

ORGANIC COMPOUNDS AT THE SRP OLD BURIAL GROUND FOR
LOW LEVEL RADIOACTIVE WASTE

Steven B. Oblath
E. I. du Pont de Nemours and Company
Savannah River Laboratory
Aiken, South Carolina, 29808

ABSTRACT

Between 1953 and 1972, the Savannah River Plant (SRP) disposed of its solid, low-level radioactive waste in a 31 hectare shallow land burial site. A grid of 63 monitoring wells covering the site were used to sample for organic species in the groundwater which might enhance the mobility of radionuclides in the soil/water system. Total organic carbon (TOC) measurements were used as a screening method to select which wells should be used for oxalates, tri-n-butyl phosphate, and EDTA. More thorough analyses were performed using gas chromatography and mass spectrometry for a number of the wells. Using this procedure over 60 compounds were identified. Spent solvents, scintillation wastes, and decomposing cellulosic wastes are believed to be the primary sources. None of the compounds were identified as strong complexing agents which would enhance migration. Preliminary experiments indicated that as much as 40% of the organic carbon may be humic material. These substances were not further characterized. However, humic materials have been implicated in increasing mobility of radionuclides in soil/water systems.

INTRODUCTION

The low-level waste burial grounds at the Savannah River Plant (SRP) comprise approximately 79 hectares and are centrally located on the site. The old burial ground began operations in 1953, and comprises 31 hectares. It was filled in 1972, and operations since that time have been in an adjacent area. This original 31 hectare site has been the subject of extensive monitoring efforts over the years, including measurements of radionuclides and inorganic species in the groundwater beneath the site(1).

A variety of wastes have been disposed of in this low-level waste facility(2). Most of this waste is similar to what is referred to as dry active wastes in the commercial nuclear industry. A significant quantity of the waste is incidental waste from laboratory and production operations, including air filters, sample bottles, protective clothing, gloves, decontamination residues, wipes, and similar materials. A large fraction of this material was disposed of in plastic bags and/or cardboard boxes in shallow burial trenches. This provides a potentially large source of humic material, should these materials decompose in the soils. The length of time which these containers retain their integrity is not known. Contaminated equipment, spent resins, and spent lithium-aluminum targets have also been disposed of in this disposal facility. Small quantities of used oils and scintillation wastes were disposed of on absorbent materials. The types of wastes disposed of and the manner of disposal has changed over the years, due to changes in the wastes generated and the regulations in effect at the time of disposal. However, almost all of these wastes represent potential sources of organic species which may leach and be present in the soil/water system beneath the burial site.

Records were kept both of the radionuclide content and source of wastes which were disposed of in the facility, as well as the location of burials. In addition, records of operations and discussions with

employees who were involved in the early disposal operations provided information on what operations went on in what portions of the facility. While most of the records were not concerned with what organic species were being stored or disposed of within the facility, they provide useful historical information on the types of compounds which may be present.

Early in the history of the burial ground, spent solvent from the PUREX separation processes were burned in open pans at the burial ground. Later this waste was stored in single walled underground tanks within the 31 hectare site. An estimated 1.5 cubic meters of spent solvent has been released to the burial ground environment, due to leaks in tanks and solvent spills(1). These solvents have since been transferred to newer, more secure double walled tanks in another portion of the facility.

An additional source of organic species was the decontamination of large pieces of equipment, which was performed in the northwest corner of the facility during the early years of the operations of SRP. This was a source of soluble complexing agents, including ethylenediamine tetraacetic acid (EDTA)(1). These decontamination operations took place prior to waste having been buried in that portion of the facility, and would not likely have migrated through the waste-containing zone.

In the early 1970's, installation of a grid of 63 monitoring wells was completed in the 31 hectare portion of the burial site. The layout of the burial ground and the grid of monitoring wells is shown in Fig. 1. Although installed for measuring radionuclide content of the groundwater and for making water table measurements, the wells have also been used for chemical analyses of the groundwater(1). These same wells were used in the present study to determine the nature of the organic species present in the groundwater beneath the burial site. The study emphasized analysis for those species which might be complexing agents for radionuclides, and enhance the mobility of the radionuclide in the soils present at SRP.

METHODOLOGY

The 63 monitoring wells are of two types of construction. The majority of the wells have a 6 meter section of stainless steel screen centered at the normal water table elevation, with the rest of the well being constructed of polyvinyl chloride (PVC) pipe. A smaller set of wells are similar, but the screen is made of PVC and the casing is galvanized steel. Each well is provided with a 1 liter stainless bailer, which hangs within the casing, but above the water table, when not in use. The wells are capped to eliminate debris falling into the wells. Samples were collected from the surface of the water table using the bailer, and best represent the percolate waters which have most recently reached the water table. The samples were transferred from the stainless bailer to glass bottles by pouring. The samples were refrigerated immediately upon return to the laboratory. This sampling technique is likely to result in significant losses of highly volatile organic species. However, such species are not typically complexing agents, which is the focus of the current work.

If necessary, the samples were filtered through glass fiber filters in an all glass apparatus prior to analysis. All wells were subjected to total organic carbon (TOC) analyses, either by combustion methods or persulfate oxidation. Samples were collected from each well a number of times over a four year period, at different seasons. This information, coupled with the historical data, was used to limit the number of samples which were selected for additional analyses.

Samples which had TOC concentrations above the detection limits of methods for specific species were analyzed for that species. This included oxalates by ion chromatography, tri-n-butyl phosphate (TPB) by gas chromatography, and EDTA by colorimetric techniques. In addition, fifteen wells were chosen based on location, TOC measurements, and historical records for analysis by gas chromatography/mass spectrometry (GC/MS). The locations of these wells in relation to some of the known events and activities which took place during waste disposal operations are shown in Fig. 2. Finally, several wells were selected for analysis using dialysis membranes and TOC measurements to determine what fraction of the organic carbon had molecular weights in excess of 1000 daltons. This serves as a measure of the fraction that is likely to be humic material.

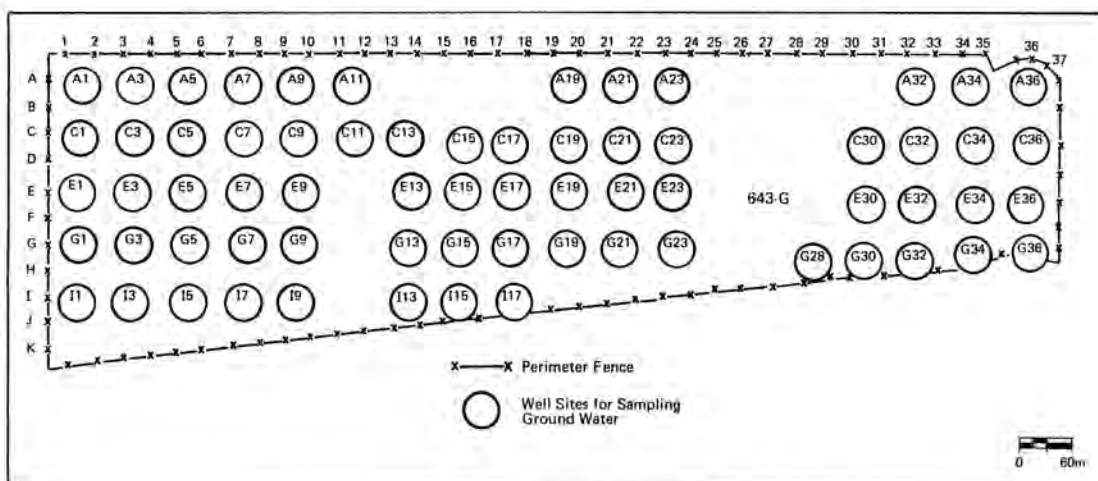


Fig. 1. Groundwater Monitoring Well Locations at the SRP Low-Level Waste Burial Ground.

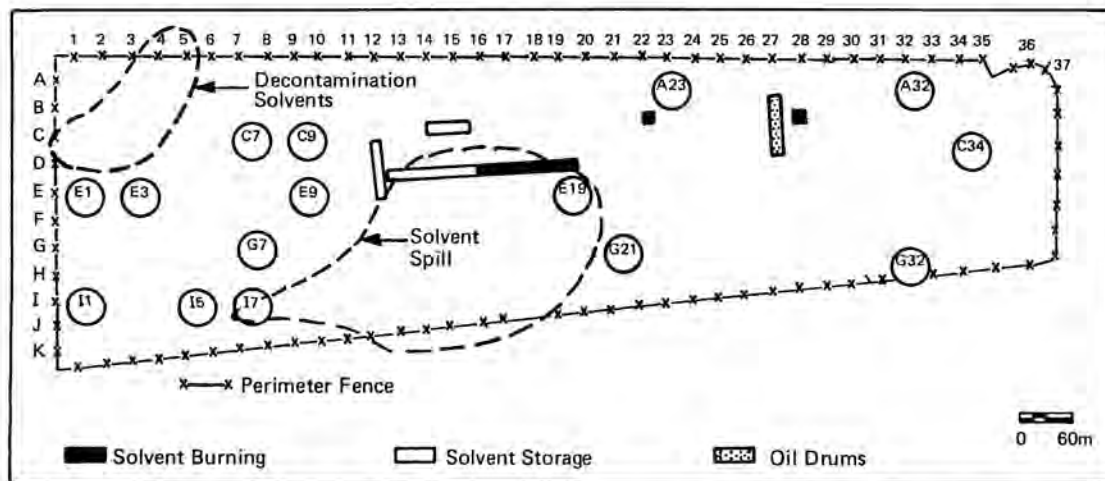


Fig. 2. Locations of Wells Selected for GC/MS Analysis and Known Sources of Organics.

SPECIES SPECIFIC ANALYSES

Total Organic Carbon

TOC levels were determined for all 63 wells over a four year period. During each sampling period, between 25 and 30 of the wells contained greater than 1 mg/L of TOC. Generally, less than ten wells contained TOC levels in excess of 10 mg/L in any given sampling. The well with the maximum concentration fluctuated between 200 and 900 mg/L. These values are generally less than has been observed in similar screening studies at commercial low-level radioactive waste burial grounds(3). It was found that the TOC levels varied significantly over the four year period, but did not seem to correlate with season. However, the wells that contained significant amounts of TOC always had detectable amounts. Most of the other wells never showed measurable TOC concentrations. For this reason, most of the remaining analyses were performed only on all or a subset of the 25-30 wells which routinely yielded samples containing organic carbon.

The groundwaters from a number of these wells were used in radionuclide sorption studies for ^{137}Cs , ^{90}Sr , and ^{60}Co . The technique used was a batch type distribution coefficient measurement which has been described elsewhere(4). No systematic decrease in distribution coefficient with increasing organic carbon content of the water was noted. With the variety of organic species which could contribute to the TOC, no systematic trend was expected.

EDTA

EDTA was detected in four of 26 wells in the burial ground. The maximum observed concentration was 0.4 mg/L, with a detection limit of 0.1 mg/L. Only two of the four wells showing EDTA were in the portion of the burial ground associated with the equipment decontamination operations. This indicates that there are additional sources of EDTA in the burial ground. If these sources are packages of waste, more material may become accessible to the environment as the waste containers become breached. As a strong chelating agent for many metals, it is possible that this species could enhance the mobility of a number of radionuclides, particularly induced activity radionuclides such as ^{63}Ni and ^{60}Co .

Tri-n-butyl Phosphate

TBP was detected at a concentration of 0.16 mg/L in only one out of nine samples. The detection limit for the method was 0.05 mg/L. For this sample, the TBP made up less than 1% of the TOC that had been measured. Since most of the samples analyzed for TBP were from the zone affected by the solvent spill, this result was somewhat unexpected. However, the analysis used was specific for TBP, and any degradation products would not have been identified. In addition, TBP floats on the surface of the water table, moves laterally, and is sorbed by the soil. With the length of time since the spill occurred, and a low water table at the time of sampling, it is likely that the TBP was not present in the water samples at that time. This does not preclude its presence when the water table again increases to near its high water mark since the spill.

Oxalates

No oxalate was observed (detection limit of 1 mg/L) in any of the eleven wells analyzed. The lack of any oxalate in the northwest corner of the burial ground probably indicates that it was not used in decontamination operations, or that it is readily degraded in the soil system.

GC/MS ANALYSES

Fifteen wells were selected for the GC/MS analysis of the groundwater. Extraction and concentration of the water was necessary both to give sufficient concentrations for detection in the mass spectrometer, and to separate the sample into acid and base/neutral fractions for ease in identification. The procedure used is outlined in Fig. 3, and is a modification of both the EPA Method 625(5), and methods developed at Pacific Northwest Laboratories for similar shallow land burial studies(3). The modifications to the EPA method include evaporating the methylene chloride extracts to dryness, and inclusion of a methylation step to give better GC separation of the carboxylic acids. While this is a useful technique for the acidic species which are typically complexing agents (and of interest to the present study), it causes the loss of any volatile organic species. Several samples were run using the EPA method without modification, which did show the presence of several volatile organic species. However, with the emphasis of the program, it was desirable to best identify the acids at the expense of the volatiles.

Analyses were performed on an Extranuclear mass spectrometer interfaced to a capillary GC with splitless injection. A 25 meter DB-5 bonded capillary 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/min. The mass spectrometer was calibrated daily with gaseous perfluorotributylamine.

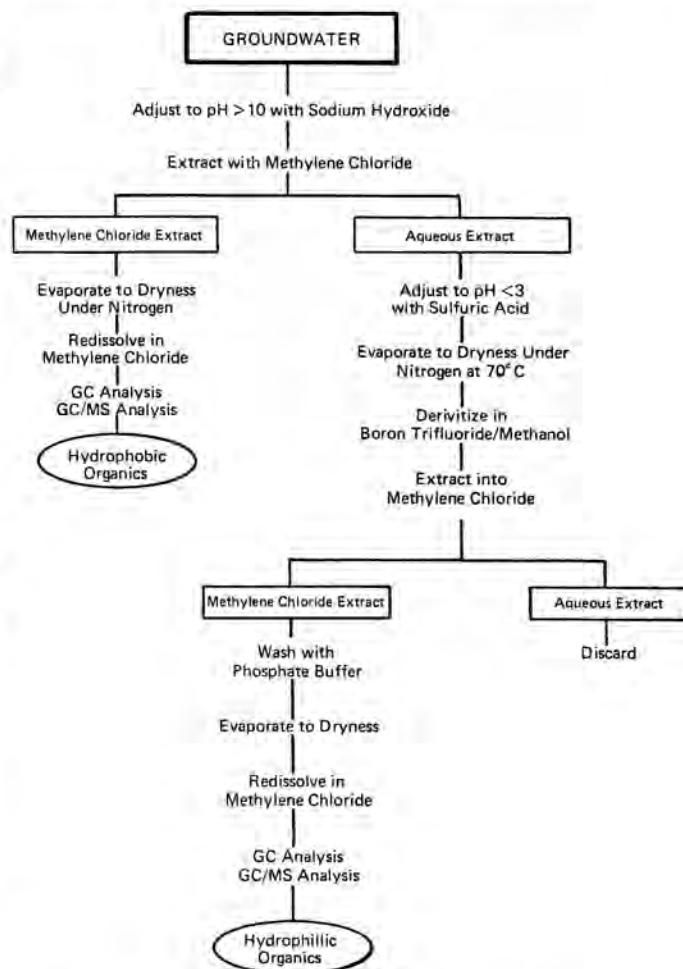


Fig. 3. Groundwater Extraction/Concentration Scheme.

TABLE I (Continued)

A considerable number of compounds were present after the extractions/concentrations, based on the peaks found in the total ion current chromatograms. Over 60 compounds have been identified, which comprises less than half of the peaks observed in the chromatograms. Some of these identifications are somewhat tentative. This was usually the case when the mass spectrometer signal was weak due to small amounts of the compound being present in the sample. A far greater number of peaks are observed when a more sensitive flame ionization detector is used with the GC separation. However, the identification of the compounds could not be made with such a detector. A list of all of the identified species is given in Table I.

TABLE I

Organic Compounds Identified in Groundwaters
(Compound in parentheses are tentatively identified)

N-paraffinic acids

acetic acid
butyric acid
pentanoic acid
(hexanoic acid)
heptanoic acid
undecanoic acid

Dicarboxylic acids

ethanedioic acid
(butanedioic acid)
(pentanedioic acid)
(hexanedioic acid)
nonanedioic acid

Phenyl acids

benzoic acid
phenylacetic acid
phenylpropionic acid
phenylbutanoic acid

Other acids

dimethoxyacetic acid
(chloromethoxyacetic acid)
dichloroacetic acid
3-methylbutanoic acid
(4-methylpentanoic acid)
2-methylhexanoic acid
5-methylhexanoic acid
2-ethylhexanoic acid
7-oxooctanoic acid
(9-oxodecanoic acid)

Sulfur compounds

(2-(methylthio)benzothiazole)
2-hydroxybenzothiazole

Phosphate compounds

diethyl pentyl phosphate

Nitrogen compounds

(trimethylhydrazine)
N,N'-dimethylurea
(n-phenylbenzamine)
4-nitro-N-phenylbenzamine
(N,N'-diphenylbenzamine)
(3,4-pyridinedicarboxylic acid)
(methylhistamine)
(phenylisocyanate)

Aliphatic compounds

1,3-dimethoxy-2,2-di(methoxymethyl)propane
3-methoxymethylbut-2-enate
hex-5-en-2-ol
(2-propyl-4-methyl-1-propanol)
2,2,5,5-tetramethylhexane
(3-methoxy-5-methylhexan-2-one)
(2-heptanone)
(5-methyl-2-furanone)
(1,3-dimethyl-2-ethylcyclohexane)
ethyl-2-methylbutyrate

Aromatic compounds

benzene
toluene
phenol
naphthalene
(acetophenone)
2-ethylphenylacetic acid
phenoxyacetic acid
4-hydroxybenzoic acid
2-hydroxy-(3-methyl)benzoic acid
2-hydroxy-(5-methyl)benzoic acid
(3-acetylbenzoic acid)
3-acetoxyphenol
(4-methylphenol)
(2,6-di(tertbutyl)-4-methylphenol)
1,2 diphenylbenzene

Eleven n-paraffinic carboxylic acids or dicarboxylic acids were identified, believed to be from spent solvent or degraded cellulosic material. Aromatic acids and hydrocarbons account for an additional 22 species. The likely source of these materials are scintillation wastes and their degradation products or degraded cellulosic materials. The remaining compounds are either sulfur, nitrogen, or phosphate containing compounds, or branched hydrocarbons. With the exception of the phosphate containing compound which is probably from degraded TBP, the sources of the other species are not known. Phthalates were also observed, probably from the large quantity of plastic material which has been disposed of in the burial ground. These are not included in the table as it was not possible to be sure that they were not introduced during laboratory processing of the samples.

None of the species which have been observed are noted as being strong complexing agents for radionuclides. This is consistent with the findings of the distribution coefficient measurements. The carboxylic acids and dicarboxylic acids may have potential for complexation, but these species have not been tested as complexants for the radionuclides of interest. Four volatile species were observed, but only in the few samples that were run without the methylation step which requires evaporation to dryness.

A poor correlation was noted between TOC levels and number of compounds and relative concentrations of species identified by GC/MS work. This suggests that much of the carbon was not extracted from the aqueous phase or was not volatile enough to be separated by the GC column. This is indicative of the presence of large organic molecules. Preliminary dialysis work, using a membrane with a 1000 dalton cutoff demonstrated that as much as 40% of the organic carbon had a mass in excess of 1000 daltons. This is likely to be humic material due to the large amount of degrading cellulosic material in the burial ground. Although these species have not been further characterized, humic materials have been shown to enhance radionuclide mobility in soil systems under certain conditions(6).

CONCLUSIONS

The concentration of total organic carbon is generally low in the groundwater beneath the SRP low-level waste burial ground. A large number of organic species are present in the groundwater, over 60 of them having been identified by GC/MS methods. None of these are known to be strong complexants, and are not expected to significantly increase the mobility of radionuclides in the soil/water system. Possible exceptions to this are the humic materials. These have not been well characterized, but have been implicated in enhancing radionuclide mobility in other soil systems. In addition, EDTA and TBP which were identified by specific methods are both likely to enhance the mobility of certain radionuclides under the correct conditions. However, these were present only in low concentrations and in a few wells, so the impact is expected to be small. In general, the low concentrations of both the radionuclide and organic complexing agents make complexation and the associated increase in mobility unlikely.

ACKNOWLEDGEMENT

The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

REFERENCES

1. J. P. Ryan, "Groundwater Monitoring in the Savannah River Plant Low Level Waste Burial Ground: A Summary and Interpretation of the Analytical Data," DPST-83-209, E. I. du Pont de Nemours and Company, Inc., Aiken, SC, (1983).
2. J. A. Stone and E. J. Christensen, "Technical Summary of Groundwater Quality Protection Program at Savannah River Plant," DPST-83-829, E. I. du Pont de Nemours and Company, Inc., Aiken, SC, (1983).
3. L. J. Kirby and A. P. Toste, "Chemical Characteristics, Migration and Fate of Radionuclides at Commercial Shallow Land Burial Sites," Proceedings of the Fifth Annual Participant's Information Meeting, DOE Low-Level Waste Management Program, CONF-8308106, EG&G Idaho, Idaho Falls, (1983).
4. S. L. Hoeffner, "Radionuclide Sorption on Savannah River Plant Soil: A Summary and Interpretation of Laboratory Data," DP-1702, E. I. du Pont de Nemours and Company, Inc., Aiken, SC, (1985).
5. "Method 625 - Base/Neutrals and Acids," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio (1982).
6. S. Boggs, Jr., D. 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).