Box 58
N60-02-10

DPST-85-783
Acc. No. 189390

TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

Keywords: Burial Ground
Groundwater
Organics

RECORDS ADMINISTRATION
R0962652

CC: W. R. Stevens, III, 773-A
G. W. Wilds, 773-A
H. F. Sturm, Jr., 773-A
J. A. Stone, 773-41A
M. A. Ebra, 773-A
M. W. Grant, 773-41A
R. E. Eibling, 773-A
D. E. Gordon, 773-42A
C. M. King, 773-42A
S. W. Hixson, 703-A
SRL Records (4), 773-A

SRL FILE
RECORD COPY

September 26, 1985

TO: E. L. ALBENESIUS, 773-A

FROM: S. L. HOEFFNER, E. L. DENHAM, AND S. B. OBLATH
SLH. ELD. SBO

ANALYSIS OF ORGANICS IN 643-G GROUNDWATERS BY GC/MS

SUMMARY

Twenty-three of the 63 monitoring wells in the 643-G burial ground consistently contain measurable (> 1 ppm) amounts of total organic carbon, TOC. Of these 23 wells, 10 that contain elevated (2-400 ppm) TOC were chosen for in-depth analysis of semivolatile organics by gas chromatography/mass spectrometry, GC/MS. A well located near the site of previous decontamination operations was also chosen for analysis. About 40% of the organic compounds detected in these well waters have been identified. Many of these compounds are indicative of liquid scintillation wastes, spent solvent wastes, and solvent degradation products. Four priority pollutants were present at low levels. Some of the organics identified are probably degradation products from humic substances. Organic compounds of unknown origin are also present. No strong chelators capable of increasing radionuclide mobility have been identified. Preliminary dialysis work indicates that up to 30-40% of the TOC may be present as nonvolatile humic substances that cannot be analyzed by GC/MS.

INTRODUCTION

This work is part of a larger study, the primary objective of which is to obtain data on migration of radionuclides from an operating shallow land burial site. Periodic analyses of the groundwaters beneath the 643-G burial ground have verified the

satisfactory containment of radioactive and hazardous wastes[1]. However, it is also important to anticipate the future performance of the burial ground.

The purpose of the identification of organics in the groundwater is several-fold:

1. Organic chelating agents may be detected. The presence of chelating agents can have a profound influence on radionuclide mobility.

2. Organics in the groundwater may account for the radionuclide sorption observed in the laboratory when the radionuclide, burial ground water, and soil are equilibrated. (Inorganic factors, especially pH, account for a portion of the observed behavior, but groundwaters with a measurable TOC decrease radionuclide sorption[2].)

3. Data on organics in the burial ground water have been very limited.

4. The identification of organics compliments the study on the effect that inorganic components have on radionuclide mobility[3].

5. Organics of concern, such as hazardous wastes or priority pollutants, may be identified.

6. The data can be used 1) in transport models and 2) to compare burial ground, lysimeter and laboratory results.

Laboratory studies of factors that can influence the mobility of radionuclides in the low-level radioactive waste burial ground have been conducted at the Savannah River Laboratory since the early 1960's. Extensive characterization of inorganic species in the groundwater and the effect of changing groundwater composition on radionuclide sorption are well documented[3]. However, only a small amount of work has been done previously to identify organics in the groundwater.

Recent organic studies[2,4] include 1) a summary of the history of organics disposal in the burial ground, 2) TOC analyses of burial ground waters, 3) specific organic analyses using colorimetric methods, and 4) results of simple correlations between TOC and other important variables. A search of SRL records and literature revealed that the major sources of organic waste in the burial ground are from disposal of liquid scintillation samples, spent solvent, waste oils, and decontamination reagents. TOC analyses of the burial ground well waters, done first in 81-82, were repeated several times in 1984. From these data, ten wells that consistently contained measurable amounts of TOC were chosen for GC/MS analysis. Well A-5, located near the site of previous decontamination operations, was also chosen. The location of wells in the burial ground is shown in Figure 1.

Specific analysis for EDTA, TBP, and oxalate ion were of limited value, mainly because of poor sensitivity. These data and the results of the TOC analyses are summarized in Table 1. Attempts to correlate TOC, radionuclide K_d (the soil/water equilibrium distribution coefficient), phosphate concentration, and observed beta-gamma and alpha activity were not successful, indicating the system is complex.

This report builds on previously reported data and concentrates on the results of gas chromatography/mass spectrometry analysis of the groundwaters.

PROCEDURE

Extraction and concentration of the organics from the groundwater was required for GC/MS analysis. The extraction/concentration procedure used was a modification of the EPA method 625 for base/neutrals and acids[5] and a method developed at PNL[6]. The procedure involves a pH 10 extraction of the base/neutrals into methylene chloride followed by a pH 3 extraction of the acids into methylene chloride. The acid fraction is brought to dryness, derivatized using BF_3/methanol, and redissolved in methylene chloride.

Considerable time was invested in developing the extraction/concentration procedure. The PNL method is satisfactory for some groundwaters but not for SRP waters, because the varying pH of the SRP waters changes the extraction efficiency of the various organics. Buffered pH extractions were found to be unrealistic because a large amount of salt would precipitate and interfere with the derivatization step. The EPA method uses pH-adjusted extractions but has no derivatization step. But, by using a pH-adjusted methylene chloride extraction and BF_3/ methanol derivatization of the acid extract, reproducible extractions are obtained. The procedure is outlined in Figure 2, and complete details are given in the Appendix. Probably the major deficiency of the current method is that the vacuum evaporations, conducted at 70 C, cause the loss of volatile organics. For such compounds the EPA has another protocol to follow.

Analyses were performed on an Extranuclear mass spectrometer interfaced to a capillary GC with splitless injection. A 25 micron DB-5 bonded column with a 0.25 micron coating of 95% dimethyl-(5%)-diphenyl-polysiloxane was used. Column conditions were: 1) 40 C for three minutes, 2) ramp to 150 C at 10 C/min, 3) ramp from 150 to 300 C at 3 C/min. The mass spectrometer was calibrated daily with gaseous perfluorotributylamine which has five prominent peaks in the range of 50 to 500 amu.

RESULTS

Of the 63 well waters, only about 23 consistently contain greater than 1 ppm TOC (see Table 1). Using the pH-adjusted extraction method, a total of 10 of these 23 waters, and well I-5, were chosen for GC/MS analysis (see Table 2). Due to the low

TOC levels, analysis of the remaining 52 well waters is impractical. Original plans were to analyze a control well outside of the burial ground to verify the low natural TOC levels of SRP groundwaters. However, both tap water and many of the burial ground waters contained no measurable organics, as determined by TOC and GC/MS analyses. It appears that even within the burial ground, organic contamination from the buried waste is very limited.

Of the eleven wells analyzed by GC/MS, three contained organics below the detection limit of the instrument. Peaks were observed by gas chromatography for these groundwaters, but specific compounds were not identified. Gas chromatography is about a factor 1000 more sensitive than GC/MS to the detection of organics. Of the other 8 groundwaters, 5 contained organics below the GC/MS detection limit in the pH 10 extract. Results are summarized in Table 2. There is no apparent correlation between TOC and number of compounds observed by GC/MS.

A summary of all the organic compounds identified to date is given in Table 3. The well(s) in which the compounds were found are listed in Table 4. Many of these organics are indicative of liquid scintillation components, spent solvents, waste oils, and humic substances (see footnotes to Table 3). No strong organic chelating agents have been identified in these waters although the carboxylic acids, dicarboxylic acids, and humic substances are certainly potential chelating agents[2,7]. Low levels of four priority pollutants were detected. Identification of those compounds that were present in low concentration and/or whose spectral match with library spectra was fair to poor is considered tentative. These compounds are enclosed in parentheses in Table 3.

Preliminary dialysis work indicates that up to 30-40% of the TOC may be present as the nonvolatile larger molecular weight (> 1000 MW in this instance) humic acid/fulvic acid type organics. Apparently a wide range of organic compounds are present in these groundwaters. In light of this, the lack of correlation observed between TOC (a significant portion of which might be humic substances), K_d, phosphate concentration, radionuclide activity, etc. is not so surprizing. Humic substances can have an effect on radionuclide mobility[7]. Because they appear to be present in burial ground waters, further characterization of the site-specific humic materials is important.

CONCLUSIONS

1. Greater than 1 ppm TOC was consistently present in 23 of the 63 monitoring wells.

2. Through GC/MS analysis of 11 of these well waters, more than 50 organic compounds were identified.

3. Many of the compounds were indicative of spent solvent, oil and liquid scintillation wastes, and degradation products of humic substances.

4. No strong chelating agents were identified, although the carboxylic acids, dicarboxylic acids and humic substances are certainly potential chelators.

5. Four priority pollutants were present at low levels.

6. About 60% of the organic compounds that were detected remain unidentified.

7. As much as 40% of the TOC is nonvolatile and not detected by GC/MS.

RECOMMENDATIONS

Because of the limited sensitivity of GC/MS and because a significant portion of the TOC may be present as humic substances, additional GC/MS analyses of the groundwaters would be of limited value. The low level organics present in the majority of the burial ground wells could be identified using GC with GC/MS confirmation. This approach would be very time consuming. Since the compounds identified to date have little or no potential chelating ability, further study would be more appropriately directed towards characterizing the humic substances present in the groundwater. It may well be that these humic substances decrease radionuclide sorption more than those organics identified by GC/MS analyses[7]. Analyses by GC/MS of lysimeter effluents (where anionic cobalt is present) and trench water leachate (where any leachate from the buried waste is most concentrated) would also be of interest.

QUALITY ASSURANCE

The concentration/extraction procedure is described in an appendix to this report. The computer printouts, spectral matches, and raw data from these studies are filed and in the posession of E. L. Denham. Work was performed by trained personnel. Reagents were analytical reagent grade and used as supplied.

REFERENCES

1. J. A. Stone, S. B. Oblath, R. H. Hawkins, R. H. Emslie, S. L. Hoeffner, and C. M. King. "Radionuclide Migration Studies at the Savannah River Plant Humid Shallow Land Burial Site for Low-Level Waste." Proceedings of the Sixth Annual Participants' Information Meeting, DOE Low-Level Waste Management Program. USDOE Report CONF-8409115, p 119, EG&G Idaho, Inc., Idaho Falls, Idaho (1984).

2. S. L. Hoeffner. "Scoping Study of Organics in Well Waters of the SRP Low-Level Waste Burial Ground." DPST-84-796. November 14, 1984.

3. S. L. Hoeffner. Radionuclide Sorption On Savannah River Plant Soil: A Summary and Interpretation of Laboratory Data. DP-1702. 1985.

4. S. L. Hoeffner. "Organics in the 643-G Burial Ground." DPST-84-738. October 5, 1984.

5. "Method 625 - Base/Neutrals and Acids." US Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. July 1982.

6. A. P. Toste, L. J. Kirby, and T. R. Pahl. "Role of Organics in Subsurface Migration of Radionuclides in Groundwater." Chapter 15 in Geochemical Behavior of Disposed Radioactive Waste. G. S. Barney, et. al., (eds). ACS Symposium Series No. 246. American Chemical Society, Washington, D.C. 1984.

7. Sam Boggs, Jr., David Livermore, and M. G. Seitz. Humic Substances in Natural Waters and Their Complexation With Trace Metals and Radionuclides: A Review. ANL-84-78. Argonne National Laboratory. Argonne, Illinois. 1984.

TABLE 1

Preliminary Characterization of
Organics Present in Burial Ground Well Waters

Well	Total Organic Carbon, ppm 80-82	3/84	6/84	9/84	EDTA, ppm	Oxalate, ppm	TBP, ppm
A-1	3.7	<1.0	<1.0	-	-	-	-
A-3	0.0	3.2	<1.0	<1.0	<0.1	-	-
A-5	0.0	<1.0	<1.0	-	-	-	-
A-7	-	<1.0	<1.0	-	-	-	-
A-9	-	<1.0	<1.0	-	-	-	-
A-11	0.0	<1.0	<1.0	-	-	-	-
A-19	0.0	<1.0	<1.0	-	-	-	-
A-21	0.0	<1.0	<1.0	-	-	-	-
A-23	5.6	1.6	1.2	-	-	-	-
A-32	5.2	1.0	2.0	-	-	-	-
A-34	0.4	<1.0	<1.0	-	-	-	-
A-36	4.0	5.6	<1.0	<1.0	<0.1	<1.0	<0.10
C-1	0.0	1.0	-	-	-	-	-
C-3	0.0	1.8	3.0	-	<0.1	-	-
C-5	0.0	<1.0	2.6	25.3	-	-	-
C-7	0.0	3.8	3.8	11.4	<0.1	-	-
C-9	6.0	<1.0	1.3	2.2	-	-	-
C-11	11.0	<1.0	-	<1.0	-	-	-
C-13	0.0	<1.0	<1.0	-	-	-	-
C-15	0.0	5.6	<1.0	<1.0	0.39	<1.0	-
C-17	20.9	<1.0	<1.0	-	-	-	-
C-19	0.0	1.0	2.2	-	-	-	-
C-21	18.0	2.8	<1.0	<1.0	<0.1	-	-
C-23	0.0	6.5	1.4	<1.0	<0.1	<1.0	-
C-30	12.1	<1.0	<1.0	-	-	-	-
C-32	0.0	3.7	3.9	-	<0.1	-	-
C-34	8.0	1.3	1.6	-	-	-	-
C-36	3.0	<1.0	<1.0	-	-	-	-
E-1	10.1	2.4	1.9	-	0.15	-	-
E-3	11.9	2.4	<1.0	14.0	0.16	-	-
E-5	3.9	3.5	<1.0	<1.0	<0.10	-	-
E-7	5.0	2.5	<1.0	<1.0	<0.10	-	-
E-9	10.0	3.4	2.7	-	<0.10	-	-

TABLE 1 (continued)

Well	Total Organic Carbon, ppm 80-82	3/84	6/84	9/84	EDTA, ppm	Oxalate, ppm	TBP, ppm
E-13	4.3	<1.0	<1.0	-	-	-	-
E-15	-	-	2.0	<1.0	-	-	-
E-17	0.4	<1.0	6.9	<1.0	-	-	-
E-19	0.2	1.5	1.2	-	-	-	-
E-21	10.0	<1.0	<1.0	-	-	-	-
E-23	3.3	1.1	<1.0	<1.0	-	-	-
E-30	3.0	<1.0	<1.8	<1.0	-	-	-
E-32	0.0	1.5	8.5	<1.0	-	-	-
E-34	0.0	<1.0	<1.0	-	-	-	-
E-36	0.0	<1.0	<1.0	-	-	-	-
G-1	0.0	2.5	<1.0	<1.0	<0.10	-	-
G-3	0.0	2.1	<1.0	<1.0	<0.10	-	-
G-5	0.0	2.2	<1.0	<1.0	<0.10	-	-
G-7	45.0	61.4	65.6	-	<0.10	<1.0	<0.10
G-9	9.0	2.9	<1.0	<1.0	<0.10	-	-
G-13	0.0	6.2	<1.0	<1.0	<0.10	<1.0	<0.10
G-15	0.0	<1.0	<1.0	-	-	-	-
G-17	0.0	<1.0	<1.0	-	-	-	-
G-19	4.0	<1.0	<1.0	-	-	-	-
G-21	225.0	400.0	317.0	-	<0.10	<1.0	0.16
G-23	0.0	<1.0	<1.0	-	-	-	-
G-28	0.0	1.5	<1.0	1.0	-	-	-
G-30	4.0	1.8	<1.0	<1.0	0.22	-	-
G-32	0.0	1.7	18.0	11.2	-	-	-
G-34	0.0	<1.0	<1.0	-	-	-	-
G-36	4.0	<1.0	<1.0	-	-	-	-
I-1	16.0	5.4	4.2	-	<0.10	<1.0	<0.10
I-3	-	5.5	2.4	-	<0.10	<1.0	<0.10
I-5	6.0	21.5	364	-	<0.10	<1.0	<0.10
I-7	8.0	30.0	26	-	<0.10	<1.0	<0.10
I-9	3.0	5.4	<1.0	<1.0	<0.10	<1.0	<0.10
I-13	1.0	<1.0	<1.0	-	-	-	-
I-15	0.0	<1.0	<1.0	-	-	-	-
I-17	1.6	<1.0	<1.0	-	-	-	-

Table 2. Summary of Number of GC/MS Peaks Found When Analyzing Burial Ground Waters.

Groundwater	TOC, ppm	Number of Peaks			
		Total	Phillic	Phobic	Identified
A-5	<1.0	0	0	0	0
A-23	1.2	0	0	0	0
C-5	38.8	6	3	3	3
C-7	11.2	11	11	0	5
C-23	<1.0	0	0	0	0
E-3	8.1	7	6	1	3
G-7	30.3	3	3	0	2
G-21	946	24	24	0	13
G-32	14.3	1	1	0	1
I-5	334	55	55	3	38
I-7	64.5	4	3	1	1

Table 3. Organic Compounds Identified in 643-G Groundwaters.

Normal Acids

1. acetic acid[b]
2. butyric acid[b,d]
3. pentanoic acid [b,d]
4. (hexanoic acid)[b,d]
5. heptanoic acid[b,d]
6. hexanoic acid[b,d]
7. undecanoic acid[b,d]

Dioic Acids

8. ethanedioic acid[d]
9. (butanedioic acid)[d]
10. (pentanedioic acid)[d]
11. (hexanedioic acid)[d]
12. nonanedioic acid[d]

Phenyl Acids

13. benzoic acid[d]
14. phenylacetic acid[d]
15. phenylpropanoic acid[d]
16. phenylbutanoic acid[d]

Other Acids

17. dimethoxyacetic acid
18. (chloromethoxyacetic acid)
19. dichloroacetic acid
20. 3-methylbutanoic acid
21. (4-methylpentanoic acid)
22. 2-methylhexanoic acid
23. 5-methylhexanoic acid
24. 2 ethylhexanoic acid
25. 7-oxooctanoic acid
26. (9-oxodecanoic acid)

Nitrogen Compounds

27. (trimethylhydrazine)
28. N,N'-dimethylurea
29. (N-phenylbenzamine)
30. 4-nitro-N-phenylbenzamine
31. (N,N'-diphenylbenzamine)
32. (3,4-pyridinedicarboxylic acid
33. (methylhistamine)
34. (phenylisocyanate)

Sulfur Compounds

35. (2-(methylthio)benzothiazole)
36. 2-hydroxybenzothiazole

Phosphate Compounds

37. diethyl pentyl phosphate[b]

Table 3. Organic Compounds Identified in 643-G Groundwaters (cont'd).

Aliphatic Compounds

38. 1,3-dimethoxy-2,2-di(methoxy-methyl)propane
39. 3-methoxymethylbut-2-enate
40. hex-5-en-2-ol
41. (2-propyl-4-methyl-1-propanol)
42. 2,2,5,5-tetramethylhexane
43. (3-methoxy-5-methylhexan-2-one)
44. (2-heptanone)
45. (5-pentyl-2-furanone)
46. (1,3-dimethyl-2-ethylcyclohexane)
47. ethyl-2-methylbutyrate

Aromatic Compounds

48. benzene[a] (PP)
49. toluene[a] (PP)
50. phenol[a] (PP)
51. naphthalene[a] (PP)
52. (acetophenone)
53. phenylacetic acid
54. 2-ethylphenylacetic acid
55. phenoxyacetic acid
56. 4-hydroxybenzoic acid
57. 2-hydroxy-(3-methyl)benzoic acid
58. 2-hydroxy-(5-methyl)benzoic acid
59. (3-acetylbenzoic acid)
60. 3-acetoxyphenol
61. (4-methylphenol)
62. (2,6-di(tertbutyl)-4-methylphenol)
63. 1,2 diphenylbenzene

Note - All acids were actually identified as the methyl esters.

- Compounds in parentheses are only tentatively identified.
- Several compounds were identified that are probably impurities in the methylene chloride: chloroform, carbon tetrachloride, tetrachloroethylene, and cyclohexene. Phthalates were also identified but are probably from laboratory containers.
- (PP) refers to priority pollutant organics.

Possible Source of Organic: a - liquid scintillation wastes
b - spent solvent
c - waste oils
d - degraded humic substances

Table 4. Wells in Which Specific Organic Compounds Were Detected.

Well	Compounds Detected (identification numbers from Table 3)
A-5	no compounds detected
A-23	no compounds detected
C-5	27, 40, 61
C-7	4, 8, 9, 10, 11, 12, 17, 33, 49, 55
C-23	no compounds detected
E-3	30, 31, 32
G-7	36, 61
G-21	9, 12, 14, 15, 18, 25, 26, 29, 36, 39, 41, 42, 46, 47, 49, 53, 55, 59, 60, 62
G-32	32
I-5	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 13, 14, 15, 16, 19, 20, 21, 22, 23, 24, 27, 28, 34, 35, 36, 37, 38, 43, 44, 45, 48, 49, 50, 51, 52, 53, 54, 55
I-7	36

solvent impurities: C-7, I-5, I-7

phthalates: C-5, C-7, E-3, G-21, I-7

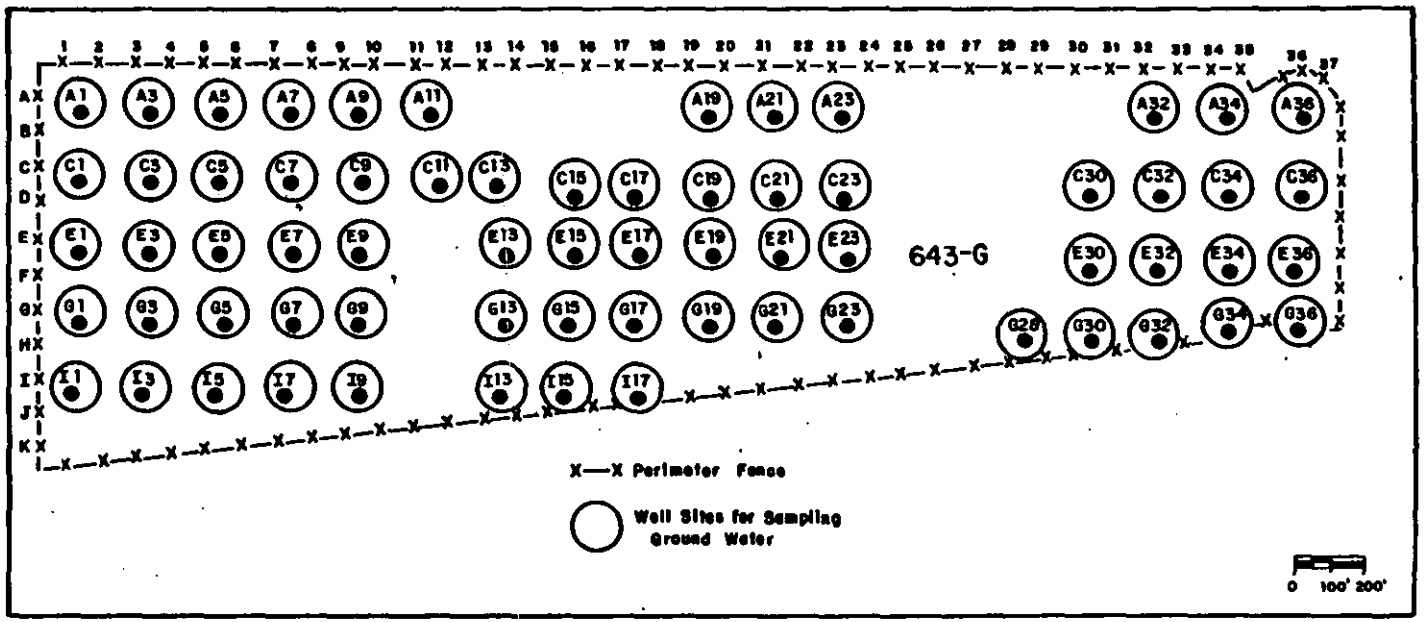

Figure 1. Groundwater Monitoring Well Locations in 643-G Radioactive Waste Burial Ground

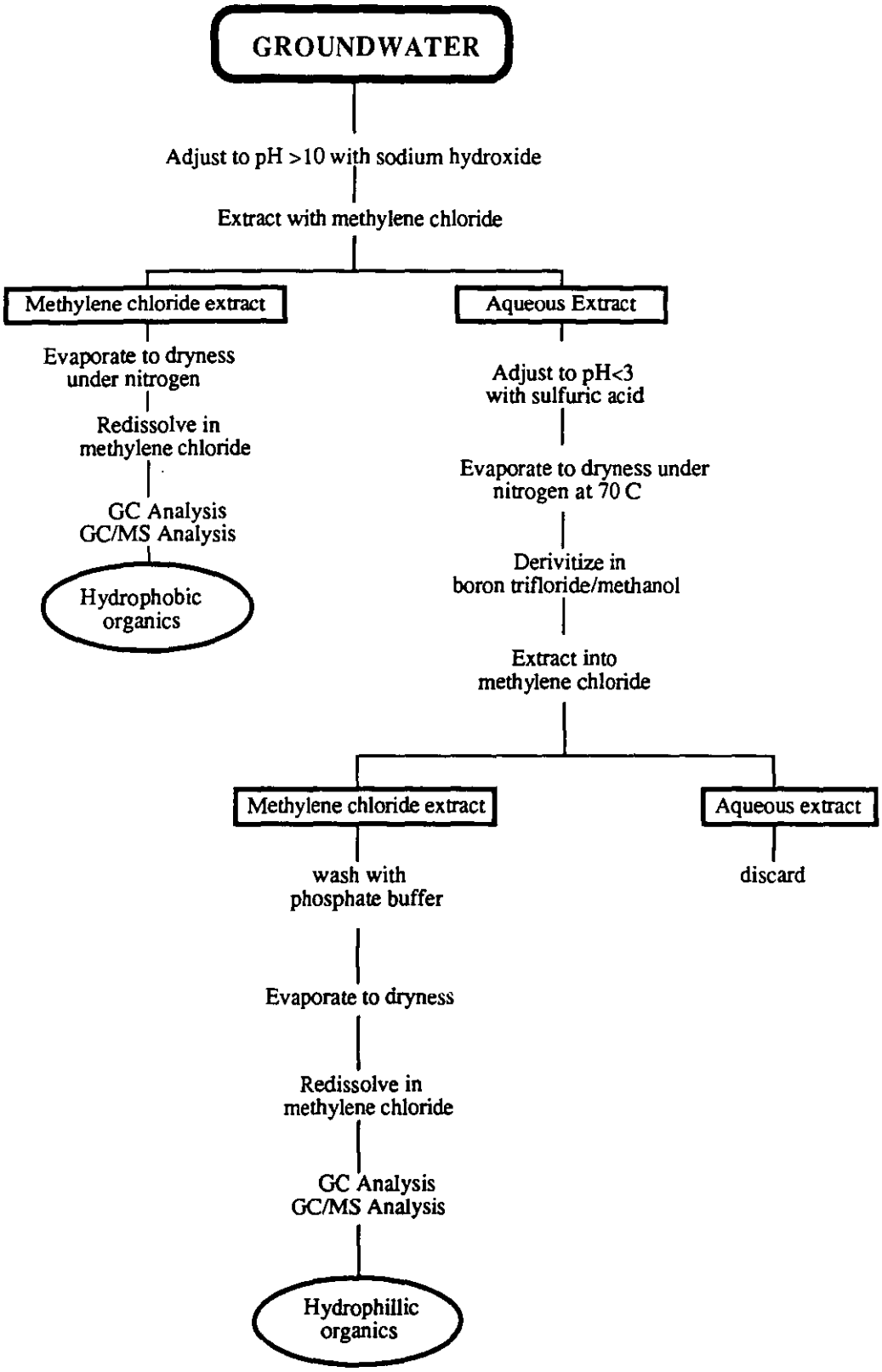

FIGURE 2. Groundwater extraction scheme.

APPENDIX
PROCEDURE FOR CONCENTRATION OF GROUNDWATER SAMPLES
May 14, 1985

Materials Required	Chemicals Required
Groundwater in 300 mL glass BOD bottle	Methylene Chloride--spectral pure grade (CH_2Cl_2)
Centrifuge and 15 mL centrifuge cones	14% BF_3/Methanol reagent (in vials)
Glass fiber filter apparatus	Nitrogen gas, purified in the lab
Cleaned glassware	1 M KH_2PO_4 buffer (13.6 g/100 mL)
-250 mL graduated cylinder	10 N NaOH (40 g diluted to 100 mL)
-25 mL graduated cylinder	1 + 1 H_2SO_4 (slowly add 50 mL of H_2SO_4 to 50 mL deionized water)
-50 and 250 mL roundbottom flasks for rotovap	
-15 mL centrifuge cones	
3 and 5 mL reactivials	
100, 500, and 1000 uL glass pipets	
Rotovap	
Heating block	
Vortex	

Safety Considerations:

Small amounts of methylene chloride and 14% BF_3 in methanol are used in this procedure. These chemicals are classified as moderately hazardous. Rubber gloves and safety glasses should be worn to avoid skin and eye contact (see DPSOL 158-2-4127 and DPSOL 158-2-4130.05). Methylene chloride is to be stored in accordance with regulations in the SRL and SRP safety manuals. About 60 mL of this organic liquid are required for each groundwater sample. Methylene chloride wastes are to be disposed of by evaporation in a hood. The BF_3/Methanol is contained in reagent vials. Each vial contains sufficient reagent (2 mL) to methylate one groundwater sample. These vials are to be stored in a refrigerator suitable for flammable solvents. Methanol wastes are to be diluted with water and disposed of down the low level drain.

As with all laboratory work, the SRL and Division safety rules pertaining to the laboratory are to be followed.

Cleaning of Glassware:

Clean all glassware as soon as possible after use by rinsing with the last solvent used in it (either water or methylene chloride). This is followed by washing with Alconox in warm water, using a brush where possible. Rinse thoroughly with tap water and then with deionized water. Dry in oven at 100 C. Wrap mouth of glassware with aluminum foil to keep dust and contaminants out.

Start-Up Procedure For Rotovap:

1. Pour 200 mL of groundwater (previously extracted 3 times with 20 mL of methylene chloride) into the 250 mL roundbottom flask.

2. Connect flask to rotovap.

3. Turn on water to the condenser.

4. Turn on vacuum pump. Turn on rotary motor and adjust to desired speed. To avoid vigorous boiling slowly close the addition stopcock. This allows the small amount of methylene chloride dissolved in the water to gently boil off.

5. Turn on heat to water bath and adjust temperature.

6. Continue evaporation until desired amount of sample has evaporated.

Shut-Down Procedure For Rotovap:

1. Turn off heat.

2. Turn off vacuum pump.

3. Open stopcock.

4. Turn off rotary motor.

5. Raise sample out of water bath.

6. Turn off condenser water.

7. Remove sample when cool.

Procedure For Concentration of Groundwater:

1. Collect groundwater samples in 300 mL BOD bottles. No air should be present in the bottles. Store in refrigerator at 4 C until ready for use. Record the date and which samples were pulled.

2. Filter the sample through a glass fiber filter using an all-glass filter apparatus.

Note: If unfamiliar with the proper usage of a separatory funnel, receive training and instruction on its use prior to proceding.

3a. Transfer 200 mL of the water to a 250 mL separatory funnel and save the remaining 100 mL for step 5. Add 10 N NaOH dropwise until the pH is > 11 (Measure the pH after each addition of NaOH by dipping a glass rod in the water and

touching the glass rod to a piece of paper. Rinse the glass rod with deionized water before dipping in the groundwater).

3b. After the pH of the groundwater has been adjusted, add 20 mL of CH_2Cl_2 to the sep funnel, shake 1 minute and allow to set for 10 minutes.

If no emulsion is present drain the bottom (CH_2Cl_2) layer into a 50 mL beaker and begin evaporation (step 4). Add a second 20 mL portion of CH_2Cl_2 to the sep funnel and repeat the extraction (shake 1 minute, etc.). Follow this with a third and final 20 mL CH_2Cl_2 extraction.

If an emulsion is present procede as follows. For the first two extractions drain off as much of the methylene chloride layer as possible and add the next portion of methylene chloride. For the third extraction further separation of the layers can be obtained as follows:
- drain off as much as possible of the bottom (CH_2Cl_2) layer into a 50 mL beaker and begin evaporation (step 4).
- drain the remaining sample (emulsion and aqueous phase) rapidly through the separatory funnel into a 250 mL beaker.
- return this sample to the sep funnel and allow the emulsion to break down further into the aqueous and organic layers.
- repeat these first three steps several times, transfering the bottom layer into the 50 mL beaker, until the amount of the organic phase that separates out of the emulsion is very small.
- transfer the emulsion that remains in the sep funnel to a 15 mL centifuge cone and centrifuge at a setting of 5 for 5 minutes. Remove the CH_2Cl_2 layer with a glass pipet. Combine with the CH_2Cl_2 phase in the 50 mL beaker.

4. Combine the CH_2Cl_2 extracts in a 50 mL beaker and set on a hot plate (setting of 1) in the hood. When the volume is 3 mL or less, transfer the sample to a 3 mL reactivial. Rinse the beaker twice with a small amount of methylene chloride (about 0.5 mL) and transfer the rinse to the reactivial. Evaporate to dryness under a stream of nitrogen gas. Resuspend the residue in 100 uL of CH_2Cl_2, mixing well with the vortex for 1 minute. This is the **hydrophobic organic fraction.** Label the reactivial with the well number, date, and the letters FO (abbreviation for water-Fearing Organic extract). Store in refrigerator at 4 C until analyzed.

5. Measure the pH of the 100 mL of groundwater remaining from step 3 (Calibrate the pH meter if necessary).

6. Transfer the extracted water from step 3 into the 250 mL roundbottom flask and concentrate on the rotovap (T = 70 C) to about 40 mL. Add dropwise a 1 to 10 dilution of 1 + 1 H_2SO_4 until the pH is less than 2. Record the final pH. Transfer the sample to the 50 mL roundbottom flask and concentrate to near dryness.

7a. Rinse the concentrated groundwater into a 3 mL reactivial. As much as possible leave behind any precipitate that has formed.

7b. Dry the sample under nitrogen in the heating block at 60 C (setting of 9 on the low temperature adjust). When dry, remove the vial and let cool. In preparation for step 9, adjust the temperature of the empty heating block to 100 C (setting of 5 on the high temperature adjust).

8. When the sample has cooled, add 2 mL of BF_3/methanol (14% w/v), tightly cap the sample and vortex for 1 minute.

9. Heat the vial in the heating block at 100 C for 50 minutes.

10. Remove the vial and cool for at least 7 minutes. Turn off the heating block. Add 1.00 mL CH_2Cl_2 and vortex the vial for 1 minute.

11. Transfer the sample into a 15 mL centrifuge cone that contains 3 mL of KH_2PO_4 buffer.

12. Add an additional 1000 uL of CH_2Cl_2 to the reactivial. Vortex 1 minute and transfer to the centrifuge cone.

13. Rinse the vial twice with less than 0.5 mL of the buffer solution (using the vortex). Transfer the rinses to the centrifuge cone.

14. Vortex the cone for 1 minute (Adjust vortex speed so that no sample is spilled).

15. Centrifuge the cone for 10 minutes at a setting of 5.

16. Transfer 1000 uL of the bottom (CH_2Cl_2) phase to a 3 mL reactivial. Record the amount of the bottom phase that remains in the cone.

17. Dry the 1000 uL sample under nitrogen. Resuspend the residue in 100 uL of CH_2Cl_2. This is the **hydrophillic organic fraction.** Lable the reactivial with well number, date, and LA (abbreviation for water-**L**oving **A**queous concentrate).

18. Cap the vial; vortex, and record the sample volume.

19. Store the sample in the refrigerator until analyzed. Check volume on a weekly basis and add methylene chloride as necessary to bring all sample volumes up to 100 uL.