances, a solvent rinsed bottle would have been sufficient. Unfortunately, somehow over the telephone we did not understand that Dr. Chian wanted three samples each for volatile organics. The lack of the two additional samples required him to use water from the 1-gallon samples for volatiles analysis. In this case, the residual solvents in the bottles did cause him some problems.

III. Sample Analysis

1. Extractable Organics. A portion (1 liter) of each of the six samples was selectively extracted to yield acids, bases, and neutrals fractions -- giving 18 samples to be run by GC/MS. The extracts were concentrated down to about 1 ml with the final solvent being benzene. The concentration process results in the loss of most volatile organics (such as acetone and toluene).

2. XAD-2 Resin Samples. The solvent used to extract the adsorbed organic material from the column is also concentrated -- once again one would expect to lose most of the volatile organics. These samples proved to be useless even though the test samples run earlier had looked good. The reagent blank (extract from a column which had not had water run through it) had many organic chemicals of high concentration which made the GC/MS runs of the sample extracts uninterpretable.

5 wells to 1st sample
2/ wells in triplicate

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3. Hexadecane Volatile Organics Extracts. We followed the method quite carefully but still came up with uninterpretable results. Even though we bought the exact grade and brand of hexadecane as specified in the method, the hexadecane itself contained so many peaks of contaminating material that the extracts were useless.

IV. Results and Discussion

The enclosed table summarizes the results of the GC/MS scans of the 18 sub-fractions of the 6 samples. The peak number is an arbitrary designation roughly corresponding to the elution order of the peaks. The base peak represents the molecular weight (usually -- actually, charge-to-mass ratio) of the most abundent mass fragment in each mass spectrum. The purpose of the table is to provide an illustration of the similarities between the various samples. An "X" in a row denotes the presence of that compound in that sample fraction (a dotted "X" indicates that the match is not perfect), a blank space denotes the absence of that compound in that sample fraction, and an "O" in the first line of a column indicates that no peaks at all were seen in that sample fraction.

Rather surprisingly, W2 showed three large peaks and one smaller one -- not what one would hope to find in a drinking water well. Upon subsequent analysis of the remaining samples an event worthy of note occurred.

The acids fraction of W27 was inadvertently checked off as having been run. Upon completion of the samples, only the Amoco PW3 was found to have the peaks present in the Artesian W2. Examination of the attached sketch map shows the dilemma -- the two wells furtherest from each other and furtherest from the landfill had similar contamination but no relation to the landfill. At this point, under mild duress, I communicated some "preliminary results" to the Regional Office. Shortly thereafter, during the preparation of this report, the omission was discovered and the acids fraction of W27 analyzed.

One can see from the Table that the contamination patterns found in the three wells (Artesian 2, Amoco PW3, and MW27) are clearly related. All four of the compounds present in W2 are also in MW27 and in PW3. Seven of the thirteen compounds present in PW3 are also present in MW27. These results suggest that chemicals are migrating from the landfill into Artesian Well 2 and Amoco PW3.

The computerized mass spectral search system lead to the tenative identification of two of the four peaks found in Artesian W2. The first peak matched chlorocyclohexanol and the second peak matched dichlorocyclohexane. One of the peaks in PW3 appears to be dichlorotoluene.

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One of the other peaks in W2 appears to be chlorinated (based upon the isotope ratio of the mass fragments) and five of the remaining peaks in PW3 appear to be chlorinated.

The contamination in the other three wells sampled did not seem related to the three wells discussed above. From the Table, one can see that no contaminents were detected in MW42 and only one peak in RW3. Ten large peaks were detected by the GC/MS scan of the sample from MW29. Several of the peaks were tenatively identified (dinonyl phthallate, tributyl phosphate, a substituted phenol) but probably are not of too much interest because they do not occur in the other samples.

An important point to mention here is that, in order for a compound to be detected by our GC/MS system run as it was for these scans, the concentration in the original 1-liter sample would have to be on the order of 50 µg/l or 50 parts-per-billion. One can see that many chemicals which are alarming at the 5 to 10 ppb level in drinking water could have been present and passed undetected.

Although we do not have standards of the chlorinated materials identified in the drinking water and therefore can not quantitate them, one can say that, judging from the sizes of the peaks observed, the levels could be 1 ppm or greater.

In conclusion, a few comments are probably appropriate about how our results compare to those of Ron Webb from EPA Athens (analyses performed in 1974).

Webb analyzed samples from three of the wells which were sampled this time -- RW3, Artesian W2 and MW29. He did not find any compounds in AW2. He did identify camphor, cresols, caprolactam, benzoic acid, and alot of aliphatic acids in RW3. Most of the materials he found were below the levels which we would have detected, so perhaps it is not too surprising that we detected only one peak. In W29, other than a suite of aliphatic acids, he detected chlorobenzene, p-dichlorobenzene, and triethyl phosphate. Of the ten major peaks which we detected, we identified dichlorobenzene, dinonyl phthallate and tributyl phosphate.

TOM/jr

cc: James W. Marks

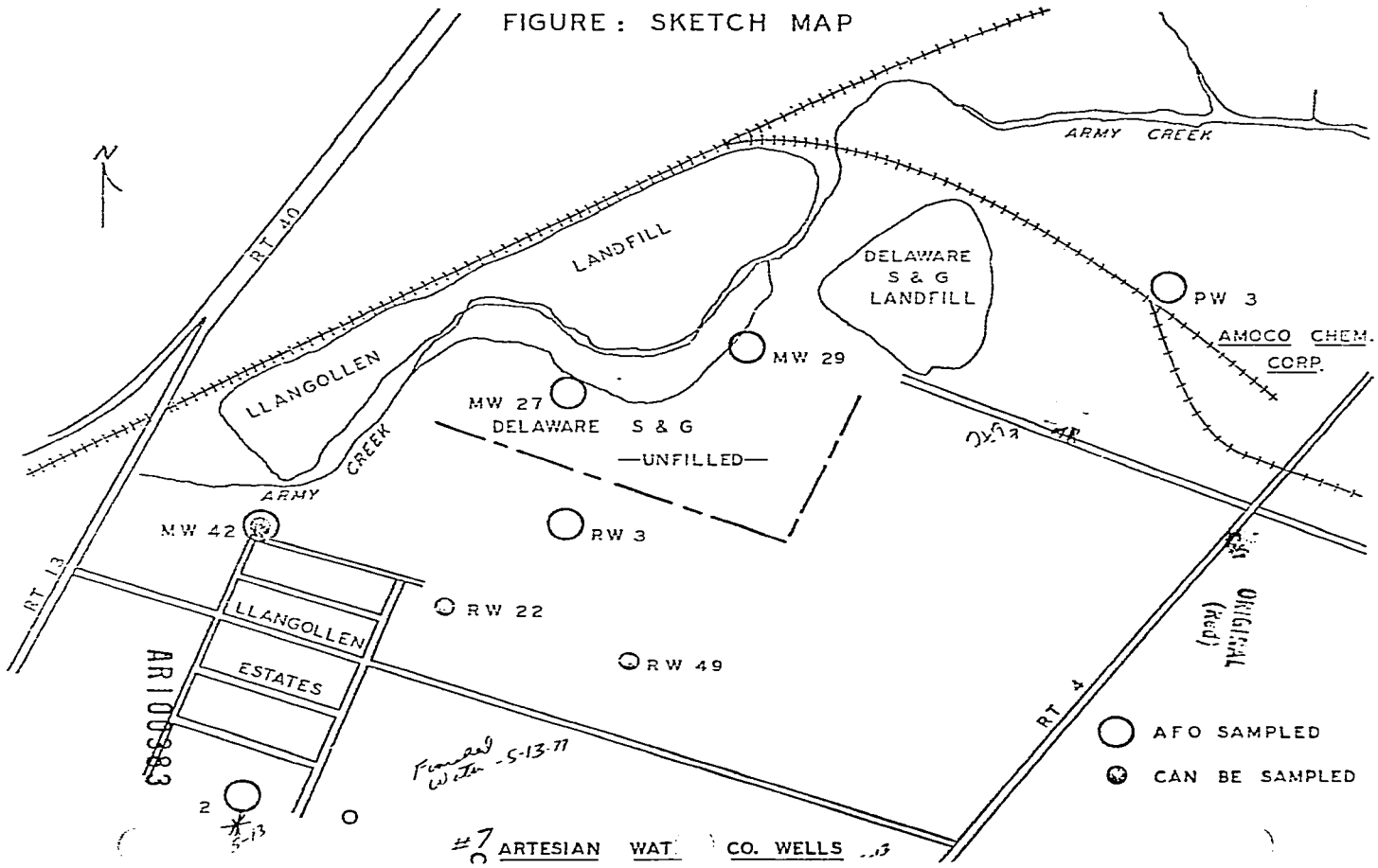
FIGURE: SKETCH MAP
N
RT 40
LANDFILL
ARMY CREEK
DELAWARE S & G LANDFILL
PW 3
AMOCO CHEM. CORP.
MW 29
MW 27
DELAWARE S & G
—UNFILLED—
LLANGOLLEN
CREEK
ARMY
MW 42
RW 3
RT 13
LLANGOLLEN ESTATES
RW 22
RW 49
RT 4
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AFO SAMPLED
CAN BE SAMPLED
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Flooded water - 5-13-77
2
5-13
#7 ARTESIAN WAT CO. WELLS

TABLE. Contamination Patterns of Sample Fractions

#	Base Peak	COMMENT	MW P W3			Interstitial W2			MW 21			MW 29			RW 3			MW 42		
			A	B	N	A	B	N	A	B	N	A	B	N	A	B	N	A	B	N
1	57	chlorocyclohexane	X	X		X	O	O	X	O	O					O	O	O	O	O
2	81	dichlorocyclohexane	X	X		X			X											
3	43		X		X															
4	125	dichlorotoluene	X																	
5	57				X															
6	146	dichlorobenzene										X		X						
7	57	chloro, bromo (?)							X											
8	83		X	X		X			X											
9	83	chloro		X		X			X											
10	68	chloro	X	X					X											
11	81	chloro	X	X					X											
12	81														X					
13	81	chloro (?)		X					X											
14	81	dichloro		X																
15	43		X		X															
16	71				X															
17	119											X								
18	119											X		X						
19	97											X								
20	63	dichloro										X								
21	97											X								
22	45	very large multiplet (?)										X	X	X						
23	305	2,6-di-tert-butyl-methylphenol											X							
24	99	tributyl phosphate												X						
25	57	dimethyl phthalate												X						

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Detection of Trace Organics around the Llangollen Landfill near Wilmington Delaware

ORIGINAL (Red)

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On May 19, a total of nine wells located in and around the Llangollen landfill (Army Creek Landfill) were sampled for trace organics by Dr. DeWalle according to procedures outlined in the previous report detailing the analytical results of the sample analysis of the first six collected samples. After collection of the well water in fired teflon capped sample vials, icing and air transporatation to the University of Illinois, the water was stripped on May 20 and 21 and the volatile organics were adsorbed onto a Tenax GC column for further GC and GC/MS analysis (Varian MAT 311 A), according to procedures outlined in the previous report.

The geographical location of the different wells is shown in Figure 1 while the construction details are listed in Table 1. The sampling rationale required the collection of an unpolluted upstream groundwater sample, a polluted sample in the landfill, a moderately polluted sample from the recovery well downstream of the landfill and the three Artesian and two Amoco wells used for drinking water. One finished water sample was also included in the analysis.

The results in Table 2 indicate that most organics are present at very low concentrations generally below 1 μg/l (1 ppb). Of a total of 41 detected compounds 23 were identified while the remaining compounds were not identified due to their low concentrations and the limitations of the GSHS computer search. The cleanest drinking water well was PW-1 while the most polluted was PW-3 both operated by Amoco. Although PW-3 and PW-1 are located

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very closely together, the data in Table 1 shows that PW-1 is retrieving waters from greater depth's that are apparently less polluted. The Artesian Water Company wells are equally polluted at very low levels of contamination. Comparison with the upstream Midvale well shows a great similarity in the type of organics present in these waters, suggesting that most organics detected in the Artesian wells are already present in the groundwater when it flows around and below the landfill. A great similarity also exists between the specific organics detected in the Amoco PW-3 well, the recovery well RW-3 and the S1 well in the landfill, suggesting that PW-3 is contaminated by the Llangollen landfill.

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Of all organics identified, benzene was detected at the highest concentrations in most of the samples, followed by hexane. Toluene was detected in highest concentrations in the landfill, suggesting that substantial amounts of industrial wastes were co-disposed of in the landfill.

The above analytical results would indicate that the recovery pumping system is effective in preventing the landfill pollution from reaching the Artesian well field. It is however, less effective in preventing low levels of contamination in Amoco well PW-3. It is therefore suggested that additional samples be taken from the Amoco wells and from sampling wells between the landfill and the Amoco well field to determine the flow path of landfill contaminants.

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	Midvale Artesian Wells	Artesian W.C. G3	Artesian W.C. 7	Artesian W.C. 2	Finished Water	AMCO PW2	AMCO PW3	Recovery Well RW 3	[illegible] le
Date Drilled	-	7-71	2-3-69	11-1-53	-	7-7-60	5-9-61	6-29-73	-
Driller	-	-	Layne, N.Y.	Kelly	-	Rubon,Cook	Shultes	Delmarva	-
Drilling Method	-	Mud Rotary	Rotary	Rotary	-	Rotary	Rotary	Mud Rotary	[illegible]ckhoe
Drilled Depth (ft)	-	200	195	-	-	629	149	153	[illegible]
Completed Well Depth	-	170	180	163	-	567	149	142	[illegible]
Screened Interval	-	115-155	115-180	-	-	-	120-149	121-142	33
ID of screen cashing(in)	-	12	12	17	-	-	16	10	4
Casings material	-	steel	steel	concrete	-	steel	steel	steel	PVC
Screen material	-	steel	steel	concrete	-	steel	steel	steel	PVC
Slot size (inch)	-	0.04	-	-	-	-	-	0.03	-
Fronting material	-	cement	-	-	-	-	-	cement	-
Formation screened	-	Potomac	Potomac	Potomac	-	Lower Potomac	Potomac	Potomac	Landfil
Measuring Pt. elevation Above MSL (ft)	-	20.6	48.1	65.1	-	20	20.5	35.5	-

TABLE 1: Construction details of the different wells sampled on May 19, 1977.

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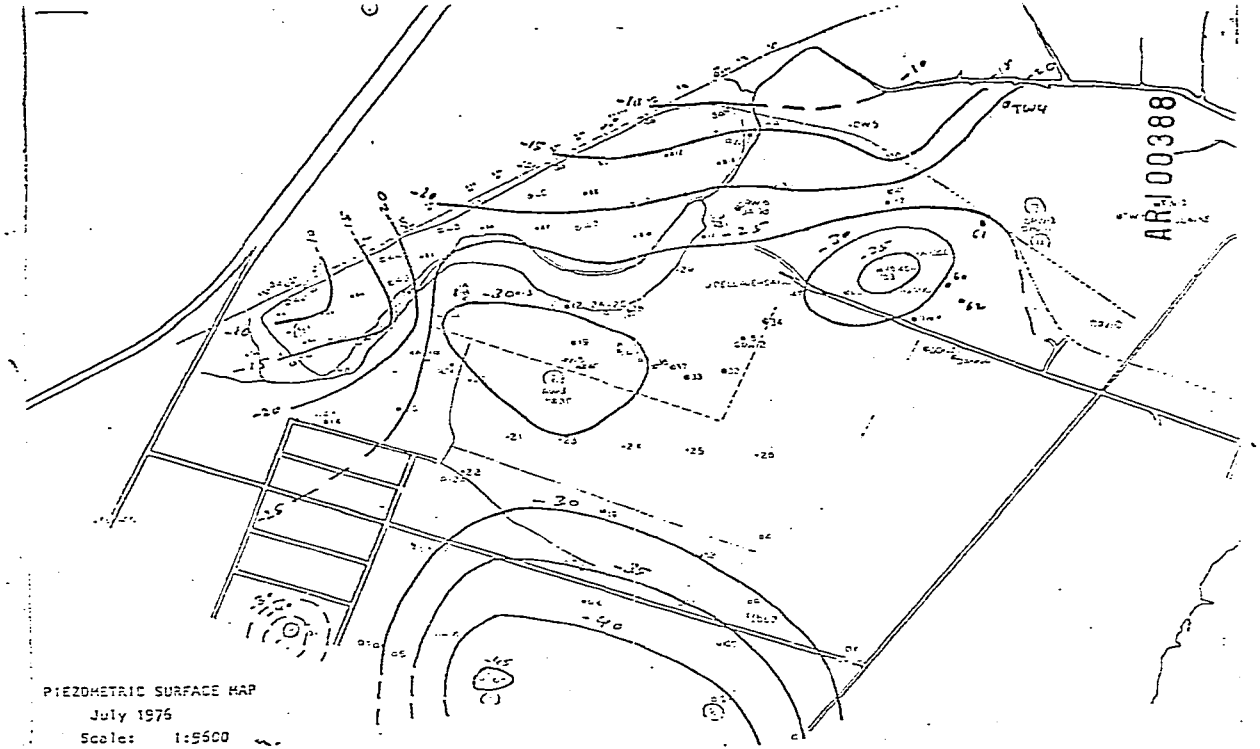

FIGURE 1: Location of the different wells compiled on May 19, 1977 and location of the piezometric surface of the

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