An Analysis of Dissolved Organic Compounds and their Contribution to Iron Complexation in the Shallow Leachate Plume of the West KL Landfill Kalamazoo, Michigan

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AN ANALYSIS OF DISSOLVED ORGANIC COMPOUNDS AND THEIR CONTRIBUTION TO IRON COMPLEXATION IN THE SHALLOW LEACHATE PLUME OF THE WEST KL LANDFILL
KALAMAZOO, MICHIGAN

by

Eric Fahle

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Western Michigan University
Kalamazoo, Michigan
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AN ANALYSIS OF DISSOLVED ORGANIC COMPOUNDS AND THEIR CONTRIBUTION TO IRON COMPLEXATION IN THE SHALLOW LEACHATE PLUME OF THE WEST KL LANDFILL KALAMAZOO, MICHIGAN

Eric Fahle, M.S.
Western Michigan University, 1991

High concentrations of dissolved iron are present in downgradient groundwater samples adjacent to the western border of the West KL Landfill. Analysis by Rudder (1988) of groundwater samples indicates oversaturation of selected iron oxides, iron sulfides and siderite in monitoring wells TW-4 and M3.

Previous research suggests that pyrogallol, gallic acid, tannic acid and similar organic compounds may retard the oxidation of ferrous iron in the shallow leachate plume of the West KL Landfill (Rudder, 1988). Present research utilizing solid phase extraction, reverse phase high performance chromatography, Fourier transform IR spectro-photometry, UV/Visible spectrophotometry, and gas chromatography/mass spectroscopy indicate that pyrogallol, gallic acid, and tannic acid are not present above detectable levels in the shallow plume of the West KL Landfill. The findings suggest that 2-Hydroxybutyric acid, a possible iron complexing agent, is present in the shallow leachate plume of the West KL Landfill.
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I also wish to express my great appreciation to my wife Victoria, our families, Rick, Steve, Eric, Ross and many friends whose faith and never-ending support have made this possible.

Eric Fahle
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INTRODUCTION

Statement of the Problem

This study is a continuation of the investigation of the problem of high dissolved iron concentrations in groundwater adjacent to the KL Landfill. Analysis by Rudder (1988) of groundwater samples utilizing WATEQF, a computer program for calculating chemical equilibrium (Plummer, Jones and Truesdale, 1976) indicates oversaturation of select iron-oxides, iron-sulfides and siderite in monitoring wells TW-4 and M3. Dissolved iron concentrations in well TW-4 and M3 groundwaters average about 50 mg/l. Approximately 1000 yards downgradient, iron concentrations are below 3 mg/l.

Previous research by Rudder (1988) and others indicates that organic and possibly inorganic iron-ligand complexes may form in contaminated groundwaters with high dissolved organic carbon content. These complexes are produced when negatively charged organic or inorganic ligands coordinate covalently to ferrous or ferric iron. A chelate is formed when the bonding of the two ions produces a ring structure. Organic ligands that produce a five-membered ring with iron form stronger complexes than those that form six-membered rings. Leachate adjacent to the KL
Landfill has a high total organic carbon (TOC) content. Earlier attempts by Rudder (1988) to isolate and identify organic anions utilized Fourier transform IR (FTIR), and anion exchange high performance liquid chromatography (HPLC). His findings suggest that organic constituents similar in structure to tannic acids are present in the landfill leachate, resulting in the production of iron complexes. Present research incorporates the use of FTIR, UV spectroscopy, reverse phase HPLC and gas chromatography/mass spectroscopy (GC/MS) to isolate and identify both fragmented and whole organic compounds occurring in the groundwaters adjacent to wells TW-4 and M3. Identification of organic species present will enable each molecular structure to be evaluated as to its ability to form an iron-organic complex.

Literature Review

Several authors have investigated the question of how appreciable concentrations of dissolved ferrous iron can be maintained in an aerobic aqueous system. Theis and Singer (1973) indicate that waters that contain humic substances or organic compounds that possess similar structural features may severely retard the oxidation of ferrous iron.

Martin and Haider (1980) demonstrated that iron occurring with humic material tends to be stabilized by the organic substance hence increasing its nutritive
availability to aquatic vegetation. Humus is a dynamic substance, changing as its constituents decompose to form new substances. The formation of humic substances via transformations of vegetation residue are influenced by soil forming conditions including plant cover and activity of micro-organisms, climate, physical and chemical properties of the soil, and human activity. The interaction of these factors determines the state of the organic matter.

Cranwell and Haworth (1972) obtained humic acids from soils and peats via extraction with sodium hydroxide and precipitation by acidification. The humic acid extract was then boiled with water, resulting in the formation of polysacharides and polypeptides.

Polysacharides hydrolysed with dilute acid produced pentoses, hexoses, aminosugars and uronic acids, whereas hydrolysed polypeptides produced x-amino acids and simple phenolic compounds. Cranwell and Haworth (1972), as well as others, suggest that humic acids are formed by the polymerization of quinone arising from the oxidation of aromatic constituents of decaying vegetation. Under weakly acidic conditions, only a few ortho-benzoquinones will polymerize. Under more basic conditions, most ortho- and para-quinones will react producing more complex polymer mixtures.
Felbeck (1971) provided estimates on what part of the humic acid molecule has been identified and which parts still need to be satisfactorily characterized. Felbeck states that the complex nature of individual humic acid molecules and the probability that there exists a great variety in the structure of the humic acid molecule are the two fundamental reasons why only a small fraction of the humic acid molecule has been characterized. Further problems arise from the different sample preparation and extraction procedures used by various scientific groups, and the assumption that the products obtained by the various degradation procedures are obtained from the fundamentally different parts of the molecule.

Depending on the degradation procedures used and the variability of the assumptions made, 50 to 55 percent of the total humic molecule is made up of amino acids, hexosamines, polycyclic aromatics, oxygen-containing functional groups, and possibly aliphatic structures and single ring aromatics. Unknown fractions appear to consist of easily oxidized heterocyclic compounds.

Flaig (1972) suggests that phenolic compounds, essential for the formation of humic substances, are produced by microbial degradation of lignin in which cleavage of C-C bonds and ether linkages disrupt the structure of the lignin molecule. Degradation products contribute to the formation of humic substances by reaction
with nitrogenous compounds. Resorcinol and phloroglucinol type phenols are microbially synthesized phenols which aid in the formation of humic acids. Some biologically derived phenols disappear from compound mixtures, suggesting that they participate in the synthesis of humic substances by benzene ring cleavage and formation of aliphatic acids which can then be used as a carbon source for microorganisms. Haidler and Martin (1967) investigated the mechanisms responsible for the biological formation of phenols and hydroxylated condensed aromatic structures. Certain phenols are produced through secondary metabolism via actinomycetes, bacteria and fungi. These include compounds such as antibiotics, fermentation products, aromatic molecules, and polymers. Flaig (1972) suggests that micro-organisms contribute to the formation of soil organic matter by extracellular decomposition of plant and animal constituents and by synthesis of humic precursors within the cell. A symbiotic relationship between the synthesis of humic precursors and fundamental metabolism of soil microbes indicates humus production may result as a metabolic by-product of carbohydrate metabolism. Secondary microbial metabolism is greatly influenced by the environment. Phenols are oxidized to polymers by autooxidative processes and phenolases.

Humus is differentiated by solubility in an acid medium to humic acid and fulvic acid. Humus acidified with HCl to
a pH of 1.5 will cause flocculation and precipitation of the humic acid fraction. Humic acid formation and precipitation in soil may contribute more to the accumulation of soil elements than fulvic acid. Studies by Tan, Beaty, McCreery and Powell (1972) on humic-fulvic acid accumulation in Georgia soils and its relationship to changes in nitrogen and organic phosphorous content indicate that when nitrogen or organic phosphorous is increased, there will be an increase in the humic/fulvic acid ratio. Nitrogen is suspected to accumulate in the soil due to the participation of nitrogen containing compounds in humic acid formation. In addition, complexation reactions between humic acid and metal ions result in the flocculation of humic acid whereas fulvic acid may remain in solution after complexation with metal ions. Further research by the group suggests that immobilization of nitrogen and organic phosphorous will more readily take place as the humic/fulvic acid ratio is increased. The relationship between soil pH and humic/fulvic acid ratio indicates that a decrease in pH results in an increase of the humic/fulvic acid ratio. Due to the insolubility of humic acid in an acid medium, the more acidic the soil solution, the greater the amount of humic acid formed.

Interactions between metallic cations and humic acids have been widely studied. Potentiometric titration
investigations by Khan (1969) with isolated humic acids from one Black Chernozem and two Gray Wooded soils of Alberta indicate that metal cations form complexes with humic acid. The drop in pH for the Al$^{3+}$ and Fe$^{3+}$ potentiometric titration curves in comparison to the other metals tested indicates a strong tendency for Al$^{3+}$ and Fe$^{3+}$ to form complexes with humic acids. Humic acid in the presence of ferric iron recorded the greatest magnitude in pH drop. Both Fe$^{3+}$ and Al$^{3+}$ were shown to be extremely effective in the coagulation of humic acids. This is attributed to trivalent cations being more effective in inducing coagulation of humic acids than divalent cations.

Chau and Lum-Shue-Chan (1972) investigated the effect miscellaneous organic ligands play in regulating trace metals via complexation in fresh waters. The amount of organic ligands in a body of water determines the complexing capacity of the water, and regulates the availability of trace metals to the system. Lakes high in metals and organic content were found to have a great potential for the production of algal growth, thus creating an environment in which natural complexation controls the availability and toxicity of metals in the system.

Akiyama (1973) investigated the coprecipitation of organic matter with ferric and ferrous hydroxide in natural waters. Coprecipitated amounts of organic carbon and iron were calculated from the difference in the amounts of
dissolved organic carbon and iron before and after coprecipitation. Dissolved organic matter was broken down into pigment, lipid, high molecular protein, low molecular protein and carbohydrate fractions. Ferric and ferrous hydroxides were found to coprecipitate dissolved organic matter under reduced conditions. Akiyama's research indicates that dissolved organic matter can prevent the dissolution of ferrous iron even under reduced conditions by coprecipitation. Coprecipitation of organic matter with iron hydroxides is variable, depending on the composition of the organic matter. Protein constituents of organic matter coprecipitate with iron hydroxides, whereas pigment and lipid materials did not due to their ability to form water soluble iron-organic matter complexes.

Ghosh, Chattopadhyay and Varadachari (1983) studied the interaction of metal ions with humic substances under sterile conditions and in the absence of nonhumic substances. Potentiometric titration curves of Fe$^{3+}$ with a reducing agent, complexing agent ethylenediaminetetraacetic acid (EDTA) and humic substances were derived. Fe$^{3+}$-humic substance titration curves were intermediate between those of the complexing agent and either oxidant or reductant. Their research suggests that the nature of the Fe$^{3+}$ titration curve perhaps owes its existence to formation of metal chelate and valence change of metal ions. Different types of groups or centers responsible for electron
transfers may be the cause of the two inflections exhibited by all of the titration curves with humic substances.

Szilagyi (1970) investigated the geochemical association between insoluble peat humic acids and the changeable valency of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ system. Laboratory experiments demonstrated that humic acids partially reduce $\text{Fe}^{3+}$ ions to $\text{Fe}^{2+}$ ions; then both are fixed by the cation exchange action of the humic acids. Changes in distribution of $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ ions in humic acid and water phases take place as a result of changing pH. Determinations of the degree of sorption of metal ions on humic acid preparations are dependent on both the sorption capacity and the reduction capacity. Szilagyi's experiments demonstrate that humic acids interacting with metal ions are producing both anion-to-cation and cation-to-cation reductions.

Schnitzer and Skinner (1964) studied the participation of carboxyl and hydroxyl groups involved in organic matter reactions with trivalent aluminum and ferric iron. Reaction mechanisms were deduced by measuring metal retention capacity of an organic matter preparation in which functional groups were selectively blocked. Functional groups selectively blocked were phenolic hydroxyls, carboxyls, alcoholic and phenolic hydroxyls, phenolic hydroxyls and carboxyls, and both types of hydroxyls and carboxyls. Ferric iron exhibited a greater retention to organic matter than trivalent aluminum.
Blocking either acidic carboxyls or phenolic hydroxyls caused a significant reduction in metal retention. The major reaction mechanism included both acidic carboxyls and phenolic hydroxyls with metal ions in a reaction of the same type that occurs between ferric iron and salicylic acid. A minor reaction mechanism occurred between less acidic carboxyl groups and the ferric iron. Alcoholic hydroxyls were shown not to partake in organo-metallic reactions. Later research by Schnitzer and Skinner (1966) focused on interactions involving divalent metal cations, inorganic soil constituents and fulvic acid. By utilizing earlier methods Schnitzer and Skinner were able to selectively block alcoholic hydroxyls, phenolic hydroxyls and carboxyl functional groups which aided in the determination of stability constants for Ca, Cu, Fe, Mg, Mn, Ni, Pb and Zn. Stability of the metal-fulvic acid complexes revealed that the strongest complexes were generally formed with ferric iron and trivalent aluminum.

Gamble and Schnitzer (1973), working with fulvic acid and its reactions with metal ions describe fulvic acid as tannin, lignin, tannin-like, lignin-like or hydroxylated aromatic compounds. Their complexing ability is due to their negative charge exhibited in surface waters and groundwater.

Theis and Singer (1974) state that high concentrations of dissolved ferrous iron can be maintained in aerobic
aquatic systems in the presence of certain types of dissolved organic matter. The oxidation of ferrous iron can be partially retarded by the presence of syringic acid, resorcinol, tartaric acid, and vanillic acid. Complete retardation of Fe(II) oxidation for several days, even under an oxygen partial pressure of 0.21 atm can take place in the presence of gallic acid, pyrogallol and especially tannic acid. Manometric measurements indicate that the rate of oxidation of tannic acid as reflected by the rate of oxygen consumption is inhibited in the presence of ferrous iron due to the formation of an oxidation-resistant complex between ferrous iron and tannic acid. The results of polarographic studies of ferrous iron and tannic acid indicate that as the tannic acid to ferrous iron ratio increases, the diffusion current which is proportional to free aqueous ferrous iron decreases, indicating a greater degree of ferrous iron complexation by tannic acid. Furthermore, the diffusion current for an equivalent amount of iron and tannic acid decreases with increasing pH, indicating an increase in the extent of complexation with increasing pH. Schematic curves depicting the kinetics of oxidation of ferrous iron in the presence of Fe(II) complexation by organic matter indicate that minimal ferrous iron is complexed by vanillic acid, vanillin, phenol, resorcinol, syringic acid and histidine. The formation of oxidation-resistant complexes resulting in
near to complete oxidation inhibition are achieved through the use of tannic acid, gallic acid and pyrogallol. Oxidation rates greater than simple aqueous media rates result when ferrous iron is allowed to complex with citric acid.

Rudder (1988) utilizing data calculations performed by WATEQF, a computer program for calculating chemical equilibrium (Plummer, Jones, and Truesdale, 1976) found that select groundwater samples from edge of the KL Landfill were oversaturated with respect to many iron mineral phases. The oxidation of ferrous iron in these groundwater samples was demonstrated to be much lower than those of simple bicarbonate waters. His findings suggest that the degree of retardation of Fe (II) oxidation in the leachate plume is due to the presence of organic compounds tentatively identified as tannic acids. His research in determining whether Fe hydroxide coatings on overburden materials could account for the dissolved iron concentrations detected in the leachate plume indicates that indigenous overburden aquifer materials contain Fe concentrations in excess of those detected in TW-4 and M3 groundwater analyses.

Investigations by Apagar and Langmuir (1971) of the groundwater pollution potential of a landfill above the water table suggest that saturation and isolation of refuse materials may prevent oxygenation of biodegradable organics.
in refuse. Under these conditions, dissolved oxygen is depleted by aerobic bacteria resulting in anaerobic decomposition. The resulting leachate is influenced by refuse composition, amount of refuse, sorting, degree of compaction, water content, and temperature. Biodegradable organic matter, soluble inorganic materials, and redox-sensitive substances, (most metals) are the main refuse constituents which affect leachate quality. In general, the greater the refuse thicknesses, the more polluted the leachate issuing from it. Iron detected in the anaerobic leachate is mostly comprised of ferrous iron with smaller amounts of ferric oxyhydroxides also present. Ferric oxyhydroxide minerals in the soil combined with the activity of anaerobic bacteria probably control redox conditions in landfill leachate containing high concentrations of BOD. Observed mechanisms for leachate renovation during downward percolation include dilution, dispersion, oxidation, chemical dispersion, cation exchange, and anion exchange. Removal of suspended ferric oxyhydroxides, particulates, and bacteria also occur.

Cherry, Gillham and Barker (1983) state that under reducing conditions, leachate will promote Fe(III) and Mg(VI) reduction and subsequent dissolution of the metal oxides. Under reducing conditions, ferrous iron concentration is controlled by carbonate minerals while under oxidizing conditions, ferrous iron concentrations are
usually controlled by oxide phases.

Kehew and Passero (1990) studied both pH and redox buffering mechanisms at the West KL Landfill Site. Buffering takes place when reactions consume hydrogen ions introduced into a solution and prevent accumulation of $H^+$ in solution. High ratios of inorganic cations to anions suggest that organic acids dissociate to organic anions resulting in an electrically balanced leachate. Leachate buffering is suggested when minimal pH variations are detected between contaminated groundwaters and uncontaminated groundwaters. Dissolution of carbonate minerals to levels of oversaturation results from acidic leachate movement into soils and aquifer materials. This dissolution probably takes place under open system conditions in soils beneath landfill refuse. Waste decomposition under aerobic and anaerobic conditions produces large quantities of CO$_2$, thus driving carbonate mineral dissolution.

Verzele and Delahaye (1983) quantitatively analyzed tannic acids by HPLC. Commercial tannic acids derived from Turkish and Middle East gall nuts (Alep), Chinese and Korean gall nuts (Chinese), Bulgarian or Mediterranean sumac (Sumac), and from the pods of "Caesalpinia spinosa" (Tara) were analyzed for purity and gallic acid content. HPLC was run in both normal and reverse phase modes with 2,3,4,-trihydroxybenzoic acid used as the internal
standard. Normal-phase HPLC of tannic acid produced six peaks showing a general Gaussian shaped pattern. According to Verzele and Delahaye, tannic acids contain from five to twelve gallic acids. If more than five gallic acid residues are bonded to a tannic acid molecule, some must be in the form of digallic acid and trigallic acid. Further research by Delahaye and Verzele (1983) of gallic, digallic and trigallic acids in tannic acids by HPLC indicates that tannic acids belong to the hydrolyzable group of tannins. Alep, Chinese, and Sumac are polygalloylglucoses and Tara is a polygallicol quinic acid. Both normal-phase and reverse-phase HPLC was used to isolate gallic, digallic, and trigallic acids. Reverse-phase HPLC was determined not to be as effective as normal-phase HPLC due to the poor separation of the four trigallic acid peaks from the main peak of tannic acids. In normal-phase HPLC the trigallic acids only produce one peak when analyzed immediately after dissolving samples in methanol. Analysis of the same samples one hour later shows digalic acid to have a close doublet. This close doublet is due to the ester function shifting, thermodynamically controlled equilibrium, from the meta to para position and vice versa.

Rajakyla (1981) studied gluconic acid, sodium gluconate and other acids formed in biochemical or catalytic oxidations of glucose through the use of HPLC. The acids were separated on a column containing cation exchanging
resin and then were eluted with dilute sulfuric acid. Gluconic acid as well as its associated salts and lactones are non-toxic, non-corrosive organic compounds which have the ability to form chelates with metal ions in caustic solutions. Products formed in the biochemical oxidation of D-glucose contain oxalic, maleic, citric, gluconic, and acetic acid.

Dimson (1983) used solid phase extraction (SPE) columns to remove phenolic priority pollutants from aqueous solutions. Octadecyl (C18), octyl (C8), cyanopropyl (CN), ethyl (C2), and cyclohexyl (CH) SPE columns were evaluated for their ability to retain phenols. Aqueous samples were drawn through SPE columns by a vacuum manifold. Nonpolar phenols were retained by all SPE columns tested. Phenolic recoveries from aqueous solutions decreased with increasing polarity. The C8 SPE column demonstrated the greatest ability to remove both nonpolar and polar phenols from aqueous solutions. Experiments, utilizing SPE proved to be convenient, rapid cost effective and to provide excellent recoveries of phenols.

Chladek and Marano (1984) applied the bonded phase extraction method to the determination of 33 priority pollutants in waste water samples. Bonded silica phase cartridges containing C2, butyl (C4), C8 and C18, were evaluated for sampling of both acidic and neutral priority pollutants, while CH, diol (DH) and CN were evaluated for
only the acidic fraction. The pH of waste water samples was adjusted prior to extraction to 1-2 in order to suppress ionization of phenols. Various amounts of NaCl were added to decrease the solubility of phenols to further improve their recovery. Optimal extractions of acidic phenols and neutral priority pollutants from waste water took place using CH and C8 cartridges each containing 1200 mg of adsorbent. The cartridge adsorbent extraction method was found to have several advantages to liquid-liquid extraction. Sampling could be undertaken in the field, hence eliminating the need for shipping and storing large volumes of aqueous sample. Selective elution procedures produced a final eluent with less background interference, hence improving the accuracy and precision of analysis.

Chian and De Walle (1977) utilized membrane ultrafiltration, gel permeation and gas chromatography to separate and determine the main class of soluble organics in different leachate samples. Significant amounts of carbohydrates and hydrolyzable amino acids were found in the high molecular weight fraction, while a fulvic-like material containing carboxyl and aromatic hydroxyl groups constituted the lower molecular weight fractions.

Barker, Tessmann, Plotz and Reinhard (1986) indicate that significant changes in leachate composition take place along the flow system. Along the flow system, adsorption of aromatics exceeds that of aliphatics and the OH group.
Even in the presence of organic ligands with significant complexing ability, minimal mobility of trace metals including Fe were found in contaminated groundwater. One explanation is attenuation of trace metals by adsorption and precipitation in reduced groundwaters with near neutral pH. Under such conditions, aqueous concentrations of the contaminants would be sufficiently low with major cations successfully competing for available complexing sites within organic matter, hence limiting the mobility of metals and transition elements.

Knox and Jones (1979) found that the ability of leachate to complex with cadmium varied greatly with the overall strength of the leachate. Low molecular weight (<500) short-chained carboxylic acids as well as organic compounds in the (500-10,000) and greater molecular weight range were found to complex cadmium in leachate.

The studies cited suggest that humic and fulvic acids are formed from the transformation of vegetative residues and polymerization from oxidative coupling of quinones formed from microbially synthesized phenols. These organic compounds, which contain aliphatic hydroxyls, aromatic phenolic hydroxyls, and carboxylic acid functional groups, have the ability to form metallic cation-organic chelates and complexes. Reductions in metal retention from the blocking of both carboxyl and phenolic hydroxyl groups in organic matter indicate their importance in forming organic...
complexes. Experiments with ferrous iron in the presence of tannic acid, gallic acid and pyrogallol indicate the formation of oxidation-resistant complexes. Pyrogallol is an aromatic phenolic hydroxyl compound, gallic acid is an aromatic organic compound containing both hydroxyl and carboxyl groups, and tannic acid is an aromatic compound containing both hydroxyl and carboxyl groups. Effective separations of phenolic and neutral priority pollutants from waste water samples has been demonstrated using SPE. Determination of organic compounds assumed responsible for elevated iron concentrations in the KL Landfill shallow leachate plume requires extraction of the aforementioned organic species followed by separation and identification of each organic compound. The goal of such research is to provide a better understanding of leachate and its interactions within the environment.

Location

Kalamazoo County is in the southwestern part of the southern peninsula of Michigan and lies approximately 35 miles east of Lake Michigan. Total county area approaches 362,880 acres, or 567 square miles. The West KL Avenue landfill (KL Landfill) is located slightly west of the center line in the north half of section 21, T.2 S., R.12 W. of Oshtemo Township (Figures 1 and 2).
Figure 1. Map of Kalamazoo County, Oshtemo Township, and the West KL Landfill Site.
(from Passero & Wilkins and Wheaton Testing Laboratory, 1981)

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Figure 2. Location of West KL Landfill, Oshtemo Township.
(from Passero & Wilkins and Wheaton Testing Laboratory, 1981)
The site is approximately seven miles due west of downtown Kalamazoo on KL Avenue, one-half mile east of the intersection of South 4th Street and one-half mile south of the junction of West Main Street and Almena Drive.

Climate

The average winter temperature of Kalamazoo County is 27.0 degrees F, with an average daily low of 19.6 degrees (United States Department of Agriculture Soil Conservation Service & The Michigan Agricultural Experiment Station, 1979). The average summer temperature is 71.4 degrees, with an average daily high of 83.3 degrees. The average annual temperature is 49.7 degrees F. The mean annual rainfall recorded during a 29 year period (1947-1976) in Kalamazoo was 34.4 inches of which 58 percent fell in a six month period encompassing April through September. The heaviest 24-hour rainfall ever recorded in Kalamazoo was 5.2 inches on May 11 and 12, 1914. The average seasonal snowfall is 71.4 inches. The number of days in which there is at least one inch of snow varies greatly from year to year. The heaviest single-day snowfall was 16 inches (40.6 cm) on December 23, 1907 (United States Department of Agriculture Soil Conservation Service & The Michigan Agricultural Experiment Station, 1979).

Lake Michigan, located 35 miles to the west, exerts a "lake effect" which has a moderating influence on the
climate of the Kalamazoo area. This "effect" combined with prevailing westerly winds, reduces extremes in seasonal temperature variation.

**Geology**

Oshtemo Township, situated on the southwestern edge of the Michigan structural basin is underlain by thick Pleistocene glacial sediments, deposited upon Paleozoic bedrock that dips slightly to the northeast. Precambrian igneous and metamorphic rocks formed during orogenesis comprise the deepest rock formations underlying Kalamazoo County. Overlying the eroded surface of the Precambrian resides 700-800 feet of Cambrian Sandstone that grades upward into siltstones and shales 800 to 1000 feet thick. Shallow seas that covered southern Michigan in the Ordovician deposited thick limestone deposits, as much as 700 feet thick, on the silts and shales. Stratigraphy of the Silurian consists predominantly of dolomites with minor amounts of interbedded shale. The Antrim and Ellsworth Shales, Devonian in age, comprise a total thickness of approximately 550 feet in Kalamazoo. These shales extend laterally through much of southwestern Michigan and subcrop beneath glacial drift in parts of Van Buren, Berrien, Cass and St. Joseph Counties. The Antrim and Ellsworth Formations function as aquitards; the Ellsworth acts as a barrier to the vertical downward movement of fluids from
the glacial drift, while the basal member of the Antrim Shale effectively seals upward migration of hydrocarbon accumulations located in the top few feet of the underlying Traverse Limestone (Passero & Wilkins and Wheaton Testing Laboratory, 1981). The Coldwater Formation, locally known as the Coldwater Shale, overlies the Ellsworth Shale and is composed predominantly of marine shale with thin, discontinuous lenses of limestone and siltstone. With an average thickness of about 1000 feet, the Coldwater Shale is relatively impermeable and severely restricts both downward and upward movement of fluids in the stratigraphic column.

The bedrock surface elevation in Oshtemo Township ranges from less than 300 feet to more than 850 feet above mean sea level, resulting in a maximum relief of more than 500 feet. Erosion of the Coldwater Formation is the result of stream activity during preglacial and interglacial periods combined with ice sculpturing during the Wisconsinan Ice Advance, which moved across southwestern Michigan approximately 65 thousand years ago. The Kalamazoo Moraine, formed approximately 16-14 thousand years ago, is distinguished by uneven, knoblike hills and pothole depressions. Its associated outwash plains, which are distinctive landscape features of Kalamazoo County, owe their existence to the erosional and depositional processes of glaciers. These gently sloping sand and gravel deposits
(Figure 3) extend southeastward from the Kalamazoo Moraine and cover several miles of Portage, Prairie Ronde and Schoolcraft townships (Passero & Wilkins and Wheaton Testing Laboratory, 1981).

**Site Geology**

The KL Landfill is located on the inner ridge of the Kalamazoo Moraine, a recessional moraine of Wisconsinan age. The landfill resides on a group of small hills and depressions (Figure 4), and is underlain by sediments characterized as moderate to well-graded sand and gravel sporadically interbedded with deposits of sandy and gravelly clay. Glacial sediments that form the till, outwash, glacial lakebeds and stream deposits reach a maximum depth of 350 feet before encountering the irregular pre-glacially eroded surface of the Coldwater Shale (Passero & Wilkins and Wheaton Testing Laboratory, 1981).

The glacial sediments overlying the Coldwater Shale are comprised predominantly of tills and outwash. Figure 5 shows the location of north-south and east-west vertical cross-sections. A glacial till, unit (I) in the following cross-sections (Figures 6, 7 and 8), forms the surface topography and is underlain by outwash sand and gravel deposits, unit (II), which varies in thickness from 20 to 65 feet. Unit (III) constitutes a second till ranging in thickness from approximately 7 to 65 feet separating
Figure 3. Glacial Landforms of Kalamazoo County.
Figure 4. Topographic Map of the West KL Landfill.
(from United States Environmental Protection Agency, 1989)
Figure 5. Locations of Cross-Sections A-A', B-B', C-C'.
(from United States Environmental Protection Agency, 1989)
Figure 6. North-South Geological Cross-Section of the West KL Landfill, A-A'.
(from United States Environmental Protection Agency, 1989)
Figure 7. East-West Geological Cross-Section of the West KL Landfill, B-B' (from United States Environmental Protection Agency, 1989)
Figure 8. East-West Geological Cross-Section of the West KL Landfill, C-C'.
(from United States Environmental Protection Agency, 1989)
overlying glaciofluvial deposits from the underlying gravelly-sand outwash deposits, unit IVa. which constitute the unconfined aquifer. Unit IVb. is a thin discontinuous layer of lacustrine clay and unit IVc. is a unit of sand and gravel outwash. A third till layer, unit V, with a maximum thickness of 178 feet, underlies unit IVa.; it caps a thin confined aquifer, unit VI, which uncomfortably overlies the Coldwater Shale (Passero & Wilkins and Wheaton Testing Laboratory, 1981).

Site Hydrogeology

The crest of the Kalamazoo Moraine, located just east of the landfill, controls the northwest trending regional hydraulic gradient (Figure 9). With an average total thickness of approximately 140 feet, the upper aquifer exhibits both vertical and lateral variability. Further variability results from changes in gravel and clay content from 0-10% and 0-100% respectively within the individual layers of till and outwash. Depths to static water level increase west of the KL Landfill with approximate depths ranging from 23 feet in TW-3 to 138 feet measured just northwest of the landfill. With the exception of possible groundwater mounding beneath the landfill, static water levels in the vicinity conform to the topography (Figure 10). Contaminants are restricted to the upper, unconfined aquifer by an underlying fine-grained till unit, averaging
Figure 9. Water Table Contours For Oshtemo Township, Kalamazoo County, Michigan.
(from United States Environmental Protection Agency, 1989)
Figure 10. Potentiometric Surface Map of the Shallow Aquifer Beneath the West KL Landfill.
(from United States Environmental Protection Agency, 1989)
100 feet in thickness. Stream valleys that eroded the till unit were filled with Wisconsinan glaciofluvial sediments.

Erosional features in overburden deposits may influence the hydrological characteristics of the landfill site. Although regional groundwater flow is to the northwest, local groundwater flows to the west. Migration of two contaminant plumes, one to the northwest and the other to the southwest, is indicated by recent groundwater monitoring by the United States Environmental Protection Agency (USEPA) (Figure 11). The presence of an east-west trough located beneath the landfill has been suggested by Passero and Wilkins and Wheaton Testing Laboratory (1981).

Beneath the till unit overlying the Coldwater Shale is a glacial outwash unit consisting of clays, sands, and gravels, which serves as a confined aquifer. The thickness of this second major glacial outwash unit is variable; the major controlling factor is the presence of buried stream valleys cut into the surface of the Coldwater Formation.

Background Water Chemistry

Non-contaminated glacial aquifers underlying Kalamazoo County contain groundwater that is slightly alkaline. Total dissolved solids (TDS), in which calcium and magnesium are the dominant cations and bicarbonate is the major anion, typically average less than 1000 parts per million (PPM) (Freeze and Cherry, 1979). These waters, described as Type
Figure 11. Total Phenol Groundwater Contamination Plume in the Shallow Aquifer Beneath the West KL Landfill.
(from United States Environmental Protection Agency, 1989)
II glacial drift waters by Freeze and Cherry (1979), are the result of carbonate-mineral dissolution under open and partially open system $CO_2$ conditions. The lack of gypsum, anhydride, and halite in the aquifer materials results in the low concentrations of chloride and sulfate. Elevated chloride and sodium concentrations indicate degradation of the groundwater by application of road-salt and septic tank contamination. Major ionic constituents (Table 1) measured

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>54.90</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>20.60</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>2.18</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.61</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>0.07</td>
</tr>
<tr>
<td>NH$_4$</td>
<td>1.00</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>6.40</td>
</tr>
<tr>
<td>HCO$_3$$^+$</td>
<td>237.80</td>
</tr>
<tr>
<td>SO$_4$$^-$</td>
<td>21.00</td>
</tr>
<tr>
<td>NO$_3$$^-$</td>
<td>5.00</td>
</tr>
</tbody>
</table>

in uncontaminated groundwater upgradient of KL Landfill were obtained from samples taken from Well No. MW-5, located approximately 700 feet to the east. (Figure 12).
Figure 12. Location of New and Existing Monitoring Wells at the West KL Landfill.
(from United States Environmental Protection Agency, 1989)
The concentrations of ionic constituents generally increase downgradient from the landfill. The KL Landfill is located in a groundwater recharge zone near a regional groundwater divide. Calculation of mineral equilibria by Rudder (1988) using WATEQF (Plummer, Jones and Truesdale, 1976) indicates saturated to slightly oversaturated conditions for calcite in uncontaminated groundwaters adjacent to the landfill.

KL Landfill Site History

The KL landfill, originally known as the "Oshtemo Town Dump," began operations in the early 1960s, a time in which it was common practice to discard refuse in a "hole" in the ground. The dump up-graded its method of refuse disposal to that of a sanitary landfill in 1965 (Passero & Wilkins and Wheaton Testing Laboratory, 1981).

In 1968, Kalamazoo County acquired the original 20 acres of landfill property along with 66 additional acres surrounding the site for future landfill expansion. Utilizing modern equipment and methods of burying refuse during the early and mid-1970s, KL Landfill was perceived as a "model" sanitary landfill by local and state officials.

In 1975, a small citizen's group composed of residents living in the vicinity of KL Landfill met with local and state officials and demanded the landfill cease operations.
due to their opposition to site expansion, unsightly debris and suspected groundwater contamination. The State of Michigan ordered the county to close KL Landfill in 1979 when it suspected landfill leachate to be the cause of volatile hydrocarbons detected in several local residential wells.

A closeout plan for KL Landfill was implemented in early 1980. The plan called for a bentonite cap to be applied to landfill surface areas which had slopes of less than 10 degrees. Landfill surface areas with slopes greater than 10 degrees were left undisturbed. In addition to partial bentonite capping, special fertilizers and grasses were used to enhance the existing vegetative cover. Installation of surface drainage systems, methane gas vents and groundwater monitoring wells completed the initial closeout plan (Passero & Wilkins and Wheaton Testing Laboratory, 1981).

Extensive volatile organic compound (VOC) and trace metal analyses of groundwaters in and adjacent to the KL Landfill have been conducted by various local, state and federal agencies. The remedial branch of the United States Environmental Protection Agency Superfund program is currently examining the KL Landfill in an attempt to determine effective groundwater treatment options.
METHODS

The first step in attempting tentative identification of organic constituents responsible for iron complexation in groundwater samples taken from KL Landfill requires extraction of suspect organic species from leachate. The second step is to separate the extracted organic species into their individual compounds using high performance liquid chromatography (HPLC). Production of volatile methyl esters of each separated organic compound collected and analysis of the methyl esters utilizing gas chromatography/mass spectroscopy (GC/MS) may provide tentative identification of organic constituents that participate in iron complexation. Reverse phase solid phase extraction was used to collect specific organic species from groundwater samples. A reverse phase application of HPLC was used in separating collected organic species into their individual compounds.

Lab Apparatus

Initial leachate-organic acid separation attempts utilized an anion exchange column consisting of a 30 cm buret in which a 100-200 mesh anion exchange resin served as the exchange matrix. Vacuum filtration to enhance sample flow through the anion exchange resin was achieved by in-
corporating the tip of the buret to a filter flask linked to a water aspirator (Figure 13).

Further attempts at leachate-organic acid separations utilized Burdick and Jackson #9004:500 mg, #9008:1000 mg, and #9009:2000 mg octadecyl matrix SPE cartridges. Also used in the study were Burdick and Jackson #9028:1000 mg and modified 2000 mg cyclohexyl matrix SPE cartridges. These cartridges also utilized a vacuum system to promote sample flow through the cartridge exchange matrix.

Separation of the collected organic constituents was performed using a Varian model 5000 series HPLC (Varian Aerograph, Walnut Creek, CA, U.S.A.) in combination with a Varian Varichrom variable-wavelength Spectrophotometric Detector and both Shimadzu C-R3A Chromatopac and Hewlett-Packard (HP) 3396A integrators. The HPLC column used was a Varian MCH-10 C18 fitted with a 5 cm guard column. Sample injections utilized a Millipore 2 cc syringe.

GC/MS analysis of collected organics incorporated a Hewlett-Packard (HP) 59822 A Gauge controller, HP 5970 series Mass Selective Detector and HP 5890A Gas Chromatograph linked to a PC unit consisting of a HP color monitor, HP 9133, HP 9000, and HP "Color Pro" 8 pen color plotter.

Analysis of major cations including total iron by the Western Michigan University Water Quality Lab, Kalamazoo was achieved using a Thermo Jarrel Ash Furnace Atomizer in
Figure 13. Anion Exchange Chromatography Column Apparatus.
combination with an Instrumentation Laboratory Video 11 E
aa/ae Spectrophotometer. A Hewlett-Packard 8451A diode
array Spectrophotometer incorporating a rectangular silica
spectrophotometric cell with light path length of 1.00 ±
0.01 centimeter was used to measure Fe (II) concentrations.

Volatile gas collected in the head space of a TW-4
tilde sample was analyzed using both the aforementioned GC/MS
apparatus and a Nicolet 5DXC FTIR Spectrophotometer. Both
2 x 5 1/2 cm normal phase fluorescent, bonded silica glass
plates and 20 x 20 cm normal phase fluorescent, bonded
silica plastic plates were used in initial normal phase
solvent studies. The normal phase TLC fluorescent plates
were analyzed with a UV Products, Inc. "Chromato-View" UV
Detector. Laboratory organic-acid standards were weighed
with a Cahn 27 Automatic Electrobalance. Buffer salts for
HPLC buffer solutions were weighed using a Mettler PJ 360
Deltarange. A Corning series 240 pH meter was utilized in
laboratory pH measurements.

Water for experiments was filtered through a Millipore
Milli-Q Water System resulting in HPLC grade water.
Experimentation glassware included graduated cylinders,
separatory funnels, drying tubes, burets, volumetric
flasks, pippets, and various sized beakers.
Field Apparatus

Initial Groundwater Sampling

Wells were sampled October 5, 1988, using a Timco bailer to collect groundwater leachate samples from EPA wells. Samples were filtered using a 0.45 micron Geo Filter and stored in both one liter glass and plastic containers. A Markson model 95 digital pH, mv, and temperature meter was used at the site to measure pH and temperature.

Field Extraction of Selected Organic Species

Groundwater samples from wells TW-4 and M3 were collected in 2000 ml glass beakers. Latex gloves were used for protection; however, latex gloves covered by nitrile gloves are recommended.

An Orion SA 230 pH meter was used to measure pH during acidification of groundwater samples with 6M HCl. During acidification the groundwater samples were agitated with a stirring rod. A package of hydronium ion concentration paper was on site for backup pH measurement.

Filtration of groundwater samples was accomplished through the use of a Masterflex peristaltic pump and Geo Filter system in which a 0.45 micron filter paper was used. Filtered samples for laboratory experiments were stored in one liter brown bottles.
Burdick and Jackson SPE #9009 and #9004 cartridges were used in the field extraction of selected organic species. Vacuum extraction apparatus included a setup stand in which a 500 ml vacuum flask was attached. A set of bored rubber stoppers were used as cartridge-to-flask adapters. Methanol, used to "activate" the SPE cartridges, was funneled into a 50 ml buret. Another 50 ml buret was used to dispense "millipore" distilled water used as a cartridge matrix rinse after vacuum extraction of the methanol. Both vacuum filtration using a MasterFlex pump and pressurized injection using a Millipore 50 ml syringe were used to introduce the leachate sample to the activated SPE cartridge matrix. Waste methanol was collected in a glass container for later disposal. A cooler was used to store samples during transportation to the laboratory facility.

Procedures

Sampling

Groundwater samples from EPA designated wells MW2, MW3, MW9, MW10, and MW11 were collected in October, 1988. See Figure 12 for monitoring well locations. Sample collection of these wells consisted of bailing because purging was not permitted without EPA supervision. Modifications to a Timco bailer included the incorporation of a nozzle to the bailer intake, a manual release system to open the nozzle, and a
four-foot galvanized steel pipe fitted on top of the bailer which provided the necessary weight required to lower the modified bailer in the closed position. With the incorporation of these modifications it was possible to lower the bailer to the well screen interval without introducing contamination from the overlying bore waters. Once the release mechanism was triggered the bailer filled from the bottom up. The relatively slow filling of the bailer (approximately three minutes) provided minimal agitation and limited groundwater-air interaction. High pH measurements obtained during sampling of EPA wells may be due to improper grouting of the wells.

Groundwater samples from county wells M3, M3A, and TW-4 were collected as need dictated. These county wells are fitted with deep rod pitcher pumps that require continuous pumping to retrieve groundwater samples. Each of these wells was purged a minimum of 30 minutes to ensure that more than five bore volumes were removed before groundwater samples were taken. Field testing of collected groundwater samples consisted of measuring temperature and pH. Both were measured using a Markson model 95 digital pH, mv and temperature meter. In-line measurement of the previously mentioned parameters was not possible due to the utilization of dedicated county pitcher pumps and EPA restrictions resulting in the bailing of EPA monitoring wells. Samples designated for metals and anion analysis
were field filtered using standard 0.45 micron filter paper. Lowering of sample pH with nitric acid in the field was not deemed necessary because precipitates formed could be disassociated in the lab before sample analysis. Mercuric oxide was added to the sample containers as an organic preservative to inhibit microbial degradation of the water samples. TW-4 sample containers used in volatile head space analysis were fitted with (rubber) septa providing direct syringe extraction of volatiles without contamination from the surrounding system. After collection, all samples were placed in a refrigerator and stored at a temperature of approximately eight degrees centigrade.

Procedures for field extraction of selected organic species from TW-4 and M3 groundwaters are broken down into five phases: (1) Collection of groundwater samples from county pitcher pump wells TW-4 and M3; (2) pH measurement and acidification of collected groundwater samples; (3) filtration of groundwater samples; (4) collection of pH adjusted and filtered groundwater samples; and (5) field extraction of specific organic constituents from pH adjusted and filtered groundwater samples using Burdick and Jackson SPE #9009 and #9004.

The first step in the extraction of specific organic constituents was the activation of the SPE #9009, and #9004 cartridge matrix. A Masterflex pump was used to provide a
vacuum source for the 500 ml vacuum flask. The SPE #9009 and #9004 cartridges were attached to the vacuum flask via specially prepared rubber stoppers. Once a cartridge was attached to the vacuum flask, the Masterflex pump was engaged and five mls of methanol, dispensed from a buret, was drawn through the cartridge matrix. The vacuum was removed before the methanol had been completely drawn off, thus leaving the cartridge matrix saturated with methanol.

This procedure was repeated for all cartridges used in the experiment. The methanol was used to activate the octadecyl cartridge matrix thus preparing it for the retention of the organic species. Once activated, the saturated cartridge was removed from the vacuum flask apparatus, and set aside. Activation of the cartridge matrix required at least five minutes. In field extractions, the methanol remained on the cartridge matrix until the cartridge was needed for the extraction process.

Thorough purging of each well, to remove borehole contamination effects, was performed prior to extraction of selected organic species from contaminated groundwater. After sufficiently purging, a 1000 ml beaker was used to collect the contaminated groundwater samples. Sample pH was adjusted to 2 with 6M HCl and measured using an Orion Sa 230 pH meter. After pH adjustment, samples were passed through a 0.45 micron filter utilizing a Masterflex peristaltic pump in combination with a Geotech filter and
collected in 1 liter pre-labeled brown collection bottles.

For quality assurance and control, three SPE #9009 and #9004 cartridges were used in each analysis performed on well TW-4 and M3. The extraction process required first the removal of the methanol in the cartridge matrix via vacuum filtration. A 4 ml rinse of distilled water was then completely drawn through the cartridge. The extracted methanol and methanol-water collected in the 500 ml vacuum flask were dispensed into a glass container for proper disposal. Each SPE cartridge was attached to a vacuum test tube via modified rubber stoppers. Both test tube and cartridge were then connected to a clamp stand. The Masterflex pump vacuum hose was then connected to the vacuum test tube. With the Masterflex engaged, 5 mls of adjusted sample were drawn through the cartridge. A flow rate of 5-10 ml/min was maintained throughout the procedure. After extraction of the five mls of sample, the SPE cartridges were labeled and placed in a cooler for transportation to the lab. The eluents collected in vacuum test tubes were dispensed into a small brown collection bottles, labeled, and placed in the cooler for lab analysis.

Iron Analysis

In order to determine iron concentration versus time of air exposure, iron concentrations were determined colorometrically utilizing the 1,10-phenanthroline method.
with spectrophotometer detection at 510 nanometers. Ferrous iron in solution with 1,10 phenanthroline forms a reddish-orange complex that increases intensity with increased iron concentration. Procedural accuracy and precision were checked by calculating standard solution accuracy utilizing the equation $A = abc$ where $A$ is the measured absorbance in absorbance units of the standard solution, $b$ is the path length of the sample cell, $c$ is the molar concentration of the solution and $a$ at 510 nanometers should be $11,100 \text{ (L}(\text{mole}^{-1}\text{cm}^{-1}))$. The results of a 5.00 mg/l iron standard complex solution produced the following $A$, $c$, and $a$ values:

$$A = 1.005$$
$$c = \frac{(1M)}{(10^5\text{mg/g})} \times (5.000\text{mgFe/L}) \times \frac{1\text{mMFe}}{55.800 \text{mgFe}} \times \frac{1\text{mMcomplex}}{1\text{mMFe}}$$
$$= 8.960 \times 10^{-5} \text{M}$$
$$a = \frac{1.005}{(1.00 \text{cm})} (8.960 \times 10^{-5})$$
$$= 11,216 \text{ (L}(\text{mole}^{-1}\text{cm}^{-1}))$$

Calculation of the relative error of the standard solutions is essential. In the aforementioned example the relative error was 1.03% which is below the 2% relative error utilized in the Hewlett Packard 8451 A Diode Array spectrophotometer accuracy measurement. Reproducibility of results alone does not inherently determine accuracy. Degradation of chemicals used in the 1,10-phenanthroline method may effectively reduce the standard solution's measured absorbance resulting in inaccurate $a$ values.
Determination of Fe(II) to Fe(III) concentrations through time was performed by using the aforementioned method. Before analysis, groundwater samples from wells TW-4 and M3 were filtered through a 0.45 micron Millipore filter. 500 ml groundwater samples from TW-4 and M3 were then placed in 600 ml beakers and allowed to air oxidize. After approximately 30 minutes, a 5 ml aliquot of sample was placed into a 10 ml beaker. 5 ml of 1,10-phenanthroline was then added to form the complex. Complexed samples were then transferred to the Hewlett-Packard 8451A diode array Spectrophotometer to measure the absorbance. Fe(II) absorbance values were then measured at hourly intervals for four hours. Fe(II) concentration levels were determined utilizing the equation $c = \frac{A}{ab}$.

Modifications to the experimental method used by Stumm and Lee (1961) included the utilization of 1,10-phenanthroline instead of 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline), and simple air oxidation of the samples instead of bubbling a mixture of CO$_2$ and air to maintain a constant partial pressure throughout the experimental procedure. The representative reaction runs were plotted as log concentration versus time.

Previous work by Rudder (1988) using x-ray diffraction techniques and UV/Visible spectrum for ferric hydroxide in distilled water, indicated that the precipitate was indeed Fe(OH)$_3$ and not FeCO$_3$. 

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FTIR Procedures

A Nicolet 5DXC FTIR Spectrophotometer was used in the analysis of a TW-4 head space and the methylene chloride insoluble fraction of concentrated extracted organic constituents from TW-4 and M3 groundwaters. Head space analysis incorporated the use of a 10.0 gas cell with NaCl windows. Nujol oil in conjunction with KBr plates were utilized in the analysis of methylene chloride insoluble organic constituents. Although the insoluble organic constituents could not be fractionated into pure compounds, the types of compounds present were determined.

Extraction Procedures

Landfill leachates are the result of a number of chemical and biological processes. Leaching and degradation of organic matter greatly contribute to leachate composition. Compositional inhomogeneities in leachates cause variations in the chemical composition of groundwaters directly beneath and adjacent to landfill refuse. Thus specialized methodologies are necessary to effectively separate select organic species from leachate samples.

Initial experimental methodology included the use of column chromatography involving 100-200 mesh chloride anion exchange resin and 1.0 M HCl in attempts to separate and concentrate suspect organic species from groundwater samples. This approach assumes that the organic species
should separate on the basis of their molecular charge with resolution and selectivity controlled by the pH of the eluent, the pKa of the organic acid and, to a lesser degree, ionic strength of the buffer solution.

The 30 cm column with an i.d. of 1 cm contained 5 cm of anion exchange medium fixed by glass wool. pH adjustment of the anion exchange medium to 7 was accomplished by flushing with de-ionized water. Baseline linearity of the anion column was measured via a Hewlett-Packard 845A diode array spectrophotometer with a cell path length of 1.00 ± 0.01 centimeter. Standards of known organic acids suspected to be present in TW-4 and M3 groundwater were produced so tentative organic acid column retentions could be determined, thereby calibrating the anion exchange column for landfill groundwater samples (Figure 14). Calibration plots of absorbance at 220 nm versus ppm were developed for selected organic acids to permit concentration determination.

The major drawback of the aforementioned method is that both inorganic and organic anions are retained on the exchange column matrix. Thus further analysis by HPLC or an anion exchange method may result in the overlapping of chromatographic peaks or inaccurate concentration estimates due to similar retention times.

Initial experiments in SPE utilized a Burdick and Jackson SPE #9004, 500 mg octadecyl cartridge, analytical
Figure 14. Model Organic Compounds Used as Standards in UV-Visible Spectra Analysis of Well TW-4 and M3 Groundwater Samples.
grade phosphoric acid, de-ionized water, methanol, 10 ml sample size, and a vacuum system. Samples of known organic acids in water were prepared so tentative organic acid cartridge retention times could be determined. Activation of the octadecyl cartridge matrix was achieved by vacuum extraction with 3.0 ml of methanol followed by a 3.0 ml aliquot of water. Re-utilization of the cartridge was possible by extracting 10.0 ml of methanol through the cartridge matrix followed by a 3.0 ml extraction of water.

Pyrogallol and resorcinol, weak organic acids with pKa values of approximately 9, exhibited minimal retention on the Burdick and Jackson SPE #9004, 500 mg octadecyl cartridge and were unaffected by subsequent 1.0 ml aliquot extractions of 1.0 M phosphoric acid. Glutamic and malonic acid, moderately stronger organic acids also exhibited minimal retention to the octadecyl matrix. Complete elution of these acids from the matrix occurred in the first 1.0 ml extraction with 1.0 M phosphoric acid. Retained portions of gallic acid, an organic acid with a pKa of 4.11, slowly moved through the octadecyl matrix with the major portion being eluted during the third elution with 1.0 M phosphoric acid. Syringic and tannic acid, which exhibited excellent retention, were also unaffected by 1.0 ml aliquots of 1.0 M phosphoric acid. Retained fractions of the aforementioned acids were eluted from the SPE cartridge matrix via a 1.0 ml aliquot rinse of methanol. The initial experiments
demonstrated that the octadecyl cartridge matrix was capable of retaining most carboxylic acids (syringic acid, tannic acid and gallic acid) but failed to retain hydroxyphenols such as resorcinol, and pyrogallol. Glutamic and malonic acids also failed to be adequately retained.

Further attempts to separate hydroxyphenols from aqueous samples included pH adjustment of the eluent to 2.0 with 1.0 M HCl, activation of the octadecyl matrix with 1.0 M sulfuric acid, and a process of phenol extraction known as "salting out."

Adjustment of the eluent medium to a pH of 2.0 and activation of the exchange matrix using 1.0 M sulfuric acid failed to improve the retention of the hydroxyphenols.

The phenol extraction methodology known as "salting out" was utilized by first conditioning the octadecyl matrix with a 3.0 ml rinse of methanol followed by a 3.0 ml rinse of water. 25.0 grams of sodium chloride was added to 100 ml of aqueous sample with a pH adjusted to 2.0 with 1.0 M HCl. Absorbance at 220 nm of the aqueous sample was then determined by placing a 4.0 ml aliquot into a cuvette with subsequent analysis with the UV/Visible Spectrophotometer. The entire 100 ml sample was then drawn through the octadecyl cartridge matrix by vacuum extraction with the eluent collected in a vacuum flask. Absorbance of the eluent at 220 nm was thus measured. This procedure failed to provide a condition in which resorcinol was effectively
retained by the SPE octadecyl cartridge.

Further literature research indicated that SPE extraction of acidic phenols from 150 ml aqueous samples was successful when utilizing a 1200 mg cyclohexyl SPE cartridge matrix in combination with NaCl at concentrations between 20 and 25% (w/v) with pH adjusted to 2 (Chladek & Marano, 1984). Laboratory analysis of the previously mentioned methodology utilized 100 ml aqueous samples containing 5 ppm resorcinol in combination with 1000 mg cyclohexyl and octadecyl matrices with pH adjusted to 2 and 8 with 1.0 M HCl and 6.0 M NH₄OH, respectively.

Both 1000 mg cyclohexyl and octadecyl SPE cartridges required conditioning the cartridge matrix. This was achieved by extracting 2.0 ml of methanol through the cartridge matrix. After five minutes the methanol was drawn off via a vacuum apparatus. A 2.0 ml aliquot of 0.010 N HCl was then extracted through the cyclohexyl cartridge whereas, a 2.0 ml aliquot of water was extracted though the octadecyl cartridge matrix. In each procedure, the matrix was not allowed to dry.

One hundred ml aliquots of 5.0 ppm resorcinol were prepared by adding 25.0 grams of NaCl to 100 ml of 5.0 ppm resorcinol with sample pH adjusted as previously indicated. The rate of elution was 5-10 ml/min for the cyclohexyl cartridge and 8-11 ml/min for the octadecyl cartridge. UV/Visible spectra between 190 and 320 nm of original
samples and extracted eluents from the 1000 cyclohexyl and octadecyl cartridges at pH 2 and pH 8 were identical indicating no resorcinol retention on the cartridge matrix.

One hundred ml samples of 5.0 ppm resorcinol were extracted through 2000 mg cyclohexyl and octadecyl SPE cartridge matrices. Matrix conditioning of the cyclohexyl and octadecyl cartridges required extraction of 4.0 ml aliquots of methanol with proper set time for matrix activation. A 4.0 ml aliquot of 0.010 N HCl was used to rinse the cyclohexyl matrix whereas, a 4.0 ml aliquot of water was used to rinse the octadecyl matrix. The UV/Visible spectra overlay plots of original sample and sample after cartridge extraction for the 2000 mg cyclohexyl and octadecyl cartridges exhibited little variation from their 1000 mg counterparts (Figure 15). A slight retention of resorcinol was detected in the UV/Visible spectra overlay plot of the 2000 mg octadecyl cartridge (Figure 16). The retention however, was not as pronounced as one in which a 5.0 ml aliquot of 5.0 ppm resorcinol was passed through a 500 mg octadecyl SPE cartridge (Figure 17). This led to the conclusion that the 100 ml sample size was too large to effectively retain the resorcinol. Breakthroughs were occurring indicating that a smaller sample size was necessary to order to retain resorcinol to the cartridge matrix.
Figure 15. UV/Visible Spectra (top) and UV/Visible Spectra Overlay (bottom) of 5 ppm Resorcinol Extracted Through 2000 mg Cyclohexyl Matrix: 100 ml Sample With 25 Grams of NaCl Added.
Figure 16. UV/Visible Spectra (top) and UV/Visible Spectra Overlay (bottom) of 5 ppm Resorcinol Extracted Through 2000 mg Octadecyl Matrix: 100 ml Sample With 25 Grams of NaCl Added.
Figure 17. UV/Visible Spectra (top) and UV/Visible Spectra Overlay (bottom) of 5 ppm Resorcinol Extracted Through 500 mg Octadecyl Matrix: 5 ml Sample With 1.25 Grams of NaCl Added.
Experiments were then performed using 1000 mg cyclohexyl and octadecyl SPE columns with a sample size of 10 ml. Matrix activation and rinsing of the 1000 mg cyclohexyl and octadecyl cartridges have previously been described. Test samples were prepared by adding 6.25 grams of NaCl to 25.0 ml of 5.0 ppm resorcinol and adjusting the pH. Flow rates were 8-11 ml/min for the cyclohexyl cartridge and 5-10 ml/min for the octadecyl cartridge. A UV/Visible spectra of the sample with pH adjusted to 2.0 indicated an absorbance maximum of 0.295. A 220 nm spectra of the extracted eluent gave an absorbance of 0.169 indicating retention of resorcinol by the 1000 mg cyclohexyl column matrix (Figure 18). At a pH of 8.0 the retained fraction of the resorcinol was nearly identical.

The UV/Visible spectra of sample and extracted eluent from the octadecyl cartridge at both pH 2.0 and pH 8.0 indicated that there was retention of the resorcinol sample. However, the difference in the 220 nm absorbance between the sample of 0.332 AU and extracted eluent 0.231 AU indicated that the 1000 mg cyclohexyl cartridge matrix was indeed more effective at retention of the resorcinol sample than the 1000 mg octadecyl SPE cartridge (Figure 19). Breakthroughs of the 10.0 ml aqueous 5.0 ppm resorcinol samples using both types of cartridges indicated that neither cartridge was effective in retaining the majority of the weak organic acid.
Figure 18. UV/Visible Spectra (top) and UV/Visible Spectra Overlay (bottom) of 5 ppm Resorcinol Extracted Through 1000 mg Cyclohexyl Matrix: 10 ml Sample With 2.50 Grams of NaCl Added.
Figure 19. UV/Visible Spectra (top) and UV/Visible Spectra Overlay (bottom) of 5 ppm Resorcinol Extracted Through 1000 mg Octadecyl Matrix: 10 ml Sample With 2.50 Grams of NaCl Added.
Further testing involved extracting 10.0 ml aqueous samples of 5.0 ppm resorcinol through 2000 mg octadecyl and 2000 mg cyclohexyl cartridges. A 10.0 ml extraction of 5.0 ppm resorcinol through a 2000 mg octadecyl cartridge was performed on a reconditioned cartridge. Reconditioning of the octadecyl cartridge matrix consisted of rinsing the matrix with 10.0 ml of methanol followed by a 6.0 ml rinse of water. The aqueous 5.0 ppm resorcinol sample was prepared and the pH adjusted to 2. Flow rates were 5-10 ml/min and 8-11 ml/min respectively for the 2000 mg octadecyl and cyclohexyl cartridges. The UV/Visible spectra of the 5.0 ppm resorcinol sample exhibited a maximum absorbance of 0.253 at 220 nm. The corresponding spectra of the extracted eluent exhibited an absorbance of 0.001 indicating that the 2000 mg octadecyl cartridge was extremely effective at retaining the 5.0 ppm resorcinol sample (Figure 20). The experiment was duplicated with similar results. Additional 2.0 ml aliquots of 5.0 ppm resorcinol were introduced to the 2000 mg octadecyl cartridge, extracted, and added to the combined eluents of the experiment to determine the maximum sample size that could be achieved before breakthrough occurs. Measured absorbances at 220 nm for 12 ml, 14 ml, and 16 ml were 0.03, 0.06, 0.11 respectively indicating that at the 10.0 ml sample size, maximum retention of the weak acid to the octadecyl cartridge matrix occurs (Figure 21).
Figure 20. UV/Visible Spectra (top) and UV/Visible Spectra Overlay (bottom) of 5 ppm Resorcinol Extracted Through 2000 mg Octadecyl Matrix: 10 ml Sample pH Adjusted to 2.
Figure 21. Breakthrough Curves of 2 ml Aliquots of 5 ppm Resorcinol.
The 10.0 ml extractions of 5.0 ppm resorcinol using a 2000 mg cyclohexyl cartridge were performed using a modified 1000 mg cyclohexyl cartridge. The top guard filter was removed from two 1000 mg cyclohexyl cartridges with the cyclohexyl matrix combined into one cartridge. The guard filter was then fitted over the combined 2000 mg of cyclohexyl matrix to produce a 2000 mg cartridge.

The UV/Visible spectra of the 10.0 ml sample and extracted eluent indicated resorcinol retention to the cyclohexyl matrix. However, the 220 absorbance maximum of the original sample with a pH of 2 was 0.367 while the eluent absorbance was 0.204. Similar results were obtained when the sample pH was adjusted to 8 (Figures 22 and 23). Further research utilizing two SPE #9004 500 mg octadecyl cartridges in series suggests that the effectiveness of the octadecyl matrix may be due to the theoretical plate height and not the amount of matrix contained in the cartridge (Figure 24).

An equimolar mixture of 5 x 10^{-5} M resorcinol, pyrogallol, gallic acid and tannic acid was extracted through a 2000 mg octadecyl cartridge to measure the effectiveness of the extraction system to the model organic compounds used in this study. The UV/Visible spectra of the original mixture exhibited a maximum absorbance of 0.845 at 220 nm. The corresponding plot for the extracted eluent produced an absorbance of 0.019 at 220 nm indicating that
Figure 22. UV/Visible Spectra (top) and UV/Visible Spectra Overlay (bottom) of 5 ppm Resorcinol Extracted Through 2000 mg Cyclohexyl Matrix; 10 ml Sample With 2.50 Grams of NaCl Added. pH Adjusted to 2.
Figure 23. UV/Visible Spectra (top) and UV/Visible Spectra Overlay (bottom) of 5 ppm Resorcinol Extracted Through 2000 mg Cyclohexyl Matrix: 10 ml Sample With 2.50 Grams of NaCl Added. pH Adjusted to 8.
Figure 24. UV/Visible Spectra (top) and UV/Visible Spectra Overlay (bottom) of 5 ppm Resorcinol Extracted Through two 500 mg Octadecyl Cartridges in Series: 10 ml Sample pH Adjusted to 2.
the 2000 mg octadecyl cartridge was quite effective at retaining the four model organic compounds used in this study (Figure 25).

The experiments indicate that under the prescribed lab conditions, the ability of the 2000 mg octadecyl cartridge to retain both hydroxyphenols and carboxylic acids is superior to its 2000 mg cyclohexyl counterparts.

**Separation Procedures**

Once SPE techniques were developed to selectively retain suspect organic acids to the column matrix, the next step was to develop a procedure enabling effective separations of the previously mentioned acids utilizing HPLC.

The variables that must be addressed when developing a set of conditions favorable for effective HPLC separations are the type of analytical column, the type of HPLC eluents used, eluent compositions, compatibility (i.e., solubility of one solvent mixture in another), the use of an isocratic or gradient elution, flow rate, injected sample size, sample concentration, and detector wavelength.

The HPLC exchange column is critical to the success of the separation. Since a 2000 mg reverse phase octadecyl cartridge matrix was chosen to extract select organic contaminants from groundwater samples, a 30 cm x 4 mm MCH-10 C18 reverse phase HPLC exchange column was chosen for
Figure 25. UV/Visible Spectra (top) and UV/Visible Spectra Overlay (bottom) of an Equimolar Mixture of $5 \times 10^{-5}$ M Resorcinol, Pyrogallol, Gallic Acid, and Tannic acid Extracted Through 2000 mg Octadecyl Matrix: 10 ml Sample pH Adjusted to 2.
the HPLC separation of the collected organic constituents.

HPLC solvents used in the mobile phase must be relatively polar since the stationary phase of the column is nonpolar. Attempts at deriving the proper mobile phase included the use of 0.01M phosphate buffer, pH of 1.95; 0.2M phosphate buffer, pH of 2.4; 0.4M phosphate buffer, pH of 2.0; acetonitrile and methanol. Compatibility (i.e., solubility) between mobile phase solvents is essential. Insolubility of mobile phase solvent mixtures leads to the formation of precipitates. Such precipitates can severely damage the HPLC column and tubing. Blockage in the flow system from precipitation also causes increased pumping pressures which can damage the pump and its seals.

The pH of the mobile phase will contribute the separation effectiveness of the exchange column. Buffer solutions are often used in reverse phase HPLC to suppress ionization of the solute which results in tailing. The low pH utilized in these experiments promoted the dissociation of acids and contributed to their stability during separation.

Both isocratic and gradient elutions were tested during the mobile phase development period. Important to the successful use of a gradient elution is the refractive index and viscosity of the mobile phase solvents. Changes in the mobile phase refractive index will affect the absorbance characteristics of the UV detector causing
abrupt deviations in the chromatograph baseline.

Changes in the mobile phase viscosity can lead to changes in inline pumping pressures which can also cause deviations in the chromatograph baseline. Properly maintained, the mobile phase viscosity will improve the separation efficiency, hence shortening the total separation time without compromising the resolution of early peaks. An isocratic elution uses one or more solvents in a constant composition throughout the HPLC separation. The principle advantage of an isocratic elution is its simplicity. Changes in baseline during isocratic elution are minimal. Baseline shifts in isocratic elution usually stem from refractive index changes between the mobile phase and the injected sample.

The mobile phase solvent flow rate affects the rate at which the organic acids are eluted from the exchange column. Increasing the flow rate decreases the retention times for the organic acids studied. Increased flow rates may also lead to better peak resolution. Disadvantages to increased flow rates include increased baseline noise and the overlapping of peaks.

The injected sample size is an important variable in effecting chromatograph resolution. This study utilized both a 20 and 100 microliter sample injection loop. Smaller injections of samples were found to work best for solutions containing an individual solute. Larger sample injections
promoted better resolution in chromatographs of organic acid mixtures in the 10 to 100 ppm range. A disadvantage to the larger sample size is its ability to change the refractive index of the mobile phase hence disrupting the chromatographic baseline or shifting the baseline off scale.

Sample concentration affects the absorbance measured by the UV detector. Sample concentrations that are too high will result in a swamping of the detector causing the chromatograph to go off scale. Sample concentrations that are too small will fail to be accurately detected.

The absorbance sensitivity assists in the detection capability of the UV detector. One disadvantage to increasing the absorbance sensitivity is that baseline noise is also enhanced.

Initial attempts in the HPLC elution of suspect organic acids utilized analysis conditions found in Table 2. Resorcinol, pyrogallol, gallic acid, syringic acid, and tannic acid were individually injected to measure individual retention times.

At a concentration of $5 \times 10^5$ M, both resorcinol and pyrogallol were not detected. Pyrogallol at 10 ppm was detected with a retention time of 6.35 minutes. Gallic acid was detected at a concentration of $5 \times 10^5$ M. More concentrated samples produced retention times of 12.8 to 13.3 minutes. Both syringic and tannic acid were not
detected at any concentration. It is believed that the

Table 2

Initial HPLC Analysis Conditions

<table>
<thead>
<tr>
<th>Column</th>
<th>4 x 300 mm packed with 10 micrometer C18 coated particle.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mobile Phase</td>
<td>0.2 M phosphate buffer, pH 2.4.</td>
</tr>
<tr>
<td>Detector</td>
<td>UV at 220 nm.</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>1.5 ml/min.</td>
</tr>
<tr>
<td>Injection Loop</td>
<td>20 microliters.</td>
</tr>
<tr>
<td>Absorbance sensitivity</td>
<td>0.1.</td>
</tr>
<tr>
<td>Sample concentrations</td>
<td>5 x 10^{-5} M, 10 ppm, 25 ppm, and 100 ppm.</td>
</tr>
</tbody>
</table>

0.2 M phosphate buffer, pH 2.4, is incapable of liberating these acids from the octadecyl matrix thus limiting the effectiveness of this mobile phase to elute suspected organic acids.

Methanol was chosen as a second mobile phase solvent because it was used in the elution of all laboratory prepared organic acids from octadecyl SPE cartridges. One disadvantage in using methanol is its insolubility with phosphate buffers. By lowering the concentration of the phosphate buffer to 0.01 M, greater concentrations of methanol could be used without precipitation of the
phosphate buffer. An isocratic elution using 95% 0.01 M phosphate buffer and 5% methanol worked well in eluting a 25.0 ppm resorcinol sample. Retention times were similar in duplicate runs. A 25.0 ppm pyrogallol sample, however, exhibited severe tailing. An isocratic elution of 50.0 ppm pyrogallol using a 90% 0.01 M phosphate buffer with 10% methanol was also run. The chromatograph exhibited a similar tailing peak for the pyrogallol sample and led to the conclusion that a gradient elution of 0.2 M phosphate buffer and methanol may be necessary to provide effective separation and resolution of early peaks while providing the methanol concentrations necessary to liberate syringic and tannic acid from the column matrix.

Initial times and solvent concentrations for the tested gradient elution are as follows (Table 3):

Table 3
Initial Gradient Elution Settings

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 to 10</td>
<td>99% 0.2 M Phosphate Buffer, 1% methanol</td>
</tr>
<tr>
<td>10 to 25</td>
<td>1% methanol to 5% methanol</td>
</tr>
<tr>
<td>25 to 40</td>
<td>5% methanol to 10% methanol</td>
</tr>
</tbody>
</table>

The 25 ppm pyrogallol and gallic acid exhibited good
resolution at 5.38 and 9.35 minutes respectively. Resorcinol was less distinct but still visible at approximately 10.5 minutes. Syringic and tannic acid, however, were almost completely masked by baseline interference due to increased methanol concentrations. Increased time changes in the gradient elution along with changes in pH, buffer concentration, and percent methanol failed to provide a condition in which all five suspect organic acids could be tentatively identified. Hence a gradient elution utilizing the present mobile phase solvents was dismissed as a viable method.

Pyrogallol, gallic acid and resorcinol could be effectively chromatographed using the 0.2 M phosphate buffer in combination with the initial HPLC settings. A set of conditions was now needed to effect separations of syringic and tannic acid.

Early separation attempts utilizing an isocratic mobile phase of 80% 0.2 M phosphate buffer and 20% methanol resulted in nearly identical retention times of 3.25 minutes. However the high methanol concentration caused pyrogallol, resorcinol and gallic acid to elute with the solvent peak. Similar results were obtained by decreasing the methanol concentration to 10%. Lowering the methanol concentration to 5%, increasing the pump rate to 2.5 ml/min, and increasing the sample injection size to 100 microliters resulted in off-scale absorbance of a combined
100 ppm syringic and tannic acid sample. The methanol concentration was lowered to 4%, the sample injection decreased to 20 microliters and the pump rate lowered to 1.5 ml/min.

Under these conditions four of the five organic acids tested individually exhibited the following retention times (Figure 26, Table 4).

Table 4
Concentrations and Retention Times of Organic Acids

<table>
<thead>
<tr>
<th>ORGANIC ACID</th>
<th>CONCENTRATION ppm</th>
<th>RETENTION TIME (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrogallol</td>
<td>50</td>
<td>4.38</td>
</tr>
<tr>
<td>Tannic acid</td>
<td>100</td>
<td>7.88</td>
</tr>
<tr>
<td>Gallic Acid</td>
<td>25</td>
<td>7.92</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>50</td>
<td>9.27</td>
</tr>
</tbody>
</table>

A 100 ppm syringic acid sample was not detected and is believed to have remained on the column. Confirmation by increasing the methanol concentration resulted in baseline interference eliminating possible chromatographic peak identification.

A chromatographic plot of a combined pyrogallol, tannic acid, gallic acid and resorcinol sample contained three absorbance peaks at 5.05, 8.79 and 9.94 minutes. Combining the organic acids caused both a shift in the retention time
Figure 26. Retention Times of Model Organic Compounds Used as Standards in HPLC Analysis of Well TW-4 and M3 Groundwater Samples.
and a single retention peak for tannic and gallic acid. Changing the concentration of the phosphate buffer to 0.1 M resulted in decreased absorbance and peak resolution. Decreasing the methanol concentration to 3% increased the resolution of the peaks but failed to separate the tannic-gallic acid peak. At 3% methanol the absorbance peaks corresponding to retention times of a combined pyrogallol, tannic acid, gallic acid and resorcinol sample indicated that decreasing the methanol concentration resulted in increased solute retention times (Figure 27, Table 5).

Table 5
Shift in Concentrations and Retention Times of Organic Acids

<table>
<thead>
<tr>
<th>ORGANIC ACID</th>
<th>CONCENTRATION (ppm)</th>
<th>RETENTION TIME (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrogallol</td>
<td>50</td>
<td>6.36</td>
</tr>
<tr>
<td>Tannic acid</td>
<td>100</td>
<td>11.70</td>
</tr>
<tr>
<td>Gallic Acid</td>
<td>25</td>
<td>11.70</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>50</td>
<td>12.97</td>
</tr>
</tbody>
</table>

Similar retention times of gallic and tannic acid from individual organic acid chromatographs further suggest that there is overlapping between the two peaks. This overlapping was also described by Verzele and Delahaye (1983) in their analysis of tannic acids and trigallic acids using reverse phase HPLC.
Figure 27. Chromatographic Plot of Pyrogallol, Tannic Acid, Gallic Acid, and Resorcinol.
HPLC Analysis of SPE Eluent From Well TW-4 and M3 Groundwaters

According to the aforementioned methods, aqueous samples containing a mixture of leachate and groundwater from wells TW-4 and M3 were passed through SPE cartridges to concentrate select organic species on the cartridge matrix. HPLC instrumentation conditions for the analysis of specially prepared field samples is presented in Table 6.

Table 6

Initial HPLC Analysis Conditions for Field Samples

| Column | : 4 x 300 mm packed with 10 micrometer C18 coated particle. |
| Mobile Phase | : 97% 0.2 M phosphate buffer, pH 2.4, 03% methanol. |
| Detector | : UV at 220 nm. |
| Flow Rate | : 1.5 ml/min. |
| Injection Loop | : 20 and 100 microliters. |
| Absorbance sensitivity | : 0.1. |

Collection of select organic species in the field consisted of passing 5 and 100 mls of sample through Burdick & Jackson SPE# 9009 and 9004 cartridges respectively. The concentrated organics were then eluted from the SPE cartridges with methanol as previously described and placed in a 5 ml volumetric flask. Distilled water was added to
bring the eluent to the 5 ml mark. The mixture was then ready for HPLC analysis.

HPLC analysis of SPE eluent/aqueous mixtures from wells TW-4 and M3 at a UV detection of 214 (nm) was conducted to determine if lowering the detection wavelength would have the same effect as with aqueous samples.

**HPLC Analysis of Well TW-4 and M3 Groundwaters**

Aqueous samples collected from wells TW-4 and M3 were analyzed via the HPLC to determine the effectiveness of the SPE cartridges in retaining select organic compounds. The analysis would also detect more polar organics that would pass through the SPE cartridges. HPLC analysis conditions were identical to those previously used for the SPE eluent/aqueous mixtures.

**HPLC Analysis of Well TW-4 and M3 Floc Samples**

Aqueous samples from wells TW-4 and M3 were allowed to air oxidize resulting in the formation of a ferric hydroxide floc. Earlier research indicated that organic compounds containing carboxyls and hydroxyphenols were combined with the ferric hydroxide floc. Dissociation of the floc occurred when the sample pH was lowered to 2. Aqueous portions containing no floc and portions containing floc were acidified, filtered (0.45 micron) and analyzed via HPLC.
Gas Chromatography/Mass Spectroscopy Procedures

Gas chromatography/mass spectroscopy analysis of well TW-4 groundwater was conducted in an attempt to better isolate and identify organic constituents. GC/MS instrumentation consisted of an HP 59822 A Gauge controller, a HP 5970 series Mass Selective Detector (MSD) and HP 5890A Gas Chromatograph (GC). The GC was linked to a PC unit consisting of an HP color monitor, HP 9133, HP 9000, and HP "Color Pro" 8 pen plotter.

Sample preparation was conducted in three phases. The first phase dealt with the separation and concentration of organics from a TW-4 groundwater sample. The second phase consisted of further concentration by evaporation. The third phase involved preparation of the soluble fraction of the organic residue for GC/MS analysis.

Organic constituents were concentrated from a 500 ml TW-4 groundwater by elution through a Burdick & Jackson SPE #9009, 2000 mg octadecyl cartridge. Activation of the cartridge required saturation of the octadecyl matrix with 4.0 ml of methanol. A set time of 5 minutes insured matrix activation after which 4.0 ml of water was completely drawn through the cartridge. A Flow rate of 8-11 ml/min. was maintained during the elution. Organics concentrated on the cartridge matrix were eluted with 2 ml of methanol. The pungent solution was poured onto a drying plate. The
methanol was allowed to evaporate. The remaining organic residue had an oily consistency and was quite odiferous.

Methylene chloride was added to the organic residue in 4, 1 ml aliquots. Each 1 ml aliquot was thoroughly mixed with the residue to maximize organic dissolution. Approximately 1/2 of the methylene chloride evaporated during the mixing process resulting in the collection of approximately 2 ml of methylene chloride/soluble organic solution. Insoluble organics were scraped off the drying plate and saved for FTIR spectroscopy analysis.

A 1 microliter aliquot of methylene chloride/soluble organic solution was injected into the GC sample port. An initial starting temperature of 46°C was obtained at the sample port before injection. Once injected, the sample was instantaneously vaporized and transported by an inert carrier gas into the column. Upon entering the column the individual organic constituents in the sample were temporarily adsorbed on the surface of the column matrix. As the temperature of the carrier gas was increased to 280°C, approximately 14 minutes, the organics were selectively desorbed (liberated) from the column matrix and subsequently entered the mass selective detector. The mass selective detector reduced the volatilized organic constituents into positively charged particles by bombardment with an electron beam. The charged particles were then accelerated in an electrical field according to
their velocities and separated in a magnetic field according to their mass/charge ratios. A mass spectrum plot of the relative abundance of each charged species against the mass to charge ratio was produced for each chromatographic peak and stored in the computer for further analysis.

**Gas Chromatography/Mass Spectroscopy Analysis of Fe (III) Hydroxide Floc of Well TW-4 Groundwater**

Gas chromatography/mass spectroscopy analysis of Fe (III) hydroxide floc from TW-4 groundwater was conducted in an attempt to better isolate and identify organic constituents associated with the floc. GC/MS instrumentation consisted of an HP 59822 A Gauge controller, a HP 5970 series Mass Selective Detector (MSD) and HP 5890A Gas Chromatograph (GC). The GC was linked to a PC unit consisting of an HP color monitor, HP 9133, HP 9000, and HP "Color Pro" 8 pen plotter.

Sample preparation was conducted in five phases. The first phase dealt with formation and collection of Fe (III) hydroxide floc from a TW-4 groundwater sample. The second phase consisted of floc dissociation and dilution. The third phase dealt with the separation and concentration of organics associated with the floc. The fourth phase consisted of further concentration by evaporation. The fifth phase dealt with the preparation of the soluble
fraction of floc residue for GC/MS analysis.

One liter of TW-4 groundwater was allowed to air oxidize promoting the formation of the Fe (III) hydroxide floc. The floc was collected from the sample by 0.45 micron vacuum filtration.

The coagulated Fe (III) hydroxide floc was placed in a 500 ml beaker containing 100 ml distilled water. Concentrated HCl was added to promote dissolution of the floc, hence liberating associated organic compounds. Dissociation of the floc occurred at a pH of 0.57.

Organic compounds liberated from the dissociated floc solution were concentrated after pH adjustment to 3 by elution through a Burdick & Jackson SPE #9009:2000 mg octadecyl cartridge. Activation of the cartridge required saturation of the octadecyl matrix with 4.0 ml of methanol. A set time of 5 minutes insured matrix activation after which 4.0 ml of water was completely drawn through the cartridge. A Flow rate of 8-11 ml/min. was maintained during the sample elution. A 10 ml aqueous wash was performed to remove any ferrous iron from the cartridge matrix. Organics concentrated on the cartridge matrix were eluted with 2 ml of methanol and stored in a small glass vial.

The methanol was allowed to evaporate. The remaining organic residue although odiferous was different in consistency.
A two ml aliquot of methylene chloride was added to the vial promoting dissolution of the organic residue. Hence preparing the organic fraction of the Fe (III) hydroxide floc for analysis.

Sample analysis of the methylene chloride/soluble organic solution by the GC/MS has previously been mentioned. The analysis provided a mass spectrum plot of the relative abundance of each charged species against the mass to charge ratio for each chromatographic peak generated by the GC. All mass spectra were stored in the computer for further analysis.
RESULTS

Leachate Chemistry

The migration and distribution of contaminants in the groundwater system in and adjacent to the KL Landfill are the result of a number of physical, chemical and biological processes. Both northwest and southwest trending contaminant plumes emanate from the landfill. The chloride contaminant plume map (Figure 28) depicts the general migration of contaminants from the site. The remedial investigation by the United States Environmental Protection Agency (USEPA) indicates that the entire thickness of the shallow aquifer contains numerous organic compounds and that stratification of organic compounds may be present due to the varying solubility of the organic compounds in water. No contamination is present in the deep aquifer above detectable limits. Sulfate values less than 1 ppm measured in highly contaminated wells suggest that organic carbon is reducing sulfate to sulfide. Microbial degradation along the flow path is suggested due to decreased TOC levels relative to chloride concentrations. Rudder (1988), assuming that chloride attenuates in the shallow leachate plume by dilution only, suggests that the trend of increased alkalinity relative to chloride-
Figure 28. Chloride Groundwater Contamination Plume in the Shallow Aquifer Beneath the West KL Landfill.
(from United States Environmental Protection Agency, 1989)
/alkalinity ratios indicates the oxidation of organic carbon to carbon dioxide. He further adds that constant chloride/alkalinity ratios downgradient relative to well TW-4 ratios, suggest loss of alkalinity by calcite precipitation.

Analytical Results

Concentration of Fe(II) Versus Time

The semilog plot of log dissolved Fe (II) concentration versus time (Figure 29) depicts a scattering of points in the plots of TW-4, and M3. This is attributed to the low initial concentrations of ferrous iron combined with slight variations in test solution temperature. The linear relationship of the reaction runs in the semilog plot indicates that the Fe (II) oxidation rate is first order and appears to be independent of concentration. The dashed line represents the plot of ferric hydroxide precipitation in a bicarbonate solution without dissolved organic compounds.

Similar linear relationships derived from log Fe(II) concentration versus time graphs by Stumm and Lee (1961) indicate that oxidation rates are indeed first order with respect to Fe(II) and are not influenced by the Fe(III) concentration. At a constant pH, the rate of ferrous iron oxygenation is dependent on the partial pressure of oxygen.
Figure 29. Semilog Plot of Log Dissolved Fe (II) Concentration Versus Time. (Dashed line represents precipitation of Iron Hydroxide in the Absence of Organic Matter.)
to the first power and follows the rate law:

$$\frac{-d[\text{Fe(II)}]}{dt} = k'[\text{Fe(II)}][\text{PO}_2]$$

An increase of one pH unit was found to produce a 100-fold increase in the ferrous iron oxygenation rate, indicating that a second order relationship exists between the reaction rate and hydroxyl ion concentration:

$$\frac{-d[\text{Fe(II)}]}{dt} = k[\text{Fe(II)}][\text{PO}_2](\text{OH}^-)^2$$

Stumm and Lee (1961) further state that complex formation via organic matter may stabilize ferric oxide colloids, lower the oxidation rate and may increase Fe (II) solubility. The organic materials tend to slow the Fe (III) flocculation rate, inhibiting the precipitation of the ferric oxide colloid.

Oxidation of the organic constituents themselves may compete with Fe(II)-Fe(III) oxidation process. Such an occurrence would produce a linear plot similar to the semilog plots derived for TW-4 and M3 groundwaters. Hence semilog plots of dissolved Fe(II) concentration versus time of TW-4 and M3 groundwaters which deviate from those of a simple bicarbonate solution may be the result of organic oxidation and not complexation of iron with dissolved organic matter.
FTIR Analytical Results

Figure 30 represents the head space analysis of a TW-4 groundwater sample. The strong absorbance at approximately 3100 and 1300 wavenumbers (cm⁻¹) is indicative of methane. The small absorbance at 2400 wavenumber (cm⁻¹) is carbon dioxide. The strong absorbance in the 800–400 wavenumber (cm⁻¹) range is suggestive of small aliphatic (straight chained) halogenated compounds. The absorbance at approximately 1000 wavenumber (cm⁻¹) is suggestive of an aromatic compound; however, the corresponding absorbance at approximately 3400 wavenumber (cm⁻¹) is not detected. Absorbances between 4000–3600 and 1800–1350 wavenumbers (cm⁻¹) are interferences from water.

The TW-4 groundwater head space analysis suggests a reducing environment containing halogenated compounds. The absence of aromatics may be attributed to their insolubility in water combined with the low sensitivity of FTIR detection.

The FTIR spectra (Figure 31) represent the methylene chloride insoluble organic constituents found in TW-4 groundwaters. The organic constituents suggested by the spectra include phenolic hydroxyls, alcoholic and carboxyl groups, aliphatic and aromatic groups, aldehydes, quinones, and ketones. The major sorption maxima around 3900–2900 wavenumber (cm⁻¹) are attributed to methylene
Figure 30. Headspace Analysis of Well TW-4 Groundwater Sample.
Figure 31. FTIR Spectra of Methylene Chloride Insoluble Fraction of Organic Constituents Collected From Well TW-4 Groundwater.
phenolic hydroxyls, carboxylic and alcoholic groups. This is in agreement with recent monitoring of TW-4 groundwaters during remedial response activities at the KL Landfill by the USEPA.

Results of HPLC Analysis of SPE Eluent From Well TW-4 and M3 Groundwaters

The HPLC chromatograph of a TW-4 sample prepared from a SPE# 9004 cartridges utilizing an injection loop of 20 microliters exhibited three peaks at approximately 1.7, 1.8 and 3.0 minutes (Figure 32). The first two peaks are produced by the solvent front. A fourth peak was detected at approximately 2.4 minutes when the injection loop was switched to 100 microliters (Figure 33).

![Figure 32. HPLC Chromatograph of Eluent From Well TW-4 Groundwater Utilizing a SPE #9004 Cartridge and a 20 ul Injection Loop.](image)

Chromatographs of TW-4 samples prepared from SPE# 9009 cartridges exhibited not only the previously detected peaks but the presence of 2 broad peaks at approximately 5 and
11 minutes. A smaller but more pronounced peak was detected at 9.7 minutes. However, the peaks at 9.7 and 11 minutes were not detected in every analysis.

Chromatographs of M3 samples prepared from SPE# 9004 cartridges exhibited non-solvent front absorbance peaks at 2.4, 3.1, and 4.8 minutes. The shapes of the peaks are similar to those chromatographed in the TW-4 HPLC analysis and are assumed to represent the same chemical constituents. No attempt was made to identify these early eluting chemical constituents. Adjustments in the methanol concentration from 0-5% had no effect in chromatograph resolution.

Chromatographs of M3 samples prepared from SPE# 9009 cartridges were nearly identical to ones produced from the
concentrated SPE# 9004 methanol eluent/aqueous mixture. No absorbance peaks at 9.7 or 11 minutes were detected in either set of chromatographs.

HPLC analysis of SPE eluent/aqueous mixtures from wells TW-4 and M3 at a UV detection of 214 nm was conducted to determine if lowering the detection wavelength would increase the detection capability of the system. Chromatographs of both TW-4 and M3 samples exhibited no change.

A mixture of 0.5 cc M3 sample and 0.2 cc 100 ppm pyrogallol was chromatographed to determine if the absorbance peak at approximately 5 minutes was pyrogallol. The pyrogallol peak emanated from the broad peak, at 5.3 minutes (Figure 34). The same test was run with 0.5 cc M3 sample and 0.2 cc 100 ppm tannic acid. The tannic acid peak appeared at 9.6 minutes (Figure 35).

Figure 34. HPLC Chromatograph of 0.5 cc Eluent From Well M3 Groundwater Sample and 0.2 cc of 100 ppm Pyrogallol.
Results of HPLC Analysis of Well TW-4 and M3 Groundwaters

Chromatographs of aqueous TW-4 and M3 contained no additional peaks. As in earlier HPLC SPE eluent/aqueous runs, the major absorbance peaks at 9.7 and 11 minutes were inconsistently chromatographed. The wavelength of the UV detector was set to 214 nm to investigate its effect on increasing the absorbance of the peaks at 9.7 and 11 minutes. Decreasing the wavelength to 214 nm did indeed
increase the absorbance of the two peaks. The two peaks, however, exhibited varying retention times. Original absorbencies of 9.7 and 11 minutes decreased as much as 0.7 minutes in M3 aqueous samples with earlier absorbance peaks remaining constant. In addition to the increased absorbance of the peaks at 9.7 and 11 minutes, a new peak was detected in the TW-4 aqueous sample at approximately 6.2 minutes. This new absorbance peak exhibited a constant retention time in all five chromatographed runs (Figure 36).

Quantification Results

Separate mixtures of 0.5 cc M3 sample with 0.2 cc 5 ppm gallic acid and 10 ppm tannic acid were chromatographed in an attempt to estimate the ppm concentration of absorbance peaks at 9.7 and 11 minutes. The test was run with UV detection at 214 nm. Chromatographs utilizing equal concentrations of tannic acid and gallic acid produce a tannic acid absorbance about 1/2 that of gallic acid. This is due to the molecular weight of tannic acid being approximately twice that of gallic acid. Hence its absorbance is decreased by the same proportion. The chromatographs indicate that if the chemical constituents have a molecular weight similar to gallic acid their concentration would not exceed 1-3 ppm (Figure 37). The concentrations would approach 3-6 ppm if the molecular
Figure 36. Three HPLC Chromatographs of Eluent From Well TW-4 Groundwater Utilizing a SPE #9009 Cartridge, 100 ul Injection Loop and UV Detector Set at 214 nm.
weights were similar to that of tannic acid (Figure 38).

Figure 37. HPLC Chromatograph of 0.5 cc Eluent From Well M3 Groundwater Sample and 0.2 cc of 5 ppm Gallic Acid. UV Detector Set at 214 nm.

HPLC Analysis Results of Well TW-4 and M3 Floc Samples

Chromatographs of aqueous portions containing no floc exhibited non-solvent front absorbance peaks at 2.7, 3.0 and 4.0 minutes. The peaks were identical in appearance to TW-4 and M3 absorbance peaks previously chromatographed, suggesting similarity of the chemical constituents.

Chromatographs of aqueous samples representing floced constituents from a M3 sample collected on November 3, 1988 contained in addition to the absorbance peaks at 2.7, 3.0 and 4.0, a large peak at 28.2 minutes. The result was duplicated. The absorbance peak accounted for 82% of the
combined total peak volume. In order to maximize extraction of the substance from the HPLC, the solvent ratio was changed to 15% methanol/85% 0.2 M phosphate buffer. Retention time of the substance was decreased to 9.4 minutes (Figure 39). Additional sample runs representing flocced constituents of an M3 sample collected on July 14, 1989 exhibited small absorbance peaks at 9.1 and 11.9 minutes but failed to exhibit the large absorbance peak at 9.4 minutes (Figure 40). Sample runs representing flocced constituents of a TW-4 sample collected on July 14, 1989 indicated similar small absorbance peaks at 9.2 and 12.0 minutes (Figure 41). No TW-4 sample from the November 3, 1988 collection date was available for testing. Exactly why such a large absorbance was detected at 9.4 minutes for the flocced constituents of the M3 sample collected on November
3, 1988 is not known. It may indicate that a greater concentration of a chemical or group of chemical constituents were present in the groundwaters proximal to well M3 during the November 3, 1988 sampling. Perhaps the Fe(III) floc in this sample was somehow able to coagulate...
the organic constituents over the eight month holding time. Accidental destruction of the sample prevented its analysis via GC/MS.

Figure 40. Chromatograph of an Aqueous Sample Representing the Flocced Constituents From a Well M3 Groundwater Sample Collected on 07/14/89.
Gas Chromatography/Mass Spectroscopy Analysis Results of Well TW-4 Groundwater

The computer-generated total ion chromatograph (Figure 42) depicts several peaks representing the methylene chloride soluble organic fraction of the TW-4 groundwater sample. Identification of the organic constituent
### Table: Compound Identification

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>% Match to Mass/Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CYCLOBUTENE, 2-PROPENYLIDENE</td>
<td>76</td>
</tr>
<tr>
<td>2. TETRACHLOROETHANE</td>
<td>62</td>
</tr>
<tr>
<td>3. PROPYL - HYDRAZENE</td>
<td>25</td>
</tr>
<tr>
<td>4. PHTHALIC ANHYDRIDE</td>
<td>43</td>
</tr>
<tr>
<td>5. 2,2 - DIMETHYL BUTANE</td>
<td>25</td>
</tr>
<tr>
<td>6. 4-PENTENAL</td>
<td>11</td>
</tr>
<tr>
<td>7. 1 - ISOXYANO BUTANE</td>
<td>37</td>
</tr>
<tr>
<td>8. 1,2 BENZIENEDICARBOXYLIC ACID, DIISOOCTYL ESTER</td>
<td>76</td>
</tr>
</tbody>
</table>

**Figure 42.** Total Ion GCMS Chromatograph of the Methylene Chloride Soluble Organic Fraction of a Well TW-4 Groundwater Sample With Tentative Peak Identification by the National Bureau of Standards file.
responsible for each peak was possible by "windowing in" on each peak, retrieving its mass spectrum, and having the computer compare the mass spectrum to mass spectrum standards contained in the National Bureau of Standards file. Tentative organic compounds were listed by the percent match of their mass spectrum to an individual unknown spectrum (Figure 43). The organic compound with the highest mass spectrum percent match was chosen to represent an unknown chromatograph peak. Each peak was analyzed by this approach; however, not every peak could be identified by the aforementioned method.

Gas Chromatography/Mass Spectroscopy Analysis Results of Well TW-4 Fe(III) Hydroxide Floc

The computer-generated total ion chromatograph depicts several peaks representing the methylene chloride soluble organic fraction of the Fe (III) hydroxide floc. Identification of the organic compounds utilized the same method as those identified in the TW-4 groundwater sample. The total ion chromatograph (Figure 44) depicts the tentative peak identification of methylene chloride soluble organic compounds present in the TW-4 Fe (III) hydroxide floc.

Suggested Complexing Agents

Of the twenty organic compounds tentatively identified by GC/MS, ferrocene and 2-Hydroxybutyric acid are logical
Figure 43. Tentative Identification of an Unknown Compound by Comparison of Mass/Charge Ratios to Those Contained in the National Bureau of Standards file.
Figure 44. Total Ion GCMS Chromatograph of the Methylene Chloride Soluble Organic Fraction of a Well TW-4 Fe (III) Oxyhydroxide Floc Sample With Tentative Peak Identification by the National Bureau of Standards file.
choices for possible iron complexing agents.

Ferrocene is formed when two cyclopentadienyl anions react with one ferrous ion. The actual structure of ferrocene is that of a "sandwich" in which the ferrous iron is imbedded between two cyclopentadienyl anions. It is very unlikely that this chemical compound would form in nature. The likely source for this compound is from GC column contamination from prior experimentation with ferrocene.

2-Hydroxybutyric acid is another chemical compound which exhibits favorable properties as a complexing agent with ferrous iron. It is a compound which could be derived from butyric acid, which is present in dairy products and in its ester form represents 4-5% of butter, or could be derived through fermentation of carbohydrates.

2-Hydroxybutyric acid exhibits properties which would favor its use in pharmaceutical research. The compound possesses a chiral center which allows the molecule to exist as an enantiomer. Enantiomers are compounds that cannot be superimposed on their mirror image. Enantiomers are used in the pharmaceutical industry due to their differing behavior to polarized light, which oscillates only in one plane. Since 2-Hydroxybutyric acid contains only four carbon atoms, it is more soluble than organic species containing greater numbers of carbon atoms. The compound contains two donor atoms which would aid in the
formation of a five membered chelate. Concentrated extracted organics from wells TW-4 and M3 exhumed an odor that was quite similar to that of butyric acid.

Due to the lack of an internal standard, no quantitative measurement of 2-Hydroxybutyric acid concentration in the chromatographed sample could be made. Solubility of the 2-Hydroxybutyric acid with methylene chloride, and the acid's ability to react with other organic constituents not soluble with methylene chloride are unknown, further complicating concentration determinations.

It is evident that there were many compounds which could not be identified by their mass/charge ratios with National Bureau of Standards software. It is suggested that these chromatographed peaks represent fragments of larger more complex compounds. It should also be noted that the percent match of compound name to mass/charge ratio for many of the compounds is low, hence indicating a measure of uncertainty in tentative compound identification. It is possible that many of the unidentified compounds thought to represent molecular fragments of larger compounds are functional groups disassociated during analysis. Therefore tentatively identified compounds not containing functional groups necessary for complexation may be derived from larger compounds possessing configurations and functional groups capable of Fe complexation.
DISCUSSION

Complexation of Iron by Organic Matter in the KL Landfill

Certain microbially synthesized phenols, carboxylic acids containing hydroxyls, and polyquinones possess structures favorable for iron complexation. Humic acids have also demonstrated their ability to inhibit Fe(II) oxidation and precipitation via ion exchange, surface adsorption, chelation, coagulation and peptization.

Rudder (1988) suggests that complexation in the KL Landfill occurs in the form of iron-tannic acid complexes. He further implies that these complexes compete successfully against Fe hydroxide complexes, hence inhibiting the precipitation of iron and other oversaturated mineral phases in the presence of H₂S.

Although high iron concentrations were not detected in the October 5, 1988 and November 3, 1988 sampling of wells MW9, M3, and TW-4, (Table 7), subsequent sampling of wells M3 and TW-4 indicate dissolved Fe (II) concentrations averaging 50 ppm. Kehew, Passero, Rudder and Howell (1988) report total Fe concentrations in wells M3 and TW-4 of 32.0 and 52.3 ppm respectively with total organic carbon measuring 698 and 890 ppm (Table 8). Remedial investigation sampling by the United States Environmental Protection
Table 7
Cation Concentrations in mg/l of Groundwaters From Selected Wells Sampled at the West KL Landfill

<table>
<thead>
<tr>
<th>WELL #</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>Fe</th>
<th>Zn</th>
<th>Ni</th>
<th>Pb</th>
<th>Al</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW2</td>
<td>4.65</td>
<td>12.00</td>
<td>14.40</td>
<td>8.00</td>
<td>0.08</td>
<td>0.61</td>
<td>0.08</td>
<td>0.10</td>
<td>0.07</td>
<td>0.01</td>
</tr>
<tr>
<td>MW3</td>
<td>11.90</td>
<td>30.00</td>
<td>7.80</td>
<td>2.00</td>
<td>0.11</td>
<td>0.08</td>
<td>0.02</td>
<td>0.10</td>
<td>0.07</td>
<td>0.01</td>
</tr>
<tr>
<td>MW9</td>
<td>3.10</td>
<td>66.00</td>
<td>66.00</td>
<td>11.70</td>
<td>0.06</td>
<td>1.00</td>
<td>0.03</td>
<td>0.10</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>MW10</td>
<td>2.35</td>
<td>27.00</td>
<td>137.00</td>
<td>10.50</td>
<td>0.04</td>
<td>0.06</td>
<td>0.05</td>
<td>0.10</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>MW11</td>
<td>11.60</td>
<td>10.00</td>
<td>124.00</td>
<td>45.10</td>
<td>0.07</td>
<td>0.74</td>
<td>0.06</td>
<td>0.10</td>
<td>0.43</td>
<td>0.01</td>
</tr>
<tr>
<td>M3A</td>
<td>40.40</td>
<td>20.00</td>
<td>6.00</td>
<td>0.70</td>
<td>0.07</td>
<td>0.70</td>
<td>0.07</td>
<td>0.10</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>M3</td>
<td>213.00</td>
<td>96.00</td>
<td>80.00</td>
<td>4.90</td>
<td>0.09</td>
<td>0.39</td>
<td>0.07</td>
<td>0.10</td>
<td>0.09</td>
<td>0.01</td>
</tr>
<tr>
<td>TW4</td>
<td>170.00</td>
<td>86.00</td>
<td>62.00</td>
<td>2.33</td>
<td>11.00</td>
<td>2.09</td>
<td>0.07</td>
<td>0.10</td>
<td>0.06</td>
<td>0.02</td>
</tr>
</tbody>
</table>

SAMPLING DATES 10/5/88 11/3/88

MW2 M3
MW3 M3A
MW9 TW4
MW10
MW11
Table 8

Measured Groundwater Parameters From Selected Wells
Sampled at the West KL Landfill

| Well | Temp. | pH | TDC | Total Alkalin. | Cl⁻ | SO₄²⁻ | NO₃⁻ | NH₄⁺ | H₂S | Ca²⁺ | Mg²⁺ | Na⁺ | K⁺ | Fe | Cu | Pb | Zn | Assumed Pe |
|------|-------|----|-----|----------------|-----|-------|------|------|-----|------|------|-----|-----|----|----|----|----|-----|-----------|
| MW-5 | 12.0  | 7.0 | <2.0 | 195.0          | 6.4 | 21.0  | 5.0  | <1.0 | --  | 54.9 | 20.6 | 2.18 | 0.61 | 0.077 | 0.028 | <0.005 | 0.409 | >6.0  |
| TW-4 | 12.0  | 7.5 | 1440.0 | 1170.0        | 142.0 | 5.0  | <0.1 | 61.0 | 2.4 | 446  | 192  | 154.0 | 12.6 | 37.6 | 0.046 | 0.062 | 15.0  | -3.6  |
| MW-3 | 13.5  | 6.5 | 164.0 | 320.0          | 69.0 | <3.0  | <0.1 | <0.1 | --  | 93.6 | 61.1 | 17.4 | 7.31 | 5.6  | 0.026 | 0.90  | 120.0  | -3.1  |
| TW-9 | 5.0   | 7.7 | 91.0  | 287.1          | 32.0 | <1.0  | <1.0 | 7.2  | <0.5 | 51.6 | 27.9 | 30.1 | 3.46 | 0.11 | --   | --   | ---   | -3.1  |
| MW-9 | 12.5  | 6.4 | 104.0 | 665.0          | 61.0 | 16.0  | <0.1 | 9.6  | --  | 100  | 61.6 | 97.6 | 9.02 | 11.8 | 0.0099 | 0.340 | 25.0  | 0.0   |
| MW-2 | 12.0  | 6.8 | <2.0  | 328.0          | 6.4  | <3.0  | 0.1  | 0.15 | --  | 95.3 | 33.8 | 6.1  | 3.15 | 9.3  | 0.016 | 0.16  | 25.1  | 0.0   |
| MW-7 | 8.5   | 4.4 | 14.0  | 377.3          | 63.0 | 2.0   | <1.0 | 45.8 | <0.5 | ---  | ---  | 61.4 | 14.9 | 0.08 | --   | --   | ---   | -3.1  |
| MW-7 | 11.0  | 6.6 | 3.4   | 256.0          | 26.0 | <3.0  | <0.1 | 0.15 | --  | 61.7 | 25.7 | 10.8 | 2.05 | 0.252 | 0.082 | 0.13  | 26.7  | 2.0   |
Agency (USEPA) in March 1988 measured iron concentrations in the shallow aquifer of between 50 and 1000 ppb (Figure 45). Significant dissolved iron concentrations extending as much as 2,000 feet beyond the landfill boundaries were not detected by Kehew et al. (1988), nor by colorimetric and atomic absorption techniques used in this study.

Hypothesized Models

High levels of dissolved iron in groundwaters in and adjacent to the KL Landfill were first studied by Kehew et al. (1988). Rudder (1988) suggests that downward migration of rainfall and snowmelt mixes with refuse materials resulting in the oxidation of inorganic and organic compounds. The movement of leachate to the water table promotes generation of carbon dioxide via organic oxidation with subsequent conversion to bicarbonate and oxygenation of ferrous iron with subsequent precipitation as ferric hydroxide. Theis and Singer (1974), and Rudder (1988), suggest that complexation reactions involving ferrous iron and select organic compounds may compete with oxygenation of ferrous iron and precipitation as ferric hydroxide, resulting in elevated dissolved iron concentrations.

The recent remedial investigation by the USEPA suggests that high levels of iron present at well TW-2 may possibly be the result of metallic household objects or well casing. They do not attribute indigenous sources to
Figure 45. Total Iron Groundwater Contamination Plume in the Shallow Aquifer Beneath the West KL Landfill. (from United States Environmental Protection Agency, 1989)
the elevated iron concentrations. No other references to dissolved iron concentrations are discussed.

Present findings utilizing HPLC and GC/MS techniques suggest that known iron complexing agents such as tannic acid, pyrogallol and gallic acid are not present above detectable limits in the KL Landfill shallow leachate plume. One suggestion for the presence of high dissolved iron concentrations involves the products of oxidative coupling. Microbially synthesized phenols and carboxylic acids in the shallow leachate plume produce quinones and products of oxidative coupling similar in structure to tannic acid when exposed to aerobic conditions (Figure 46). Molecular structures produced by oxidative coupling may contain the necessary combinations of hydroxyl and carboxyl groups favorable for the production of ferrous iron complexes. Significant concentrations of organic matter present in groundwaters in and adjacent to KL Landfill may cause complexation reactions between select organic compounds and ferrous iron to compete with oxidation of ferrous iron and subsequent precipitation as ferric hydroxide. Manometric studies by Theis and Singer (1974) indicate that Fe (II)-organic complexes are resistant to oxidation. Their findings indicate that several days may pass before significant amounts of ferrous iron are oxidized to ferric hydroxide. A semilog plot of log dissolved Fe (II) versus time derived for TW-4 and M3
groundwaters by Rudder (1988) indicates that the oxidation rate of Fe(II) is significantly slow as compared to the oxidation of ferrous iron in a bicarbonate solution without high organic content. Similar results were obtained when the experiment was repeated in this study. Theis and Singer (1974), and Rudder (1988) suggest that tannic acid and molecular compounds possessing similar structures, complex with ferrous iron resulting in elevated dissolved Fe (II) iron concentrations. While this research suggests that
pyrogallol, tannic acid, and gallic acid are not present above detectable levels in the shallow leachate plume, GC/MS analysis of a TW-4 groundwater sample indicates the presence of 2-Hydroxybutyric acid. This organic compound exhibits characteristics favorable for complexation with iron. The FTIR spectra of the methylene chloride insoluble fraction of organic constituents previously presented indicates a strong transmittance in the range suggestive of carboxylic, phenolic, and alcoholic compounds, thus further supporting the possibility of this compound being present in the KL Landfill shallow leachate plume. Cleavage of aromatic hydroxyl compounds via microbial fermentation processes resulting in the formation of aliphatic compounds is suggested by several authors. Thus under reducing conditions, as indicated by head space analysis, the production of 2-Hydroxybutyric acid may occur.
SUMMARY

Elevated Fe (II) concentrations and the retardation of Fe (II) oxidation have been detected in the shallow leachate plume of the KL Landfill. Previous research indicates that iron will form complexes with organic compounds containing both hydroxyl and carboxylic acid functional groups such as pyrogallol, gallic acid and tannic acid. Rudder (1988), utilizing high performance liquid chromatography (HPLC) techniques, suggests that tannic acid and its degradation products formed stable complexes with ferrous iron.

Present research utilizing HPLC and gas chromatography/mass spectroscopy (GC/MS) suggest that tannic acid, gallic acid and pyrogallol are not present above detectable limits in the shallow leachate plume of the KL Landfill. 2-Hydroxybutyric acid was tentatively identified in the GC/MS analysis of the methylene chloride soluble portion of organic matter obtained from a TW-4 groundwater sample. This aliphatic organic compound contains both hydroxyl and carboxylic acid functional groups and its molecular structure indicates it to be an excellent iron complexing agent. The Fourier transform IR (FTIR) spectrum of the methylene chloride insoluble portion of organic matter obtained from a TW-4 groundwater sample indicates a
strong transmittance in the range indicative of aliphatic compounds containing hydroxyls and carboxylic acid functional groups.

Groundwaters with high dissolved organic content facilitate the formation of metal complexes; hence, increasing the mobility of metals. Such interactions between metallic cations and organic compounds should be suspected in waters with high total organic carbon (TOC) content.
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