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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

STUDIES OF GROUND WATER QUALITY UNDER A SANITARY LANDFILL

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

CHING-CHANG EUGENE LI

Norman, Oklahoma

1975

STUDIES OF GROUND WATER QUALITY UNDER

A SANITARY LANDFILL

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I INTRODUCTION

Ground water is one of the most important economical resources of man. It is widely distributed around the earth and two-thirds of the people in the United States are using it as a water supply.[1] But it has been found that large quantities of ground water are undesirable for use. The causes of these pollution problems in ground water are not understood very well. They are partially the result of natural processes; but the careless and deliberate acts of man also contribute. Whatever the reasons for this pollution, ground water quality is deteriorated gradually and once this happens, it is difficult to remedy this condition.

The production of solid waste is on the increase and has been for the past two decades. The disposal of this solid waste by burning and open dumping has been gradually replaced by sanitary landfill operations. Normally, the wastes are dumped into an excavated area and then covered. These wastes contain organic and inorganic substances and undergo natural decomposition. Initially, the decomposition of organic matter is carried out by aerobic bacteria when an available source of oxygen is present. This process oxidizes the organic matter to carbon dioxide and water, and nitrogen and sulfur to nitrate and sulfate. When the oxygen becomes exhausted, anaerobic bacteria continue the degradation process. In the first step, anaerobic bacteria break down organic compounds including carbohydrates, proteins and fats into

organic acids such as propionic, acetic, butyric and pyruvic acid. Then these organic acids are further broken down to mainly gaseous end products such as carbon dioxide and methane.

Surface water, rainfall or ground water moving through the landfill dissolve organic and inorganic degradable substances and produces a leachate which is capable of contaminating the ground water. Investigations of the pollution associated with ground water in landfills have demonstrated that solid waste disposal can directly and indirectly affect the physical characteristics, biological quality and chemical composition of ground water.

Since the ground water table under the Norman sanitary landfill located south of Norman is only about 4-10 feet below the ground surface, contamination of the ground water by past trenching methods for refuse disposal has occurred. Preliminary studies have partially demonstrated the increase of nutrient contents in the ground water underlying this landfill.[2]

OBJECTIVE

The objectives of this study were: (1) to determine the organic/inorganic components from a landfill which can significantly pollute ground water; (2) to study lab column leachate components to evaluate the possible extent of initial release of pollutants into ground water from the leaching of refuse; (3) to determine the feasibility of an indicator test of ground water quality using

organic and inorganic as parameters; (4) to study the sulfur cycle in the laboratory column leachate-ground water-mud soil environments; (5) to conduct ecosystem studies of the inter-relations of the chemical characteristics, biological quality and mineralogical composition of the ground water mud; (6) to determine quantities of organic matter, bitumen and hydrocarbons in order to estimate the amounts of organic pollution in the ground water muds.

II LITERATURE SURVEY

Leachate and Ground Water

The natural decomposition of solid waste deposited in a sanitary landfill results in the formation of a variety of chemical and biochemical products. Some of the soluble fraction of these products dissolve in rainfall and other liquids which may be trapped in the pores of the fill and thus constitute a source of leachate.

The processes of leaching produce a solution consisting of gases, minerals and dissolved organic matter, derived from the degradable refuse, which are capable of potential effects on the quality of ground water.

Composition of the leachate is thus important to determine the quality and quantity of contaminants which may cause impairment of ground water. The characteristics of leachates vary widely depending on the composition of refuse, type of decomposition and the amount of water present. The studies of numerous workers[3,4,5] exhibit a wide range of variation in the quality of leachate. In general, the leachate materials have a high value of BOD, sulfate, chloride, alkalinity, total hardness and total dissolved solids.

Leachates from landfill percolate through the underlying soil and are subject to attenuation. This natural purification process involves physical, chemical and biological systems and has some ability to remove contaminants.

To retard the movement of refuse leachate, a number of studies have been conducted.[6,7] A permeability of earth material less than 10^{-2} gal/day/ft^2 was considered to retard movement of contaminants from the disposal sites. The most common materials used as liners are shale, silt and glacial till.

The quality of ground water directly beneath a landfill is effected significantly by leachate. A study at Riverside, California[8] showed that high concentrations of calcium, sodium, chloride, sulfate, BOD, alkalinity and total hardness were observed in ground water below the fill. However, the quality of the ground water improves as the water moves from the landfill. From this study, it is apparent that a sanitary landfill, located as to be in intermittant or continuous contact with ground water, will cause the ground water in the vicinity of the landfill to become polluted and unfit for domestic or irrigational uses.

Another study of the effects of dumping refuse on ground water quality was conducted in South Dakota.[9,10] They found that chloride, total hardness and specific conductance were good sensitive quality parameters which indicate leaching effects on ground water quality. A similar investigation was carried out in Illinois.[11] The authors pointed out that high concentrations of organic acids and high CODs occur in leachate from relatively new refuse. These materials did not appear to travel far from the landfill area. Hardness, which also occurred in high concentrations in the leachate, decreased rapidly with distance away from the disposal site.

Cloride, the most sensitive parameter, traveled farther than any of the other dissolved solids, and can be considered as the best indicator of leachate migration.

There are numerous other references which include a general discussion of the sanitary landfill associated with ground water pollution problems.[12,13,14,15] The conclusion derived from these studies was that the ground water pollution problems from sanitary landfills were mainly chemical concerns. Bacterial and organic contamination were limited principally to soils.

Clay minerals

Soil usually contains a number of minerals. These minerals, especially those constituting the clay fraction, control both the physical and chemical properties of the soil. Thus identification, characterization and an understanding of the properties of these different minerals materially aid in the evaluation of the soil in relation to classification, agronomic practices and engineering properties.

According to Grim,[25] the clay minerals of phyllosilicates are composed of two basic structural units: tetrahedral and octahedral layers. In the tetrahedral unit, a silicon atom in the center is surrounded by four oxygen or hydroxyls forming a tetrahedron. The silica tetrahedral groups are arranged to form a sheet with the composition, $Si_4O_6(OH)_4$. The tips of all the tetrahedrals point in the same direction with the bases in the same plane.

In the octahedral unit, an aluminum, iron, or magnesium ion is surrounded by six oxygens or hydroxyls to form an octahedron. When aluminum is present, only two-thirds of the possible positions are filled to balance the structure, which is the basic gibbsite structure and has the formula, $Al_2(OH)_3$. When magnesium is present in the center, all the positions are filled to balance the structure, which is the basic brucite structure and has the formula, $Mg(OH)_3$.

The basic structural unit of kaolinite consists of a single

silica tetrahedral layer and a single alumina octahedral layer combined by a O-H linkage. This lattice is fixed rigidly and is not capable of expansion. Cations and water molecules are not able to enter the interlayer position of the kaolinite unit. Kaolinite has the characteristics of low plasticity, cohesion, shrinkage, and swelling plus a low cation-exchange capacity.

The basic structural unit of montmorillonite is composed of two silica tetrahedral layers with a central alumina octahedral layer. This structural unit is held together loosely by very weak O_2-O_2 linkages. Cations and water are able to enter into the interlayer positions causing expansion along the C axis. The crystal size of montmorillonite is much smaller than that of kaolinite. The characteristics of montmorillonite are high cation-exchange capacity, plasticity, cohesion and shrinkage.

Illite has a similar basic structure to that of montmorillonite. Both are made up of two silicon tetrahedral layers and one alumina octahedral layer. In the tetrahedral layer of illite, 15% of the silica is replaced by alumina and the resultant charge deficiency is balanced by potassium ions in the interlayer position of the two mica layers. Therefore illite can not expand as montmorillonite.

The basic structural unit of vermiculite is similar to that of illite. The interlayer position is separated by water molecules occupying a definite space of 4.89 A, which is about the

thickness of two layers of water molecules. This structure is unbalanced chiefly by substitution of aluminum(Al^{+3}) for silicon (Si^{+4}) and the charge deficiency is satisfied by cations(Ca^{+2} or Mg^{+2}) which exist between the mica layers and are largely exchangeable. Vermiculite is an expandable mineral. But the expandibility of vermiculite is less than that of montmorillonite and higher than that of illite.

Chlorite has a basic structural unit of a mica-layer and a brucite-layer. These layers are continuous along the a and b dimensions and are stacked along the c direction with basal cleavage between the layers. The mica layer is unbalanced by the substitution of Al^{+3} for Si^{+4} and this deficiency of charge is balanced by an excessive charge in the brucite($Mg(OH)_6$) layer as a consequence of substitution of Al^{+3} for Mg^{+2}.

Cation-exchange capacity

Cation exchange in soil is a reversible chemical reaction. The cations are on the surface of soil minerals, within the crystal framework, or consist of a part of certain organic compounds which can be reversibly replaced by other cations or anions. The cation-exchange capacity is the sum of the exchangeable cations of soil expressed as meq/100g. of soil. This value can be used for estimating the total storage capacity of soils for a specific cation.[16]

Cation exchange usually takes place in an aqueous environment and the ions generally have considerable solubility. In clay minerals, the common exchangeable cations are Ca^{++}, Mg^{++}, NH_4^{++}, H^+, K^+, Na^+. The clay minerals have a large cation-exchange capacity ranging from 3 to more than 100 meq/100gr. Kaolinite has a cation-exchange capacity of 3-15 meq/100gr. Illite and chlorite have a cation-exchange capacity of 10-40 meq/100gr. Montmorillonite has 80-150 meq/100gr while vermiculite has 100-150 meq/100gr.[17]

All inorganic minerals in soil have a small cation-exchange capacity. The sand fraction has a cation-exchange capacity ranging from 2.8 to 38 meq/100gr, while the silt fraction ranges from 25 to 41 meq/100gr.[18] Generally, this cation-exchange capacity increases as the particle size decreases. Some organic materials have a cation-exchange capacity ranging from 150 to 500 meq/100gr.[19]

Cation-exchange capacity caused by broken bonds around the edges of the silica-alumina units give rise to an unsatisfied charge. This charge is balanced by adsorbing cations. In kaoli-

nite, illite, and chlorite, broken bonds are the major cause of exchange capacity. In montmorillonites and vermiculites, broken bonds are responsible for a relative small portion of the cation-exchange capacity. About 80% of cation-exchange capacities result from lattice substitutions.[20]

Clogging of cation exchange positions causes reduction of the exchange capacity. The addition of aluminum in the exchange position serves to reduce the cation-exchange capacity of the montmorillonite lattice.[21] Large, flat organic ions adsorbed basal surfaces of montmorillonite blanket in more than one exchange position thereby reducing the exchange capacity.[22] Sulfur compounds may form on the adsorbing surface of clay minerals reducing the sorption activity.[23]

Various cations are not equally replaceable and do not have the same replacing power. Cation replaceability is controlled by a considerable number of factors. According to Way,[24] the replacing power of the common ions is

$$Na < K < Ca < Mg < NH_4$$

The sulfur cycle

Sulfur is an essential element for living organisms. It is a component of protein molecules in the form of sulfur-bearing amino acids. Its compounds play a basic role in the biogeochemical cycle of aquatic environments.

Sulfur may be present in a variety of forms in nature. The interconversions of the different sulfur forms in nature's cycle are of considerable geochemical importance.[26] A schematic description of these interconversions is diagrammed in Figure 1.[27]

The most important link of the sulfur scheme for consideration here is sulfuretum which Galliher defined as the anaerobic environment where the sulfate to hydrogen sulfide to sulfate biogeochemical cycle occurs;[28] although the conditions are anaerobic, elemental sulfur is oxidized to sulfate by a process which is the equivalent of dehydrogenation. In this sulfuretum, microorganisms contribute to the entire cycle and are significantly important in the cyclic process.

Hydrogen sulfide

Hydrogen sulfide occurs frequently in natural gas. It is also found in a dissolved form in springs, sewage and sulfuretum. The aqueous solution of hydrogen sulfide holds an important central position in the sulfur cycle.

The major sources of hydrogen sulfide in water are anaerobic sulfate reductions. Another source is the putrefaction of protein,

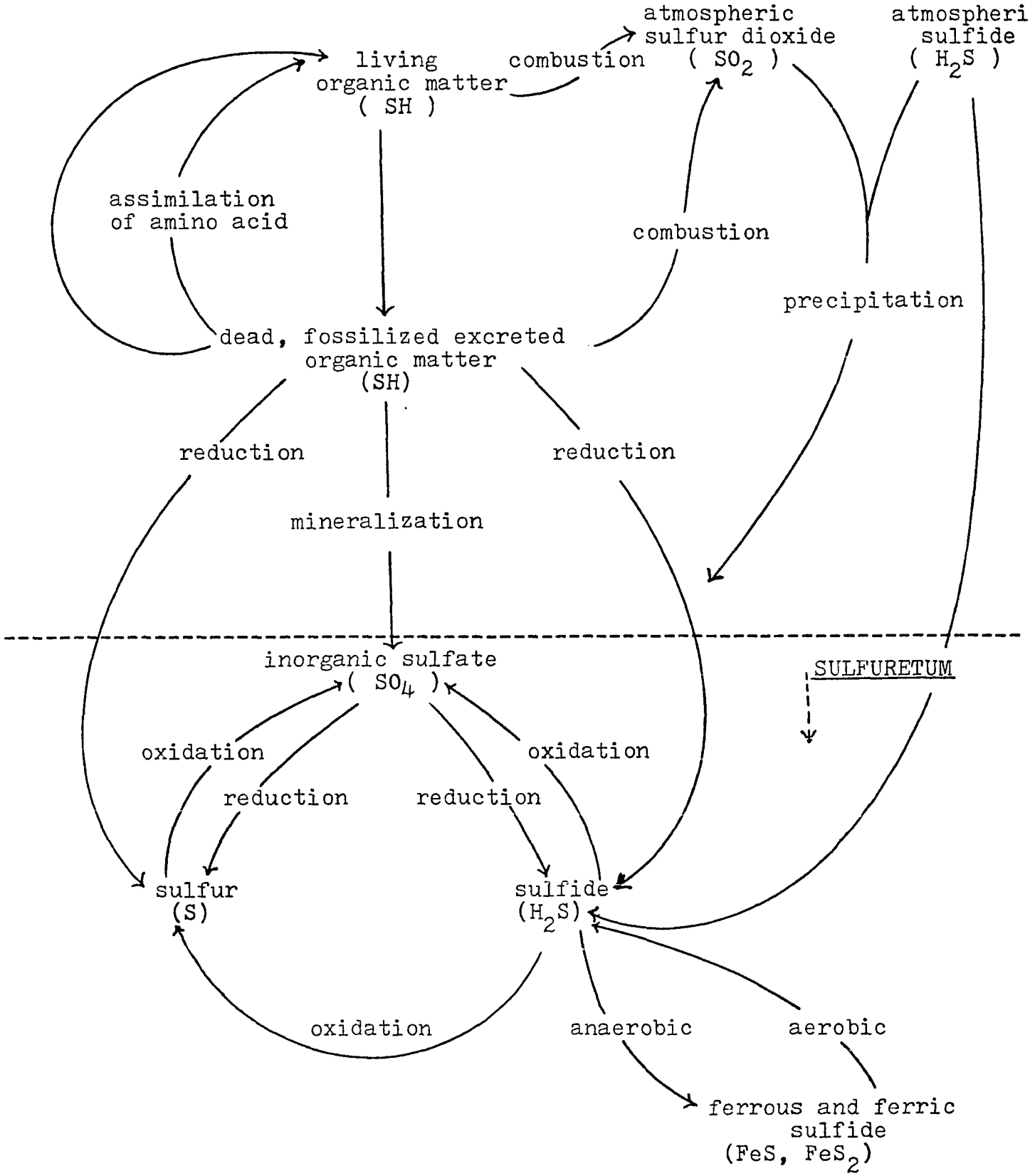
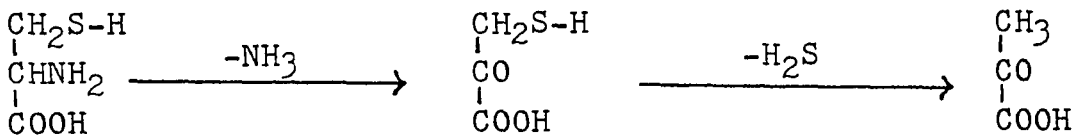


Fig. 1. The sulfur cycle in nature

as many organisms are able to remove hydrogen sulfide from sulfur containing amino acids. Large amounts of hydrogen sulfide may be liberated from iron sulfide in black mud where the acidity of the water is high enough to decompose the mud.[29]

Putrefaction

Great numbers of bacteria in soil, water, intestines and sewage can decompose organic matter. One of principal forms of this organic matter is protein. There are three amino acids containing sulfur present in protein: cystine, cysteine and methionione. These amino acids can be broken down in various ways by bacteria subsequently releasing hydrogen sulfide. This degradation is carried out by enzymes. The enzyme cysteine desulfhydrase can remove the amino- and sulfhydryl groups from cysteine as follows



The pyruvate generated from this degradation is used by bacteria. The ammonia and hydrogen sulfide which are also produced by this degradation are released into the environment.[30]

The organisms contributing to putrefaction are:

Clostridium ----------rod-shaped anaerobic bacteria.

Escherichia, Proteus --------intestinal bacteria.

Serratia, Bacillus ---------waterborne bacteria.

Assimilatory sulfate reduction

Bacteria can synthesize sulfur containing amino acids from inorganic sulfate. They convert the sulfate ion to PAPS, which is 3-phosphoadenosine-5-phosphosulfate, a nucleotide, which then yields hydrogen sulfide.

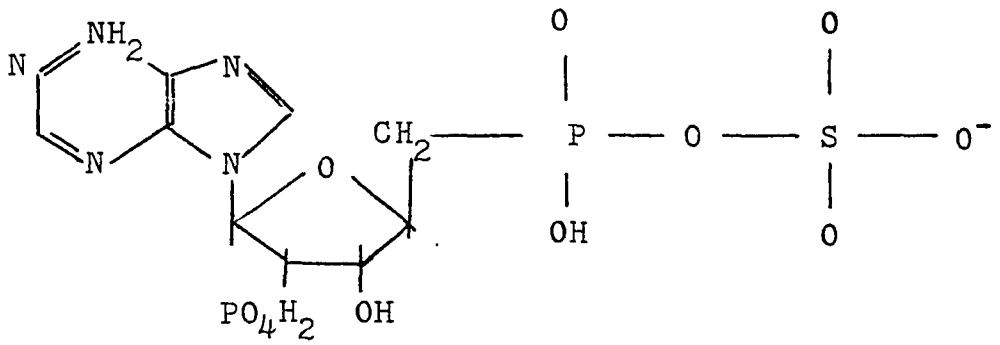


Fig. 2. Structure of 3-phosphoadenosine-5-phosphosulfate(PAPS).

Hydrogen sulfide reacts with serine in an enzymic process (serine sulfhydrase) which leads to the formation of the amino acid cysteine. This product is then methylated to the second important amino acid methionine.[31]

The major products of assimilatory sulfate reduction are:

Cysteine : $SH \cdot CH_2 \cdot CHNH_2 \cdot COOH$

Methionine : $CH_3S \cdot CH_2 \cdot CH_2 \cdot CHNH_2 \cdot COOH$

Minor products are co-enzymes such as glutathione, biotin, thiamine, co-enzyme A and S-adenosyl methionine.

The pathway of synthesis of sulfur-containing amino acids in the bacterium Escherichia coli is shown in Figure 3.[32] The first step in the metabolism of sulfate is the formation of PAPS,

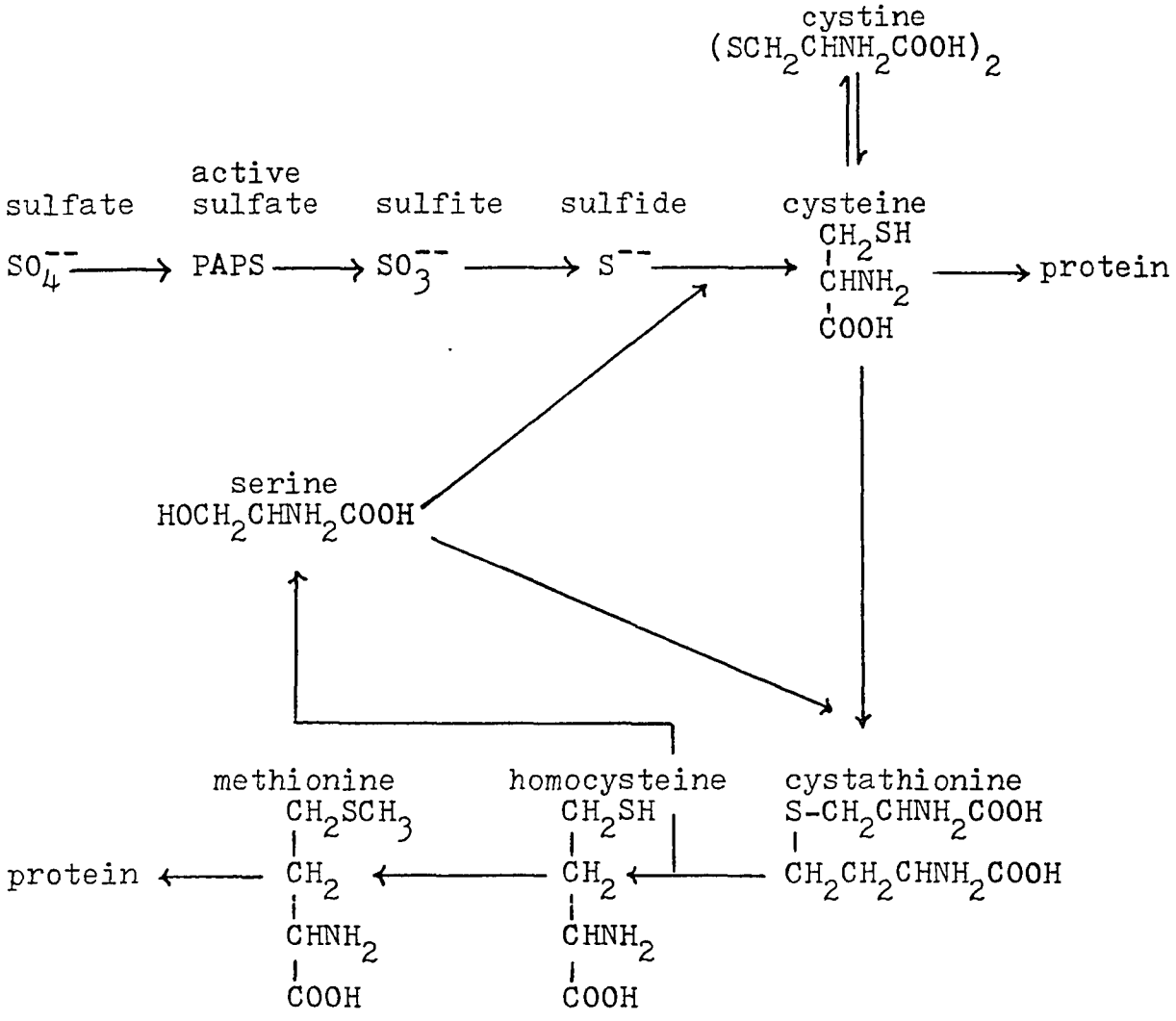


Fig. 3. Pathway of sulfur assimilation by Escherichia coli

which is so-called active sulfate. In the presence of the appropriate enzyme, PAPS can transfer sulfate to phenol, lipids, protein and carbohydrates.

Organisms that reduce PAPS in assimilatory sulfate reduction are:

Escherichia coli	Enterbacter aerogenes
Proteus mirabilis	Pseudomonas punctata
Proteus vulgaris	Clostridium kluyveri
Baker's yeast	Bacillus terminalis

Dissimilatory sulfate reduction

This process is conducted by a few types of bacteria under anaerobic conditions and produces large amounts of sulfide which lead to heavy pollution in aquatic environments.

Dissimilatory sulfate reduction is characterized by APS formation. The active sulfate(APS) is a nucleotide which differs from PAPS. The structure of this nucleotide, adenosine-5-phosphosulfate is:

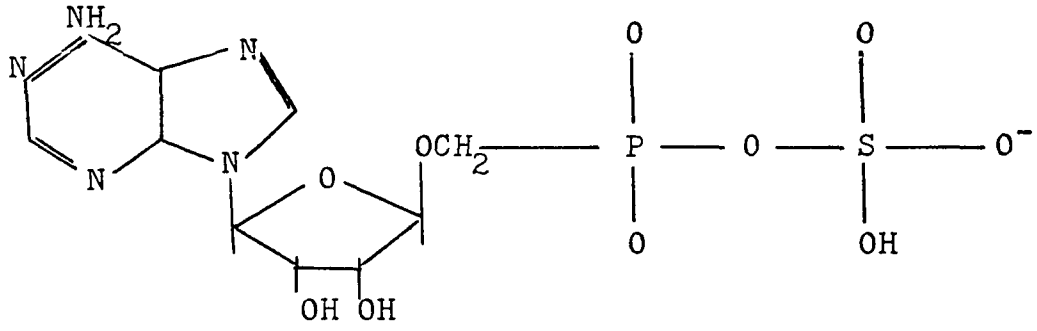


Fig. 4. Structure of adenosine-5-phosphosulfate (APS).

It is formed from adenosine triphosphate(ATP) and sulfate by the enzyme APS-sulfurylase. The initial steps of sulfate reduction can be expressed as:

$$SO_4^{--} + ATP \rightleftharpoons APS + PP$$

Pyrophosphate(PP) can be hydrolysed to orthophosphate.

$$PP + H_2O \rightleftharpoons 2\ PO_4^{--}$$

The APS is then reduced by the enzyme APS-reductase which yields adenosine monophosphate(AMP) and sulfite

$$APS \rightleftharpoons SO_3^{--} + AMP$$

Organisms that reduce APS in dissimilatory metabolism are.[33]

Desulfovibrio desulfuricans

Clostridium nigrificans

Vibrio cholinicus

Thiobacillus thioparus

Thiobacillus thiooxidans

Thiobacillus denitrificans

Sulfide oxidation

Hydrogen sulfide generated as a result of biological sulfate reduction, putrefaction or industrial activity, can be reoxidized to sulfur or sometimes to sulfate.

The first method of reoxidation is the metabolic oxidation of hydrogen sulfide by oxygen or nitrate. These processes yield

free energy which can be used by chemoautotrophic bacteria in the reduction of carbon dioxide.[34]

Hydrogen sulfide is also oxidized by the photosynthetic green and purple bacteria. These organisms can use hydrogen sulfide as an oxygen acceptor in the photosynthetic reduction of carbon dioxide. The purple forms of the bacteria which occupy the surface of mud where large quantities of hydrogen sulfide can be generated, are much more significant quantitatively. Colorless sulfur bacteria which exist in the free water above the purple forms in the mud also can oxidize free sulfide.

Colorless sulfide-oxidizing bacteria include:[35]
Thiobacillus, Thiospirillum, Thiovulum, Thiothrix, Beggiatoa.

Colored sulfide-oxidizing bacteria are: red and purple bacteria: Chromatium, Thiopedia, Lamprocystis, Rhodochromatium, Amoebobacter, Rhodothiospillum.

Green bacteria: Chlorobium, Chloropseudomonas.

Sulfur oxidation

Most sulfide oxidation bacteria can oxidize sulfur when sulfide becomes exhausted. The aerobic bacterium Thiobacillus is common genus which can oxidize sulfur or thiosulfate ions to sulfate as a source of energy for growth. Figure 5 provides a scheme of pathways for inorganic sulfur processes by Thiobacilli.[36]

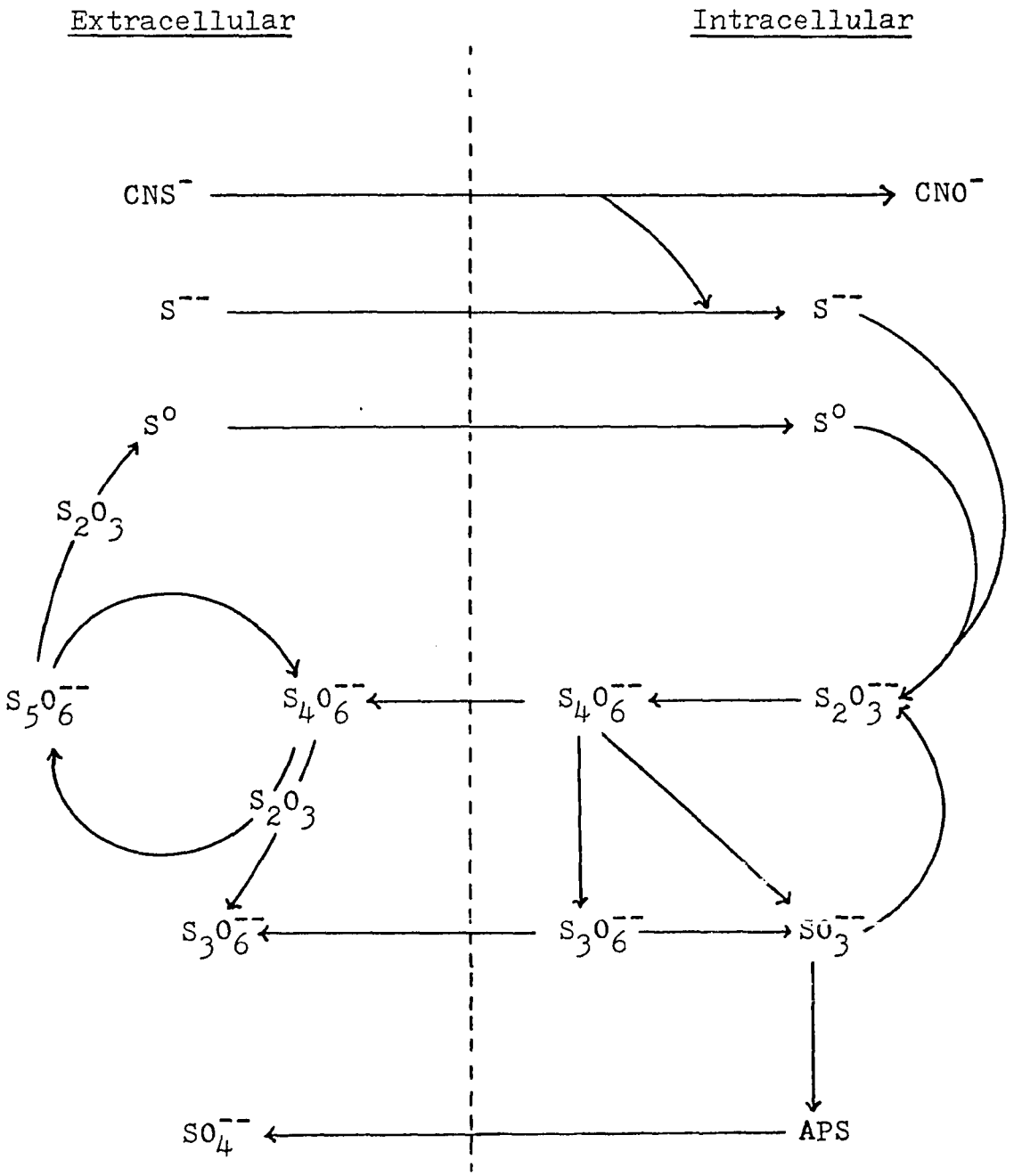


Fig. 5. Pathway of inorganic sulfur in Thiobacillus

Ultraviolet absorption of nature water

For organic pollution studies, the ultraviolet absorption technique was developed to estimate the degree of contamination in water. This technique is based upon the absorption of ultraviolet light between 220-800 μm caused chiefly by electronic excitation. The spectrum also provides some information about the particular substance being studied.[37]

Application of ultraviolet absorption to pollution was started in 1955. Armstrong and Boalch conducted an ultraviolet absorption study on sea water in 1961. They found that the ultraviolet absorption of sea water was twice as great as that of a solution containing only inorganic salts at the same concentration, thus suggesting that the high absorption of the sea water was due to the presence of organic matter. They also found that nitrate affected the ultraviolet absorption and was important to the ultraviolet absorbance characteristic of water.[38]

Ogura and Hanya conducted a four-year study on natural waters, involving sea water, lake water, rain water, river water, and snow. They found that nitrate and bromide were the only two effective inorganic substances which could be absorbed significantly at wavelengths below 235 μm and that the dissolved organic matter contributed to the ultraviolet total absorbance at longer wavelengths. Therefore, they proposed that the ratio of absorbance at 250 μm to 220 μm gives an indication of the

ratio of organic and inorganic substances and could be used as an index of water quality.[39,40]

A similar investigation was conducted by Foster and Morris. They reported that a high ultraviolet absorption of river water from 250 um to 350 um was obtained and they attributed this to the relatively large amounts of dissolved organic matter present. However, the quantity of dissolved organic matter in sea water was small because it was only supplied by land drainage, excretion and decomposition of biological materials. The natural fresh water, upon mixing with sea water, caused an increase in absorbance. Hence, increases in the absorbance of sea water were associated with increasing fresh water influence. Consequently, the magnitude of the ultraviolet absorption of sea water increased toward the coast and estuarine regions.[41]

A strong inverse relationship between salinity and intergrated ultraviolet absorbance was also observed. They suggested that the value of the salinity to absorbance indicated the quality of sea water. Samples having negative salinity residuals were high in organics, while those having positive salinity residuals were low in organics. These two parameters provide definitive criteria for depicting inhomogeneities within a sea water and for identifying the source of natural water giving rise to these inhomogeneities which make it a useful tool for characterizing water mass in inshore water.[42]

Organic matter, humic acid and hydrocarbons in soils

Soil organic matter is defined as the organic portion of soil substances.[43] It is a natural product of the soil environment, initially derived from plants, animals and microorganisms. The plant and animal polymers, including polyssacharides, lignins and proteins, are degraded into small organic molecules. Some of these substances are utilized by organisms for synthesizing cell material, and some undergo enzymatic or chemical reactions to form new polymers which are relatively resistant to decomposition, and constitute an important fraction of soil organic matter.[44]

The organic materials present in soil are a heterogenous complex consisting of numerous compounds of plant, animal and microbial origin, and their decomposition and transformation products. This complex serves as a source of energy and various organic and inorganic nutrients essential for microbial population growth. It modifies the physical and chemical nature of soil to make a more favorable environment for microbial development and characterizes the soil as a brown to dark colored amorphous substance.[45] Chemically, the soil organic matter contains carbohydrates, proteins, lignins, fats, waxes, resins, and some inorganic elements.[46]

The organic matter found in water basins resembles that found in land soil. That matter found in rivers, lakes and seas

is originally allochthonous and exists in solution, in suspension, or incorporated in the bottom deposits.

The content of organic matter in the bottom sediments was determined by numerous workers. It was usually found to be 1-12% of the total dry materials.[47]

Humic acids are the most important constituents of organic matter in soil. They may constitute 50% of the total organic matter. These materials, which are the most stable compounds in soil, are soluble in alkali, precipitated by acid, and brown to almost dark in color.[48] It is believed that humic acid is a complex polymer of various phenolic units with linked peptides, amino acids and possibly some polysacharides. The phenolic units could be formed through microbial degradation of lignin and other plant polyphenols or through synthesis by soil microorganisms.[49]

The humic compounds have large cation-exchange capacities and metal complexing abilities. They can form complexes with various metals resulting ultimately in the migration and accumulation of metals in soil, sedimentary deposits, or natural materials.[50] It has been demonstrated that a high concentration of iron is often associated with organic matter which posesses the structural features of humic substances in many natural aquatic systems. The humic acid found in ground water, surface water and municipal wastewater can severely retard the oxidation of ferrous ion, therefore, appreciable concentrations of dissolved ferrous ion can be maintained in aerobic aquatic systems in the presence of humic

substances of natural origin.[51] The stabilization of iron by humic substances increases its nutritive availability for the growth of aquatic species.[52]

Appreciably large amounts of the humic substances are present in soil and sediments. These materials in land soil are capable of complexing metal more than that of marine origin, because of the higher acidic characteristics of soil organic matter.[53]

Bitumen is defined as a hydrocarbon of nature or of pyrogenous origin or a combination of both, which can be liquid, semi-liquid or solid and is largely soluble in carbon disulphide.[54] It is extracted from soil or sediments by using a solvent mixture of benzene and methanol. It was found that bitumen in Japanese soil contains 31-67% of the total organic matter; in lake sediment it contains 4-17%; in marine sediment, 7-51%.[55] By using chromatographic techniques, bitumen can be separated into hydrocarbons and asphaltic compounds.

The widespread occurrence of mixtures of hydrocarbons in living organisms and in the organic matter of recent sediments has been clearly demonstrated.[56] A significant quantity of solid paraffin hydrocarbon was recovered from recent sediment. A complex mixture of hydrocarbons was also isolated from kelp and fresh water algae. These hydrocarbons are now considered to be common constituents of organic matter in soil and marine sediments, although they may occurred in small concentrations. Some of the hydrocarbons are probably of biological origin, whereas others are the product

of the gradual decomposition of organic matter in the sediments.

Recently, petroleum-derived hydrocarbons were found in the bottom sediment of rivers and lakes, because of the petroleum products spilled into the rivers and lakes which are then accumulated in the sediments and superimposed over the background of indigenous hydrocarbons. The large amounts of hydrocarbons found in the sediments close to densely populated shores were presumably derived from fossil fuels while those found in the sediments near the less populated shores, were presumably derived from aquatic organisms.[57] These petroleum products can retard the biodegradation in the sediments and affect the growth of the biota.

III EXPERIMENTAL PROCEDURES

Description of the study area

The sanitary landfill used for this study is located approximately one mile south of Norman, Oklahoma, on the north bend of the South Canadian River, in Section 18-T8N-R2N of Cleveland County. The landfill site which occupies 180 acres, averages 32 inches of precipitation as rain per year and a mean monthly temperature range from 39.7°F in January to 82.9°F in August.

This landfill is operated by the area method. Inert, bulky materials including demolition debris and tree stumps are dumped in a separate area of the landfill. Refuse is compacted and covered with a final layer of river sand ranging from a few inches to 2 feet in thickness.

Before 1970, the city of Norman used the present landfill as an open rubbish dump. Any type of materials could be deposited without restriction, and open burning was sometimes practiced. Ground water exists under water table conditions at depths of 2.5 feet to 6 feet. During the past four years, a private firm operated the fill on a fee basis and developed the sanitary landfill operation.

Preliminary studies concerning the direction of ground water flow and the rate of flow indicated that the direction was considered to be normal to the contours and approximately seven degrees west of south while the rate was 0.13-0.18 feet per day.[58]

Studies showed that the soil permeability in this area was 6.3-9.9 feet per day. Other studies indicated that a variety of organic compounds were found in the underlying ground water.[59,60]

Ground water and mud sampling

Three drilled wells were selected as sampling wells, one well was a control well located 0.7 mile upstream from the new landfill site. This well was drilled in October 1973, and cased with galvanized iron pipe to a depth of 42 ft. It was perforated in the bottom 12 ft and held 37 ft of standing water. The second well was in the southeast portion of the new landfill. It was drilled in November 1972 and cased to a depth of 32 ft with 20-22 ft of refuse layer and held 17 ft of standing water. The third well was one mile downstream from the new landfill site. This well was drilled in October 1973 and cased to a depth of 42 ft with 34 ft of water. Both the upstream and downstream wells were drilled to the red bed, the landfill well was not drilled to the red bed but have solid iron plates at the bottom to prevent sand intrusion. Figure 6 is a map showing the location of these wells.

Water samples were taken at weekly intervals from April 1973 to May 1974. These samples were collected by Kemmerer bottle, placed in appropriate containers and brought into the laboratory. Routine analyses were made in the field upon sample collection of temperature, pH and TDS. Other analyses run duplicate or triplicate and the samples were filtered through 0.45 um member

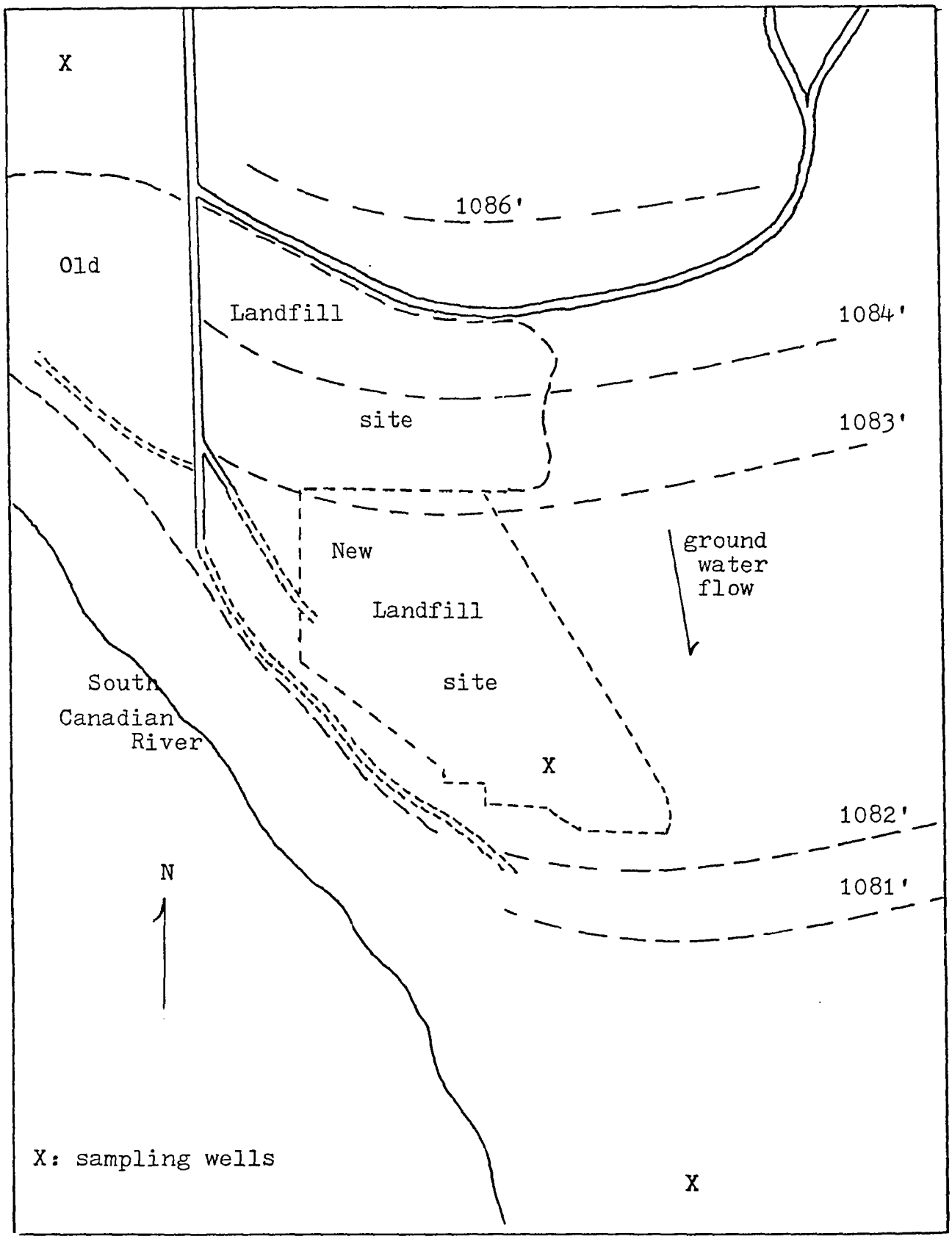


Figure 6. Well Locations at Norman Landfill

filters before being analyzed.

Mud samples were collected by Phleger cone sampler. These samples were air-dried, ground to pass through a #10 sieve, and quartered to provide for various analyses.

Ground water chemical analyses

Chemical analyses were performed on ground water samples from the three wells. The pH was measured using a digital pH meter model 801. The redox potential was measured by a potentiograph E336. Specific condutance was found by using a Beckman conductivity bridge model RC-1982 with a dippling glass conductivity cell. Density was determined by Westphal Balance. All other chemical study procedures were according to the 13th edition of Methods for the examination of water and wastewater.[61] They included alkalinity(titration method); chromium(1,5-Dephenylcarbohyrazide); copper(superthol method); cyanide(pyridine-phrazalone method); fluoride(SPADNS method); hardness (EDTA titrimetric method); manganese(periodate method); iron (phenanthroline method); nitrogen(Nesslerization method); nitrate(phenoldisulfonic acid method); nitrite(diazotization method); phenol(calorimetric method); phosphate(stannous chloride method); silica(gravimetric method); hydrogen sulfide(methylene blue method); ferrous(1,1-phenanthroline method); carbon dioxide (titration method); tannin and lignin(tyrosine method); turbidity (formazine method); dissolved oxygen(azide modification method); COD(dichromate reflux method); and BOD(5-day incubation of diluted samples).

Mud samples chemical analysis

The mud samples collected from the three wells were air-dried, ground and analyzed for a variety of chemical parameters. Cation-exchange capacity was measured by the ammonium saturation method using a boric acid solution for titration; organic matter and organic carbon were determined by the Walkley-Black method; total nitrogen, by the Kjeldahl method; iron, by the orthophenanthroline method; copper, by colorimetric analysis using diethyldithiocarbamate; carbonate, by the gravimetric method for loss of CO_2; phosphorus, by the ammonium molybdate-stannous chloride method; manganese, by the colorimetric method; organic sulfur, by a method for oxidizing organic sulfur with hydrochloric acid; sulfate, by the turbidimetric method of $BaSO_4$; sulfide, by the acid-volatile method described in Berner;[62] elemental sulfur, by the modified method as outlined by Fliermans and Brock;[63] the particle size distribution, by the hydrometer method using a calgon solution as a dispersing agent. All these analytical techniques are described in Methods of soil analysis.[64]

Simulated experiment

A simulated landfill set up in the laboratory consisted of a 3.8 inch diameter by 63 inch tall plexiglass column which was filled with refuse obtained from the Norman sanitary landfill. Fill materials contained paper, food products, metal, glass, yard waste, wood rubber, leather, cloth, dirt, ash, and soil.

Each of these materials was weighed respectively, mixed and compacted together into the column and covered with 6 inches of sandy clay. The composition of the refuse was given in Table 1.

Quantities of rain water were supplied to the column based upon the amount of precipitation for central Oklahoma in 1973, as shown in Table 2. Rain water was applied to the column at one-week intervals. After six months, leachate samples were collected from the bottom of the column and analyzed in the laboratory for chemical quality. The parameters of the analysis and the analytical procedures for leachate were similar to that described in ground water chemical analyses.

Identification of clay minerals in the bottom mud

Clay minerals in the ground water mud were identified from d-spacings obtained by x-ray diffraction procedures. Other techniques used were those including ethylene glycol expansion and heat treatment in accordance with Wong.[65] The treatment using ethylene glycol to expand the d-spacings of expandable clay minerals permitted the detection of minerals such as montmorillonite in the presence of the other 14 Å clay minerals. By this method even small amounts of montmorillonite can be detected in the presence of minerals such as vermiculite and chlorite. The heat treatments resulted in the collapse of the d-spacings permitting the separation of vermiculite and montmorillonite from chlorite.[66]

Table 1. Solid waste composition in simulated landfill column

Component	Weight (lb)	Percent (%)
Paper	22.0	44
Food product	10.0	20
Yard waste and wood	5.0	10
Rubber, leather and cloth	4.0	8
Metal product	3.0	6
Glass product	2.2	4
Plastic product	2.0	4
Dirt, ash and soil	2.0	4
Total	50.2	100

Table 2. Rainfall in Oklahoma(1973)

Month	inch/month	ml/month	ml/week
January	1.29	1062.58	265.6
February	1.11	914.31	228.5
March	2.48	2042.79	510.7
April	3.48	2866.50	716.6
May	5.37	4423.30	1105.8
June	3.80	3130.10	782.5
July	2.61	2149.90	537.4
August	2.79	2298.14	574.5
September	3.15	2594.67	648.6
October	3.23	2660.57	665.1
November	2.17	1787.44	446.8
December	1.61	1326.17	331.5
Total		27256.42	6813.6

Study on the prevalence of bacteria in the bottom mud

In this experiment, different microorganisms were isolated and identified by using nutrient agar and selected media. Samples were placed on agar plates and incubated in a Brewer anaerobic jar at 20-22° C temperature for ten day periods. At the end of this time the plates were transferred several times using the streak plate technique to obtain pure cultures and examined morphologically and physiologically to identify the genera of the bacteria grown.

Differential procedures including gelatin hydrolysis, litmus milk production of hydrogen sulfide, and gram staining were used.

Isolation of Desulfovibrio from the well muds was conducted using Bacto-sulfate API Broth.[67] This medium contained Bacto-yeast 1.0 gr, ascorbic acid 0.1 gr, sodium lactate 4.0 ml, magnesium sulfate 0.2 gr, dipotassium phosphate 0.01 gr, ferrous ammonium sulfate 0.1 gr, and sodium chloride 10 gr. Incubation took place in a Brewer anaerobic jar at 20-22° C for a minimum of three weeks. The cultures were examined daily for blackening of the medium.

For the detection of Thiobacilli, the Bacto-Thiobacillus Broth was used. This medium contained sodium thiosulfate 5 gr, ammonium sulfate 0.4 gr, monopotassium phosphate 4 gr, calcium chloride 0.25 gr, magnesium sulfate 0.5 gr, ferrous sulfate 0.01 gr.[68] Incubation was maintained at room temperature for one to two weeks until evidence of growth appeared.

For the detection of Beggiatoa, hay medium was used.[68] Dried hay was extracted at 100° C from a large column of water. The hay was then drained and placed on trays at 37° C to dry. The enrichment medium consisted of 0.8% extracted and dried hay in tap water which was distributed in 70 ml amounts in 125 ml Erlenmeyer flasks. Five ml portions of mud samples were placed in the flasks of hay medium and incubated at room temperature about ten days.[69]

In the innoculation experiment, Clostridium perfringens was innoculated to study the survival characteristics under a simulated ground water environment. A pure culture of Clostridium perfringens, obtained from the Department of Microbiology, University of Oklahoma, was grown in an enrichment broth under anaerobic conditions for 36 hours at 20-22° C, and yielded 26,700 organisms/ml. Two ml of this culture was introduced into a 500 ml Erlenmeyer flask containing 200 ml of sterilized ground water with 30 ml of sterilized bottom muds, and incubated under anaerobic conditions at 20-22° C. Samples were withdrawn at 4-day intervals and assayed for a number of viable colonies by dilution and plating on nutrient agar plates which were then incubated under anaerobic conditions at 20-22° C for 48 hours. This is a study of the growth and development of Clostridium perfringens as affected by the pollutants in the landfill environment.

Study of sulfur distribution and migration

A study of the distribution and migration of various forms of sulfur and the sulfur metabolism in ground water sulfuretum was conducted. The various forms of sulfur in column leachate, ground water and the bottom muds of ground water were determined. Sulfate-reducing bacteria, Beggiatoa and Thiobacilli, were detected and their population estimated by growth in appropriate selective media according to the MPN procedure. All the methods used in this part were described in a separate section.

Ultraviolet absorption study in ground water

An ultraviolet spectrometer Cary 118 with 1 cm silica cells was used for all measurements. The absorbance between 200 to 500 ~um was recorded in terms of the absorbance coefficient using distilled water as the reference.

Fresh ground water was collected and divided into three portions. One portion was treated with aeration for 24 hours; one was boiled in a water bath for 10 minutes; while the rest of the sample was measured immediately using a continous recorder.

The ground water samples were stored in plastic bottles which were immersed in a water bath at 20-22^{o} C for three months, and then measured again using the same ultraviolet spectrometer.

Study of bitumen, humic acids and hydrocarbons in the bottom muds of ground water

Mud samples were extracted for fifty hours by using a mixture of one part benzene to one part methanol. The solvent was then removed from the organic extract by evaporation at 40° C and the soluble organic matter, called bitumen, obtained.[70]

By using column chromatographic techniques, the bitumen was separated into hydrocarbons and asphaltic compounds. This bitumen was first dissolved in n-heptane and chromatographed on activated silica gel(diameter 1.5 cm, height 20 cm) by using n-heptane, benzene and methanol in sequence, as eluting agents. The n-heptane fraction was composed of paraffin saturated hydrocarbons. The benzene fraction contained aromatic hydrocarbons and the methanol fraction contained asphaltic compounds.[71]

The extracted residue of the mud was dissolved in a 0.1 N NaOH solution and extracted after two hours. This extracted solution was centrifuged to obtain a solution containing humic acids and fulvic acids mixtures. Concentrated sulfuric acid was added to the solution to precipitate the humic acid.[72]

An infra-red spectrometer(Beckman IR 8) and Nuclear Magnetic Resonance spectrometer were used to study the nature of the functional groups present in the hydrocarbons and humic compounds.

IV RESULTS AND DISCUSSION

Characteristics of the lab column leachate and the ground water

The physical and chemical qualities of lab column leachate and ground water were studied, and the results are presented in Tables 3, 4, 5 and 6. The leachate sample, collected from the bottom of the column, showed a light brown color and became dark green after collection. Physically, the leachate solution contained high values of density, specific conductance and turbidity. The density of this solution, defined as the mass of unit volume of the liquid, was 2.01902. It was two times higher than the density values of the ground water. Specific conductance, measured as the capacity for conveying electrical current, is proportional to the number of ions and the charge on each ion.[73] The high value indicated a high concentration of various ionized substances present in leachate solution. Resistance is inversely proportional to the specific conductance; the higher resistance, found in upstream ground water, demonstrated the less ionized clean water quality. Turbidity is caused by a wide variety of suspended materials, and substantial quantities of organic and inorganic substances contributed to the high value of turbidity in the leachate sample. The level of turbidity in landfill ground water, although much less than the leachate solution, was relatively higher than that of other ground water samples. This can be attributed partially to the leaching of organic and inorganic substances into this ground water. These substances also serve as food for microbial growth thus producing additional turbidity.

Table 3. Physical characteristics of laboratory column leachate and ground waters

Sample	Density g/cm^3	Specific Conductance $ohm^{-1} cm^{-1}$	Resistance ohm	Turbidity
Laboratory column leachate	2.01902	0.0029273	330	197
Landfill ground water	0.99899	0.0012694	761	66
Downstream ground water	0.99799	0.0007431	1300	42
Upstream ground water	0.99699	0.0003389	2850	36

Some of these substances flowed gradually downstream and contributed to the turbidity of downstream ground water.

Table 4 shows pH values of leachate ranging from 5.0 to 5.3; values of landfill ground water ranging from 6.9 to 8.1; downstream ground water ranging from 7.1 to 8.1 and upstream ground water, from 7.3 to 8.1. The redox potential and dissolved oxygen measurements indicate that the leachate solution, landfill and downstream ground water were in reducing states with anaerobic environments, and the upstream ground water was in a reducing state with a microaerophilic environment.

Concentrations of BOD as high as 12,000 mg/l and COD as high as 3,142 mg/l were obtained in leachate sample. These high values of COD and BOD were associated with the low pH indicating the presence of organic acids produced from the anaerobic decomposition. The difference between the BOD and COD values, approximately 8,858 ppm initially, also showed that the leachate materials were composed of certain organics which were biologically degradable, but resisted chemical oxidation. These organics include phenolic and ring structure compounds. Inversely, the COD of the ground water was greater than the BOD indicating lower concentrations of phenolic and ring structure compounds.

Alkalinity is defined as the presence of salts of weak acids and to a lesser degree the salts of strong bases.[74] The high value of alkalinity in the leachate indicates the presence of large amounts of strong alkaline products. The major form was bicarbonate

Table 4. Chemical characteristics of laboratory column leachate and ground waters

Sample	pH	E_h mv	DO mg/l	COD mg/l	BOD mg/l	Alkalinity mg/l as $CaCO_3$	TDS mg/l
Laboratory column leachate	5.0-5.3	-60	0	3142.0	12000.00	3200	14000
Landfill ground water	6.9-8.1	-65	0	49.6	13.33	1710	1300
Downstream ground water	7.1-8.1	-67	0	34.3	11.62	716	1150
Upstream ground water	7.3-8.1	-70	0.8	15.2	4.08	630	365

which acts as a buffer resisting the drop of pH caused by the organic acids of anaerobic decomposition products. The high concentration of carbon dioxide also contributed to the alkalinity and existed in equilibrium in this system.

The extremely high concentration of carbon dioxide in the leachate solution indicated that a very active biological process was occurring. The comparatively low concentration of carbon dioxide in the ground water probably resulted from the fact that the portion of the landfill studied was 4-7 years old and the rapid generation of carbon dioxide had already occurred in this portion of the landfill.

Chloride was present in considerable amounts in the ground water. It has been demonstrated that chloride can leach with very little containment by soil. Table 5 shows that large amounts of chloride had leached into the underlying ground water and apparently contributed to downstream ground water pollution one mile away.

The microbiological decay of plant and animal proteins contributes to the high level of ammonia nitrogen often present in ground water. This component is released normally from natural microbial reduction processes. A low level of ammonia nitrogen upstream, shown in Table 5, increased to a higher level in the fill and maintained this high concentration downstream.

Nitrate, the final stage of stabilization of waste biological materials, was high in leachate sample. This was presumably due

to the nitrification which took place involving the breakdown of ammonia to nitrate under aerobic conditions. An appreciable amount of nitrate existing in the upstream and downstream ground water was due probably to the migration of fertilizer from agricultural sources and also from natural sources within the water table.

On the contrary, the nitrite concentration was the highest in the area of upstream, lower in the area of the fill and none in the column leachate. The existence of heterotrophic bacteria under microaerophilic conditions which natrually contribute to the presence of nitrite from nitrification can be inferred in the upstream ground water. Under anaerobic conditions, the conversion of nitrate to nitrite, was possibly due to the action of facultative anaerobes which use this process as a form of anaerobic respiration.

It can be seen from the Table 5 that the concentration of ortho- and meta-phosphate was high in the leachate sample. Comparatively, the concentration of phosphate was quite low in ground water and did not appear to be significant in assessing the potential of contamination. Phosphate is readily absorbed by soils and does not travel very far in ground water. The high level of metaphosphate in downstream ground water might be associated with the high value of phosphorus in its bottom muds. It has been demonstrated that anaerobic soils release more phosphate to soil solution low in soluble phosphate.[75]

The extremely high sulfate concentration in the leachate sample indicated that significant biological degradation of proteins occurred. A more detailed discussion on the varieties of sulfur is provided in a separate section.

Total hardness is caused by divalent metallic cations. The principal cations are in the form of calcium, magnesium, ferrous and manganese. Those cations associated with bicarbonate, sulfate, chloride and nitrate also contribute to total hardness. Total hardness is also increased by total solids. The levels of total hardness in ground water were found to greatly increase in the fill area and decline slowly downstream. These levels followed the same general pattern of total dissolved solids in these areas.

Apparently, the low concentrations of phenols, tannins and lignins demonstrated the slow rate of degradation of cellulose and hemicellulose which constitute a great portion of paper and wood. These constituents are degraded even more slowly under anaerobic conditions.

Table 6 gives the results of the trace element analyses in the lab column leachate and ground water. The concentration of boron in the leachate sample was 27.5 mg/l, while the levels for ground water were low, and all these values were below the mandatory levels for drinking water quality.

Bromide was present in the upstream area in concentrations approximately eight times higher than those in the other two areas. The source of bromide upstream might have come from natural sources such as minerals. Upon reaction with water, bromide forms HOBr, NBr_3 and $NHBr_3$ which serve as the effective disinfectants.[76]

Table 5. Chemical characteristics of laboratory column leachate and ground waters

Sample	CO_2 ppm	Cl ppm	NH_3 N ppm	NO_3 N ppm	NO_2 N ppm	PO_4 (ortho) ppm	PO_4 (meta) ppm	SO_4 ppm	Phenol ppm	Total hardness ppm	tannin & lignin ppm
Column leachate	62625	2650	2620	125	0	6.25	10.5	1290	5.2	10500	30
Landfill ground water	165	2794	3.86	31	0.02	0.14	1.1	200	0.03	1360	1.8
Downstream ground water	104	464	3.78	22	0.01	0.06	2.8	8	0.004	1000	0.9
Upstream ground water	93	234	0.25	22	0.15	0.07	1.1	15.5	0.002	460	0.5

Bromide was not found in the leachate sample.

Cyanide is a toxic element and no more than 0.2 ppm is permissible in drinking water. Fortunately, there was not a trace of cyanide present in the column leachate and in the ground waters.

The chromium level in the leachate sample was 5.7 mg/l and the levels for all of the ground waters were above the recommended limit of 0.05 mg/l. The concentration in the landfill area was 0.14 mg/l, in the downstream area was 0.12 mg/l and in the upstream area was 0.07 mg/l.

The levels of copper in the column leachate solution were as high as 10.5 mg/l, while the values for all the wells were less than the recommended limits. The level in landfill ground water was more than five times greater than the levels of the other areas. This high level was assumed to be the result of leaching from the landfill refuse.

Fluoride exists naturally in some ground waters, although the column leachate contained a small amount of fluoride, the concentration of fluoride in all the studied areas was not in excess of the standard set for drinking water.

It is interesting to note that concentrations of total iron as high as 340 mg/l and of ferrous iron as high as 56.5 mg/l were obtained from the column leachate solution. The values of iron in ground water were very low and the data showed that the concentration in the landfill area was 0.43 mg/l, in the downstream

area was 0.2 mg/l and in the upstream was 0.08 mg/l. Ferrous iron existed in the anaerobic reducing conditions of the landfill and downstream ground water environments. High organic matter levels in the landfill area capable of combining with iron could help explain the low level of ferrous ion in that area. The transformation of ferric to ferrous did not occur in microaerophilic conditions of the upstream area.

A high level of manganese was found in the leachate solution. This soluble Mn^{++} is only present in large amounts in low dissolved oxygen content or high carbon dioxide content[77] The levels in landfill and downstream areas were much greater than recommended limits.

The concentration of silica in the column leachate was 30 mg/l. The values of silica in the wells studied were approximately the same. The silica-layer clay minerals partially provide this concentration.

Table 6. Trace elements in the laboratory column leachate and ground waters

	B	Br	CN	Cr	Cu	F	Fe (total)	Fe (ferrous)	Mn	Si
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Column leachate	27.5	0	0	5.70	10.5	1.01	340	56.50	48.75	30
Landfill ground water	0.6	0.027	0	0.14	0.20	0.25	0.4	0.035	3.65	1.76
Downstream ground water	0.2	0.022	0	0.12	0.02	0.64	0.2	0.10	1.68	1.47
Upstream ground water	0.1	0.185	0	0.07	0.06	0.43	0.08	0	0.05	1.43

In order to study the best chemical parameters used to evaluate the ground water pollution, the graphical analyses were made in Figures 7,8,9 and 10. Figure 7 presents the levels of the chemical components in the fill well which increased one to two times the levels in the upstream control well, Figure 8 presents the levels of the components which increased three to six times and Figure 9 presents the levels of the components which increased more than ten times. Apparently, those components shown in Figure 9 were the excellent tracers. However, the components such as ammonia nitrogen, sulfate, manganese and ferrous involved in the unique aerobic-anaerobic systems and biological and geological reaction contributed to the transformation in various forms. Therefore, chloride was considered to be the best indicator of inorganic parameter and phenol was the best indicator of organic parameter.

Figure 10 showed that the levels of the chemical components in the landfill well decreased. This study demonstrated that the ecosystem of these areas was quite complicated and many factors influenced the chemical change.

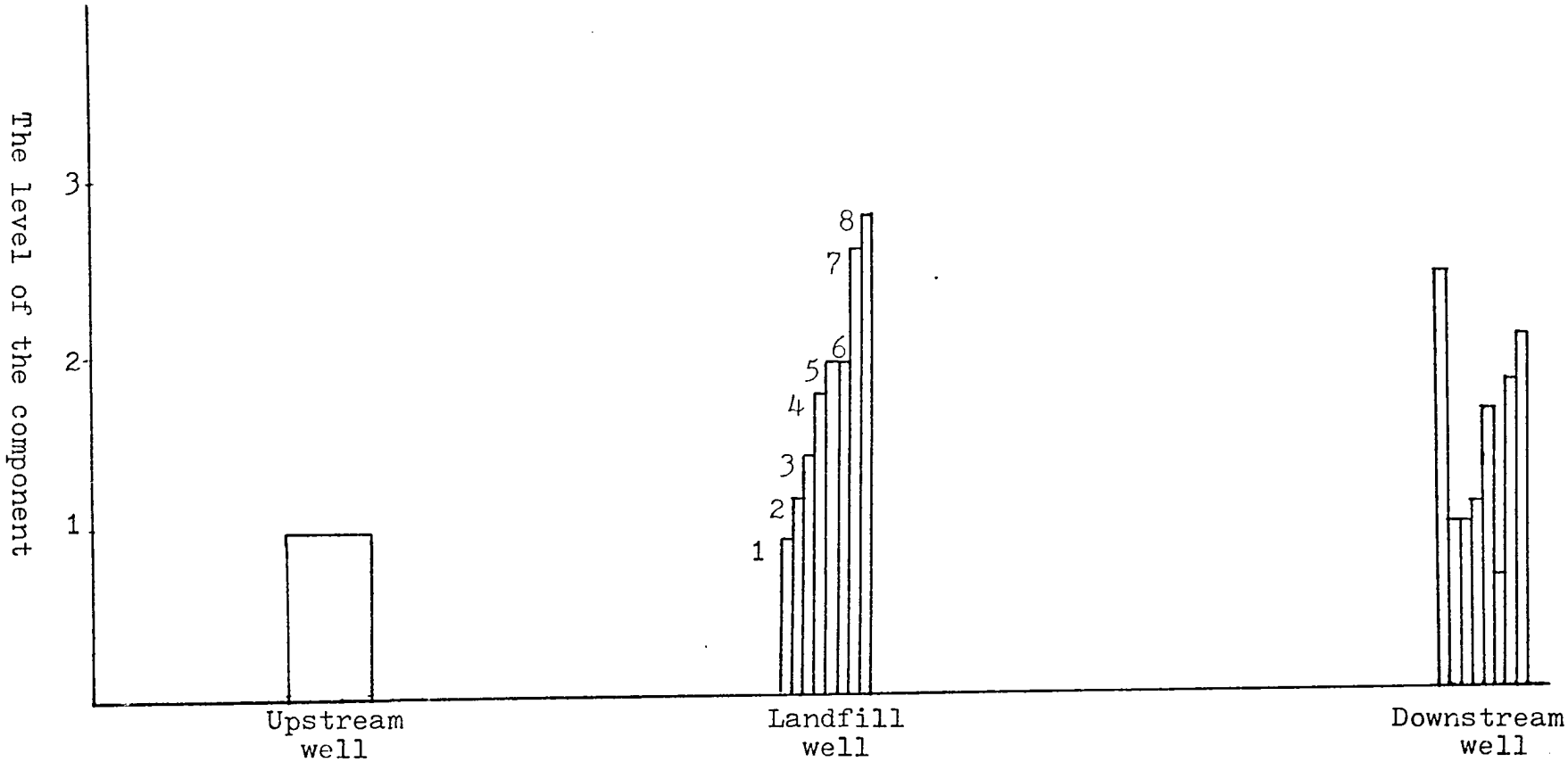


Fig. 7. The levels of the chemical components in wells (1"= 1320')
1:meta-P; 2:Si; 3:NO_3; 4:CO_2; 5:Cr; 6:ortho-P;
7:alkalinity; 8: total hardness.

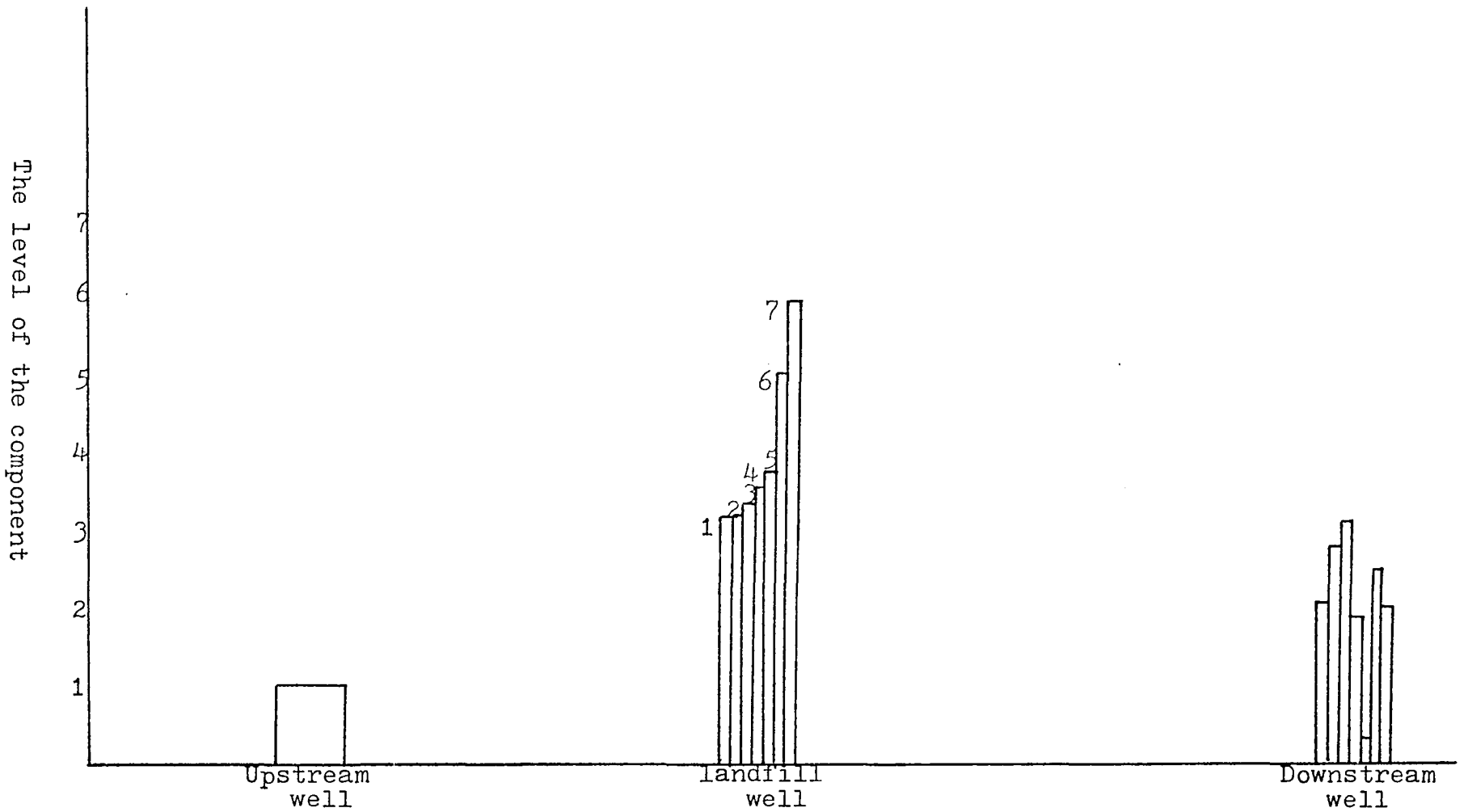


Fig. 8. The levels of the chemical components in wells (1"=1320').
1:COD; 2:BOD; 3:Cu; 4:TDS; 5:tannin & lignin;
6: total Fe; 7:B.

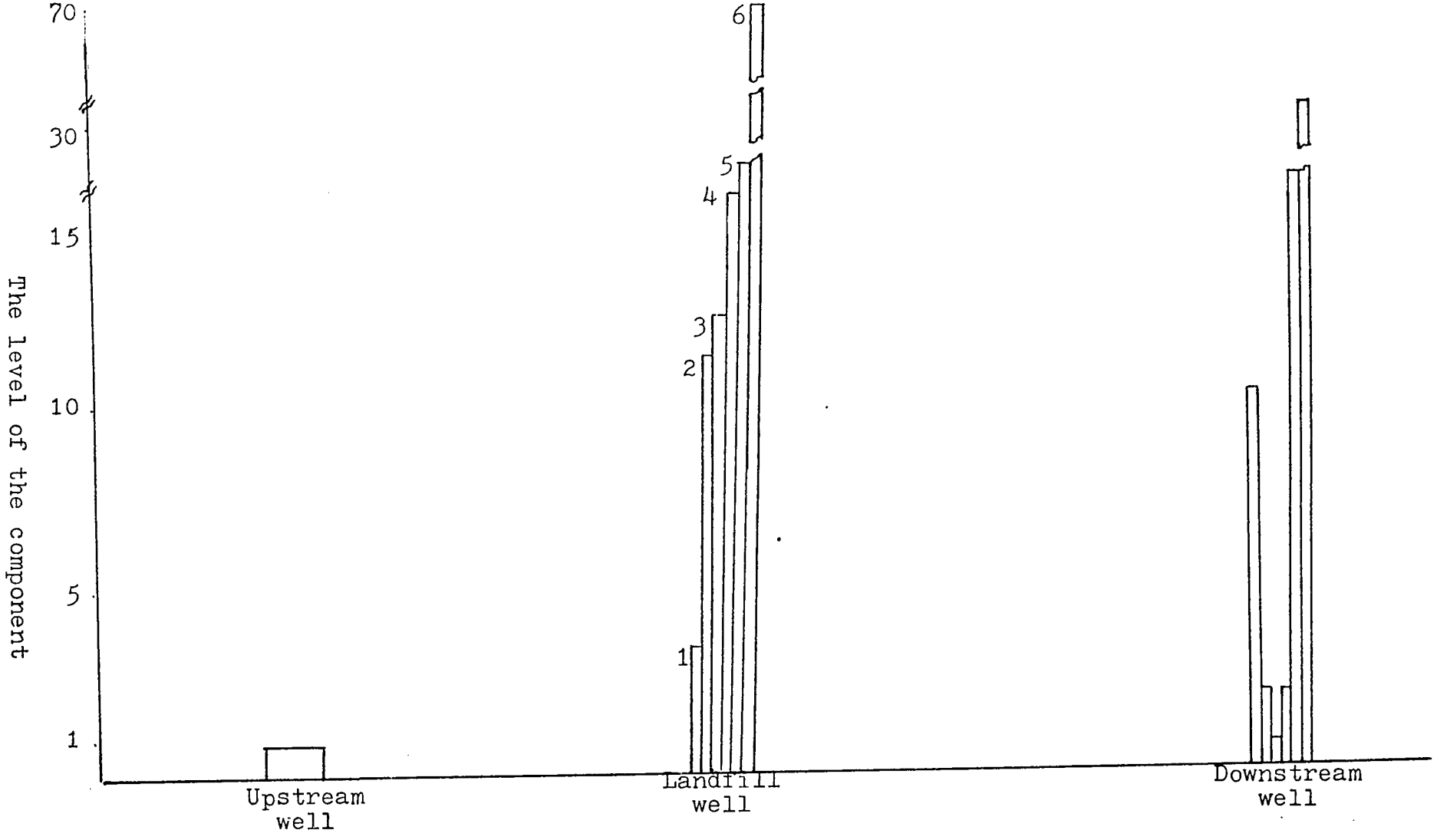


Fig. 9. The levels of the chemical components in wells(1"=1320')
1:Fe^{++}; 2:Cl; 3:sulfate; 4:phenol 5:ammonia nitrogen
6:manganese.

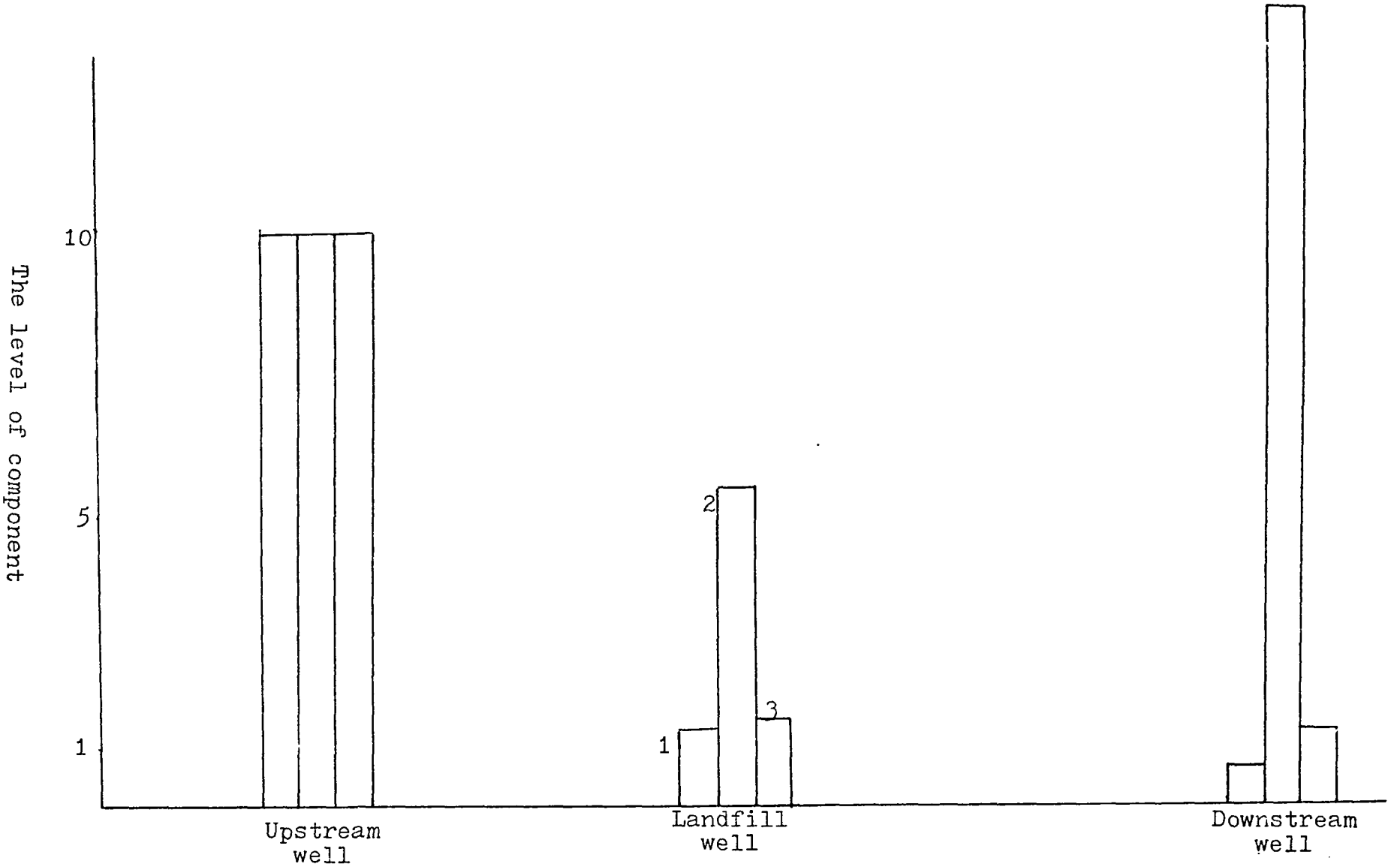


Fig. 10. The levels of the chemical components in wells(1"=1320').
1:nitrite; 2:fluoride; 3:bromide.

Characteristics of the mud soil in the water table

The chemical composition of the mud soil was investigated in order to study its interrelationship with leachate materials. The results of this study are given in Table 7. As seen from this Table, the particle size fraction in the mud samples of the landfill had a sand content of 54.4% and silt content of 37.7%. The clay content was at a minimum. In the samples of upstream and downstream muds, clay and sand composed predominantly the whole fraction while the silt content composed only a small percentage. These size analyses characterized the bottom mud of the landfill as sandy loam, while the bottom mud downstream and upstream was clay.

The cation-exchange capacities and chemical compositions have a significant relationship to the particle size fractions of the soils. It has been demonstrated that cation-exchange capacity in soil usually increases with decreasing particle size. The effective cation-exchange capacity in all the samples was high. Comparatively, the lowest content was found in the landfill sample with 63 meq/100gr. This content is compatible with that when sand is a major fraction. Higher values of cation-exchange capacity were found in the upstream and downstream mud samples.

The organic matter level, shown in Table 7, was high in the landfill mud sample. It was three times as high as in the

samples from both upstream and downstream. Apparently, it was the organic deposition from the landfill during the 35 years of operation which gave the abnormally high level.

The extractable iron level was considerably higher in the bottom mud of the landfill. This indicated that more iron deposition was occurring at this site. In the ferrous-ferric system, the ferric iron that is precipitated is transformed into dissolved ferrous iron under the conditions of absence of dissolved oxygen, presence of decomposing organic matter and the presence of adequate amounts of carbon dioxide.[77] Since the ground water environment was in a highly reduced state, the iron which had been precipitated as ferric hydroxide or ferric phosphate, was reduced in the bottom mud and dissolved as ferrous bicarbonate into the ground water. The iron which was not completely reduced still existed in the bottom muds and was associated with minerals in complex compounds. The high content of iron in the landfill mud could also allow the formation of specific compounds with organic matter. It was found that calcium ferric phosphate and potassium ferric phosphate were not reduced until the redox potential achieved -200mv.[78]

Manganese behaves similar to iron but is easier to reduce than iron. Manganese starts to dissolve as the redox potential reaches +400 mv and becomes largely dissolved as the redox potential goes below +300 mv.[79] Small quantities of extractable manganese were obtained in the mud samples. This element is

associated with minerals and exists in nature. The high concentration of manganese in the mud of the landfill was probably due to the presence of dolomite, shown in Figure 11.

The extractable copper was low in the bottom muds of the wells studied. The higher concentration of copper in the mud of the landfill was associated with the high concentration of carbonate because the ability of the sediment to hold copper is proportional to the carbonate content.[80]

Higher concentrations of carbonate revealed that there were appreciable quantities of calcareous minerals existing in the bottom muds. Dolomite in the landfill and calcite in both upstream and downstream muds were found in the clay minerals experiment. In addition, carbon dioxide produced by microorganisms within the landfill probably contributed to the total amount present.

The extractable phosphorus level was very low in all of the samples. The relatively high phosphorus level in the downstream samples, when compared to the other samples, could suggest that phosphorus fertilizers by the farmers along the river had diffused into the soil. The behaviour of phosphate leaching into the soil profile was established.[81] Polyphosphate forms soluble complexes with metallic ions and moves farther with soil solutions than orthophosphate.[82]

A comparison of the results for phosphorus and nitrogen

showed that the nitrogen content in the bottom mud was apparently higher than the phosphorus content. Naturally, relatively appreciable amounts of nitrogen existed already in the soil with small amounts accumulating either from leaching or from the loss of the nutrient from crops, grass and plants. It has been demonstrated that when large amounts of nitrogen are supplied as fertilizer it can migrate into subsoils.[83] Thus the high value of nitrogen in the mud samples downstream was possibly due to the heavy nitrogen fertilization.

Table 7. Chemical characteristics of the bottom muds of ground water

Sample	size distribution sand %	clay %	silt %	CEC meq/100g	organic matter %	organic carbon %	carbonate ($CaCO_3$) %	Cu %	N %	Mn %	Fe %	P %
Landfill mud soil	54.40	7.84	37.76	63	6.17	3.58	13.34	0.075	0.07	0.010	1.05	0.0005
Downstream mud soil	42.88	55.84	1.28	123	2.41	1.40	11.96	0.074	0.20	0.009	0.54	0.0011
Upstream mud soil	44.24	48.20	7.56	108	2.14	1.24	9.75	0.052	0.01	0.004	0.42	0.0004

Mineralogical study from ground water mud

Qualitative interpretation of diffraction patterns involved identification of crystalline species from the array of diffraction maxima obtained from the bottom mud samples. Generally, montmorillonite, vermiculite, kaolinite, illite, quartz, calcite and dolomite were found in these areas.

Kaolinite

The x-ray diffraction characteristics of kaolinite are peaks of 7.19 Å, 3.58 Å and 2.34 Å d-spacings. It is a stable clay mineral which does not change its d-spacings with ethylene glycol treatment but the crystal structure can be destroyed by heating to 600°C for one hour. Kaolinite was found to exist in the upstream and downstream ground water muds but not in the landfill ground water mud.

Montmorillonite

The x-ray diffraction characteristics of montmorillonite are the strong peak of the 13.39 Å d-spacing and weak peaks of the second and third order diffractions. The first order diffraction expands to 17.35 Å d-spacing when it is treated with ethylene glycol which enters into the interlayer position of the crystal structure. With heat treatment, up to 300°C, the 13.39 Å peak collapses to 9.9355 Å to intensify the first order diffraction of illite. From Fig.11, it has been shown that montmorillonite exists in the upstream, downstream and landfill ground water muds.

Vermiculite

The x-ray diffraction characteristics of vermiculite are the strong peak of the 13.39 Å d-spacing and weak peaks of the second and third order diffractions. Vermiculite is usually mixed with chlorite and montmorillonite in the first order diffraction. After the treatment with ethylene glycol, vermiculite is separated from montmorillonite, the former still shows a peak of the 13.39 Å d-spacing and the latter expands to 17.355 Å d-spacing. With heat treatment, up to 300° C, the peak of 13.39 Å d-spacing collapses to 9.9355 Å to intensify the first order diffraction of illite. Vermiculite exists in the upstream, downstream and landfill ground water muds(Fig. 12).

Illite

The x-ray diffraction characteristics of illite are the peaks of the 10.04 Å, 4.98 Å, 3.35 Å and 1.99 Å d-spacings obtained from a mud soil slide. It is a stable clay mineral which will not change its d-spacing by either ethylene glycol treatment or heat treatment to 600° C. Illite was found in the upstream, downstream and landfill ground water muds.

Quartz

Quartz is a framework silicate mineral(SiO_2) which is not a kind of clay mineral but it is usually mixed with clay minerals in the soil. The x-ray diffraction characteristics are the peaks of the 4.27 Å, 3.35 Å d-spacings. This mineral exists widely in any soil and is quite stable. It may be derived from the original rock as a deposit. Quartz was found to exist in the upstream,

downstream and landfill ground water muds.

Calcite

Calcite is a carbonate mineral($CaCO_3$) which is easy to dissolve in solution and easy to precipitate when the solution is over-saturated. Therefore, this mineral can be either derived from the original rocks or an authigenic one. The x-ray diffraction characteristics are the peaks of the 3.03 Å, 2.28 Å and 2.13 Å d-spacings. Calcite exists in the upstream and downstream ground water muds but not in the landfill ground water mud.

Dolomite

Dolomite is a carbonate mineral($CaMg(CO_3)_2$) which has characteristics similar to calcite. It can be formed primarily with secondary alteration rather than direct precipitation. This mineral can be either derived from the original rock or an authigenic one. Generally, dolomite is more stable and more insoluble than calcite to the attack of solutions. The x-ray diffraction characteristic is appearance of a strong peak of 2.85 Å d-spacing. Dolomite only exists in the landfill ground water muds.

Conclusively, clay minerals found in the landfill bottom muds were montmorillonite, vermiculite, and illite. Dolomite, a carbonate mineral, was also found in landfill mud soil. This mineral is associated with manganese and provided the high content of manganese in these sites.

Clay minerals found in the upstream and downstream samples

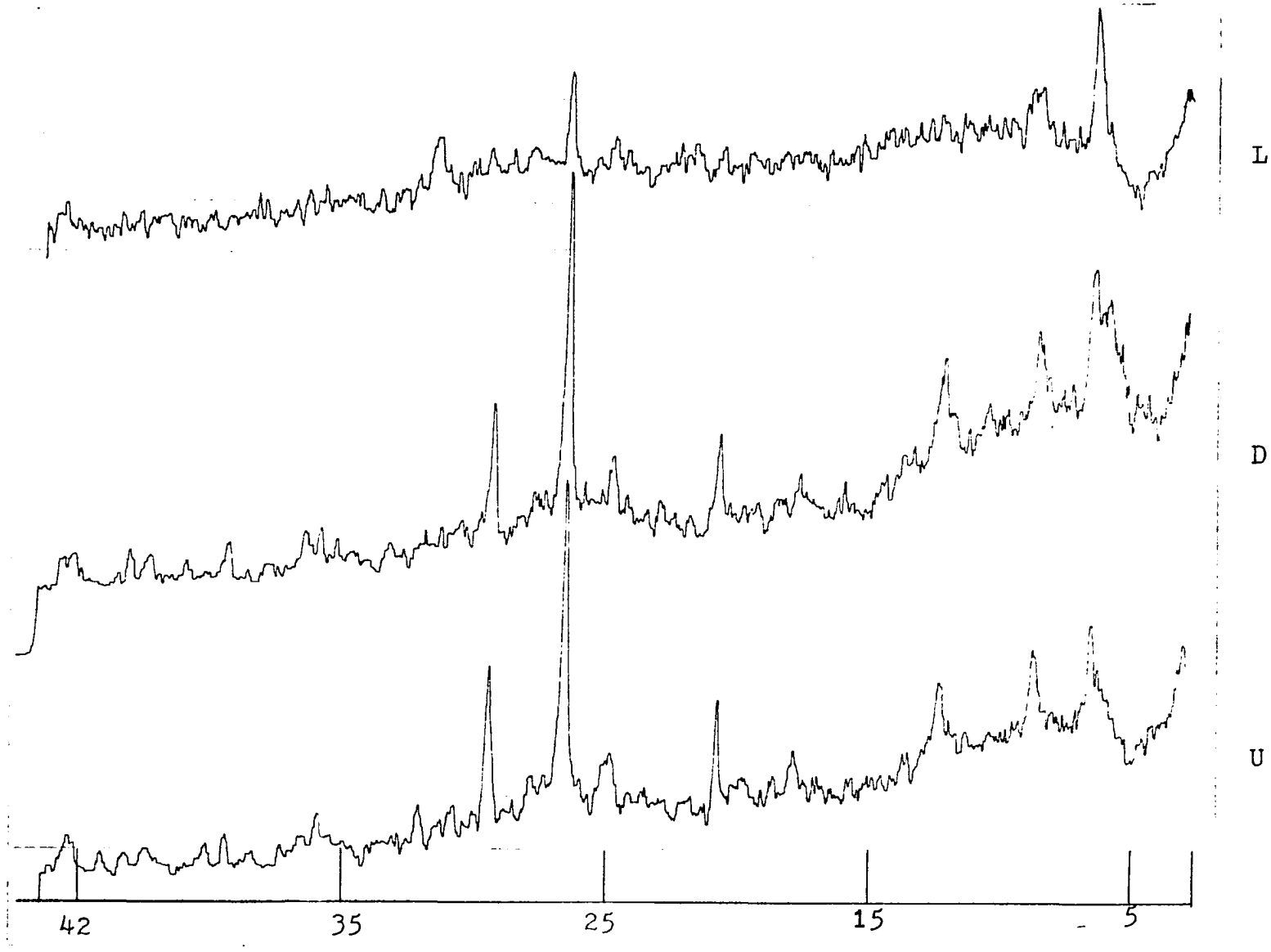


Fig. 11. X-ray diffraction patterns from ground water mud soil slides. L: Landfill ground water mud soil. D: Downstream ground water mud soil; U: Upstream ground water mud soil.

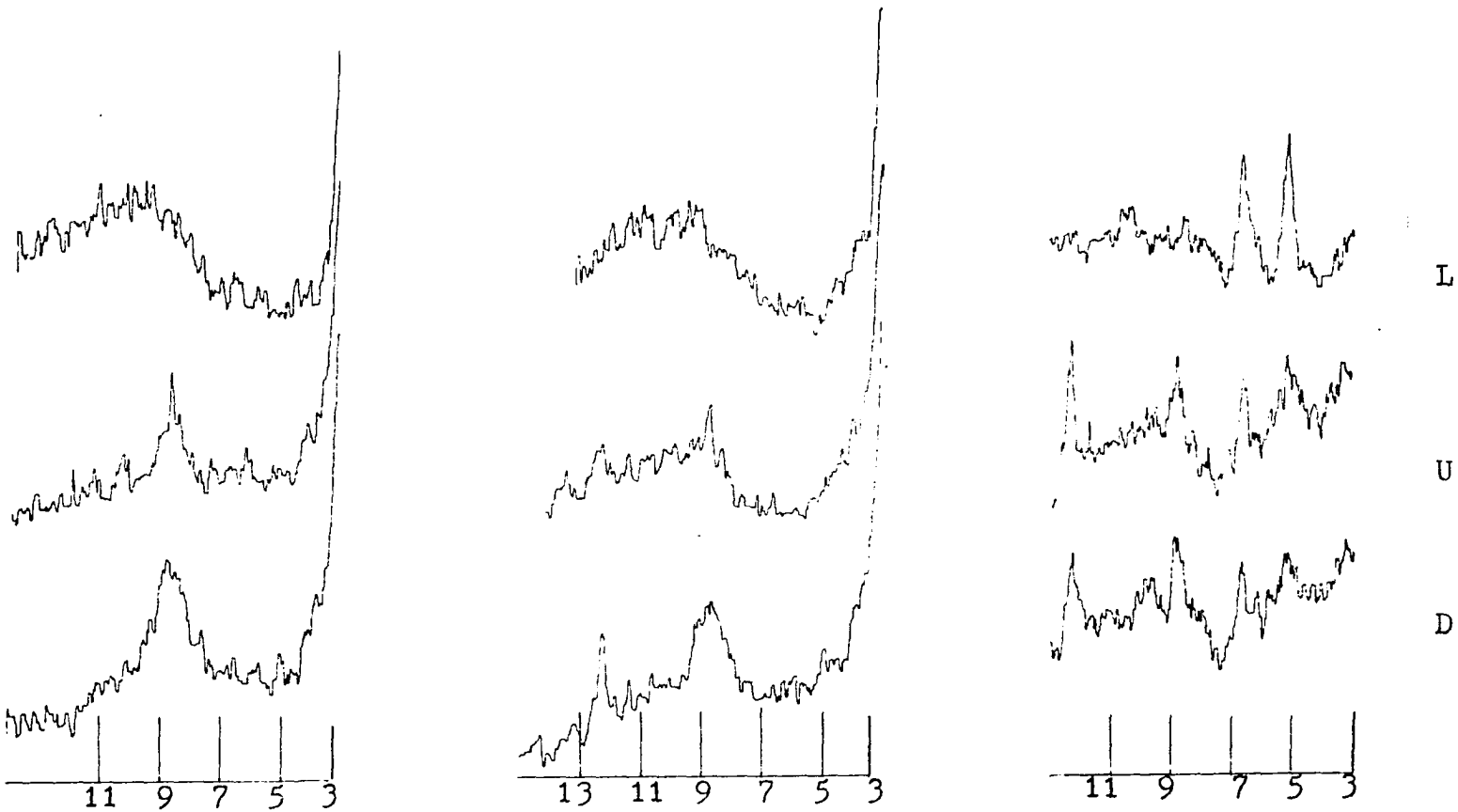


Fig. 12. X-ray diffraction patterns with treatment.
A: with ethylene glycol treatment;
B: heat treatment up to 300° C;
C: heat treatment up to 600° C.

Study on the prevalence of bacteria in the ground water mud

Qualitative tests for the presence of specific types of bacteria were made using nutrient agars and selective media. In order to obtain pure cultures, a series of transfers was made in the appropriate medium followed by plating on agar. Great difficulty was encountered in identifying the different genera accurately. The results obtained were based on a detailed study of a series of morphological and physiological tests. Tables 8, 9 and 10 give the results of this study.

Table 8 shows a number of characteristics which was used to determine the genera. It is obvious that the bacteria colonies obtained from the samples upstream were different from those obtained in the area of the landfill and downstream. White, yellow or orange colonies were cultured from the former samples. The ability to produce yellow or orange pigments, a short gram negative rod, and grow on both water and soil is limited to the genus Flavobacterium. Morphological examination revealed that the white colonies had irregular masses of gram variable spherical cells suggesting that they were probably in the genus Micrococcus. These two genera which were found in the area upstream were aerobic or facultatively anaerobic. Typical species of Flavobacterium and Micrococcus are found prominantly in soil, water and deep wells.[84]

The colonies grown in the samples from the area of the landfill and downstream were circular, flat and opaque. From the morphological

Table 8. Characteristics of bacteria isolated from the ground water mud soil

Characteristics	Upstream mud soil I	Upstream mud soil II	Landfill mud soil	Downstream mud soil	Pure culture *
Shape	rod, singly round end.	cocus irregular mass.	rod, straight with round end singly, in pairs short chain.	rod, singly or in pairs	rod, singly or in pairs
Spore	-	-	+	+	+
Agar Slant	yellow, smooth glistening	white	white opaque	white opaque	white opaque
Agar colonies	yellow circular convex	circular smooth, raised center	circular flat opaque	circular flat opaque	circular moist, raised opaque
Gram reaction	-	- or +	+	+	+
Gelatin colonies	yellow liquefied slowly	white circular not liquerfied,	liquefaction and blacken	liquefaction and blacken	liquefaction and blacken
Gelatin slant	yellow surface growth	white surface growth	liquefied	liquefied	liquefied
Litmus milk	unchanged	unchanged	acid and early coagulation	acid and early coagulation	acid coagulation
oxygen requirement	aerobic and facultative anaerobic	aerobic and facultative anaerobic	strict anaerobic	strict anaerobic	strict anaerobic
Genus	Flavobacterium	Micrococcus	Clostridium	Clostridium	Clostridium perfringens

* : Pure culture obtained from Department of Microbiology, University of Oklahoma.

and physiological examination and comparison with a pure culture Clostridium perfringens obtained from the Department of Microbiology, the colonies were proved to be Clostridium species. This genus is anaerobic or microaerophilic, can ferment carbohydrates to produce various acids and gas, and is widely distributed in nature and commonly found in soil.[85]

Investigation of the specific types of bacteria was made using selective media. The results indicated that Beggiatoa and Thiobacillus species were not isolated from any of the mud samples. By periodically examining the Bacto-sulfate API broth tubes for blackening for 40 days, it was determined that the genus Desulfovibrio was present in all the tested samples. Enumeration by the most probable number technique in liquid media, showed that approximately 160,000 sulfate reducers per 100 ml were present in the bottom mud of the landfill ground water, and about 80 per 100 ml sulfate reducers were distributed in the muds of both the upstream and downstream areas(Table 9).

Members of the genus Desulfovibrio are slightly curved rods of of variable length and usually occur singly but sometimes in short chains, have a polar flagellum and can move actively. These bacteria can only exist under strict anaerobic conditions and can reduce sulfate to hydrogen sulfide. They are found in sea water, marine mud, fresh water and soil.[86]

Innoculation of a pure culture of Clostridium perfringens into the ground water environment was investigated. A culture of

Table 9. The Most Probable Number of Sulfate-reducing Bacteria in the column leachate and in the ground water muds

Sample	Dilution				MPN index population bacteria/100 ml
	1.0 ml	10^{-1}ml	10^{-2}ml	10^{-3}ml	
Column leachate	1/5	0/5	0/5	0/5	20
Landfill ground water mud soil	5/5	5/5	5/5	3/5	160,000
Downstream ground water mud soil	3/5	0/5	0/5	0/5	80
Upstream ground water mud soil	3/5	0/5	0/5	0/5	80

Clostridium perfringens, grown in nutrient agar, was innoculated into sterilized ground water with mud from the landfill, upstream and downstream wells and incubated at 20-22° C under anaerobic conditions. Viable plate counts were made each four-day period. It was observed that the viable population for the bacteria which was tested in all samples including the control, apparently increased after the first four days. This increase reflected a fairly rapid acclimation to the new substrates and environment. During the next eight days, a significant increase of viable population was observed in the landfill samples. A large decrease in the viable population occurred in all three muds after 16 days incubation indicating the cells were in the log death phase due to either depletion of substrate or accumulation of toxic products.

In these growth experiments, attempts were made to simulate the natural environment in the laboratory but problems still existed. For example, the organisms that happened to grow under confined laboratory conditions were not necessarily those found to be active under the natural conditions in the bottom mud and vice-versa. Thus the plate counts indicate that the natural population was capable of growing at a rapid rate for only a few days under the imposed laboratory conditions. Clostridium perfringens and other anaerobes undoubtly grow very well under the more nearly steady state conditions found in the ground water mud of the landfill.

Table 10. Innoculation of Clostridium perfringens into the sterilized ground water with muds

Sample	Innoculated bacteria/ml	4-day growth bacteria/ml	8-day growth bacteria/ml	12-day growth bacteria/ml	16-day growth bacteria/ml	20-day growth bacteria/ml
Landfill ground water with mud	26,700	44,000	114,000	423,000	166,000	137,000
Downstream ground water with mud	26,700	57,000	86,000	396,000	160,000	65,000
Upstream ground water with mud	26,700	74,000	85,000	389,000	169,000	90,000

Study of sulfur distribution and transformation

The analytical data for the various sulfur components in the laboratory column leachate and in the ground water is given in Table 11. The high concentration of sulfate in the column leachate reflected the high percentage of biodegradation of plant and animal proteins. These sulfur-bearing organic proteins were broken down by the bacteria activity and consumed in the metabolism of bacteria, thus the sulfur transformed into a different chemical set-up. In the presence of oxygen, the sulfur could be oxidized into sulfate, and the principal forms of sulfur in the column leachate was this dissolved sulfate. The supply of air for oxidation of sulfur in the column, partially existed when this simulated landfill was built and partially came from the filtration of air into the upper part of the olumn. Aerobic decomposition occurred in this portion causing the transformation of organic sulfur to sulfate and its accumulation in the bottom of the column. In the lower part of the column, oxygen was exhausted and consequently developed anaerobic conditions which led to the growth and development of the facultative and strict anaerobes. These bacteria putrefied the waste and produced the hydrogen sulfide. The gaseous hydrogen sulfide diffused into the pores of the column and the rest dissolved in the leachate and reacted with metallic compounds. The low concentration of dissolved sulfide and small quantities of sulfate-reducing bacteria in the column leachate indicated that the column environment had

Table 11. Distribution of various forms of sulfur in the column leachate and the ground waters

Sample	sulfate ppm	sulfide ppm
Column leachate	1290	8.5
Landfill ground water	200	0.72
Downstream ground water	8	0.16
Upstream ground water	15.5	0.15

not attained anaerobic conditions in the entire column.

In the ground water, there was a considerable amount of sulfate existing naturally, and the sources of this compounds might be from the soil which precipitated from the air or decomposed from organic matter, and the minerals such as gypsum. The relatively high concentration of dissolved sulfate in the landfill ground water, which was in excess of that in the upstream and downstream ground water indicated that decomposed products containing large qualtities of sulfate were leaching into ground water beneath the landfill.

The low concentrations of dissolved sulfide were found in these ground waters. Most of dissolved sulfide were diffused from the mud surface where the sulfate-reducing process occurred. This transformation of inorganic sulfur compounds was intimately connected with the enzyme metabolism of the dissimilatory sulfate reducers and Mg^{++} catalyzed this enzyme activity.[87]

The sulfur found in the bottom muds of the area studied was made up of organic sulfur, elemental sulfur, sulfate sulfur and sulfide sulfur. Table 12 revealed that sulfide sulfur was the dominant form present in the bottom mud of the entire area.

The extremely high concentration of sulfide sulfur found in the landfill mud sample was probably associated with the large amounts of sulfate-reducing bacteria(Table 9) within the landfill. These bacteria used sulfate as terminal electron acceptor for their respiration and produced great quantities of hydrogen sulfide.[88]

Table 12. Distribution of various forms of sulfur in the mud soils of ground waters

Sample	Sulfate sulfur ppm	Sulfide sulfur ppm	elemental sulfur ppm	organic sulfur ppm
Lardfill mud soil	56	3600	67	115
Downstream mud soil	14	86	30	80
Upstream mud soil	12	160	34	43

It has been demonstrated that the sulfate-sulfide phase of the sulfur cycle is largely dependent on organic matter for its activity[89] thus the sulfate-reducing process probably occurred near the mud surface where the concentration of utilizable organic matter was highest and where there was contact with an essentially large reservoir of sulfate ions in the overlying ground water. Since the organic matter and sulfate ions leached from the refuse stagnated and accumulated in the landfill area, the hydrogen sulfide production would be most rapid and stayed in this mud surface. The analytical data for the concentration of sulfide sulfur and the population of sulfate-reducing bacteria shown in Tables 9 and 12, indicated that the serious pollution occurred in this area.

The great dissimilatory sulfate reduction process took place within the landfill site and most of sulfate was utilized, so the concentration of sulfate downstream was low with a consequent low formation of sulfide sulfur in downstream mud.

The high concentration of elemental sulfur and organic sulfur in the landfill ground water mud could be associated with the deposition of organic matter. The mineralization of this sulfur-bearing organic matter contributed to a part of the sulfur build up in this bottom mud.

Organic sulfur downstream which was about twice as large as that in the upstream mud could be brought from the landfill dissolved organic matter to the downstream mud so that the amounts

of sulfate sulfur was somewhat higher than that upstream

It was found that the color of the downstream mud sample was blacker than the upstream mud sample. This color difference might suggest that hydrotroilite, which was an amorphous hydrous sulfide of iron, present in the downstream ground water mud.

The yellow color of the landfill ground water mud indicated the relative absence of ferrous sulfide in the bottom mud. It is assumed that most of the iron which reacted with hydrogen sulfide to generate iron sulfide existed as a chelate complex or formed chemical bonds and inhibited the transformation of hydrogen sulfide to ferrous sulfide such as hydrotroilite or pyrite. That most of sulfide exist as the metallic sulfide such as lead, copper or zinc sulfide in the mud soil.[90]

In general, the transformation of sulfur compounds occurring in these areas are important in basic biological and geological phenomena that are in some cases of great pollution consideration.

Ultraviolet absorption study of ground water

The typical ultraviolet absorption spectra for the ground waters studied are illustrated in Figure 13. The absorption tends to decrease with an increase in wavelength. Within the spectral region from 350-250 μm, the water samples of the landfill show a consistently high absorption. This high absorption could be attributed to the relatively large amounts of dissolved organic matter in the ground water. The absorption in this range was found to decrease in the downstream samples. In upstream ground water, the small quantities of dissolved organic matter which can be attributed to biological degradation caused the low absorption.

A comparison of the spectra below 250 μm for these three water samples showed that the upstream ground water had a great increase in absorbance from 250 μm to 200 μm. It has been found[91] that nitrate and bromide are the only two effective inorganic substances which have an absorbance below 250 μm and the concentration of bromide in the upstream sources was eight times as high as that in both the landfill and downstream samples.

The absorption of the upstream samples in the spectra below 250 μm became lower than the landfill and downstream samples after the water had been stored for three months. It was found that the content of the bromide greatly decreased, from 0.185 mg/l to 0.022 mg/l. during this storage period.

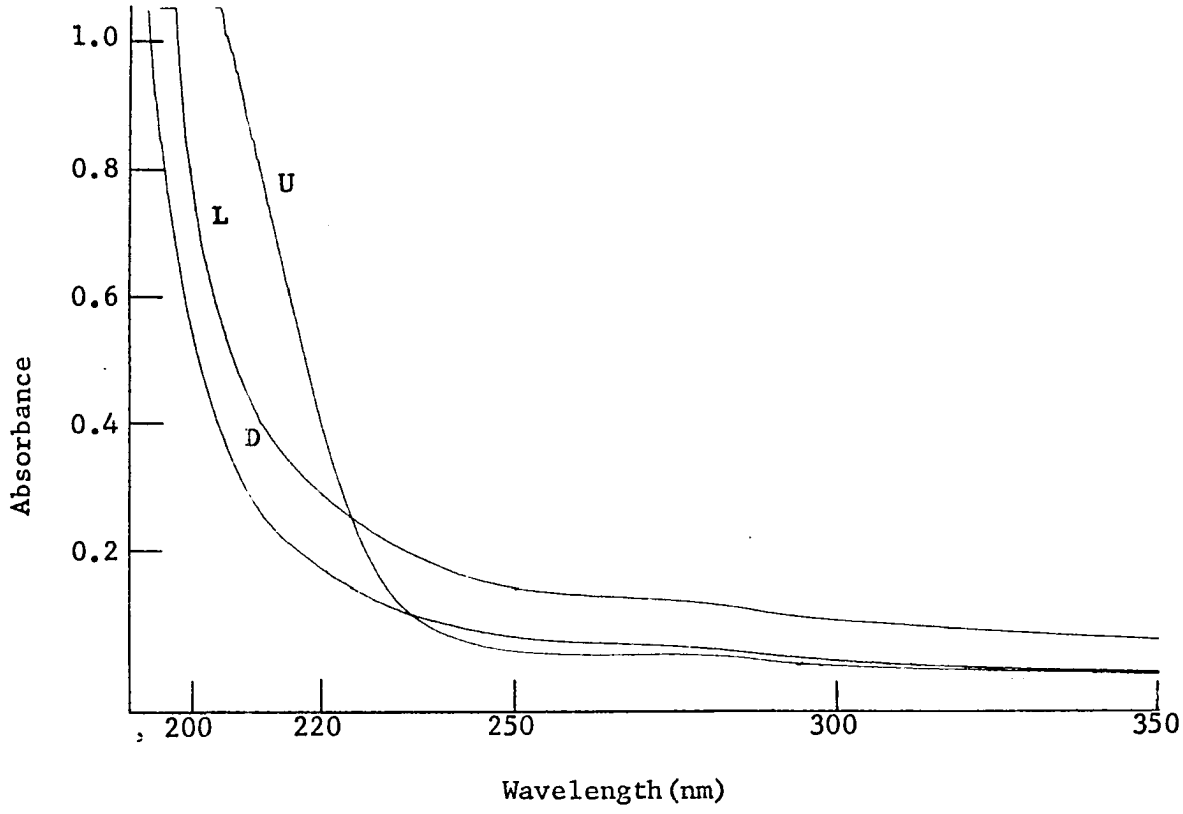


Fig.13. Typical ultra-violet absorption spectra of ground water.
L = landfill ground water; D = downstream ground water;
U = upstream ground water

As shown in Table 13, the pre-treatment by aeration and heating of the ground water caused a change in the absorption. The aerated water increased its absorption in the short wavelengths and decreased in the long wavelengths. This change in the absorption might be explained by the conversion of the organic compounds which contributed toward the high wavelength absorption into inorganic substances. The heated water samples had a decreased absorption with both wavelengths which indicated that both organic and inorganic substances were evaporated by the high temperature.

The results of the water quality studies are summarized in Table 14. The high ratio of E_{250}/E_{220} in the landfill ground water indicated a relatively poor quality while the upstream ground water with its low ratio exhibited an organically clean quality. The water treated had a lower ratio than the fresh water. The ground water which was stored three months had the lowest ratio.

Table 13. Ultraviolet absorption for fresh and pretreated ground water

Sample	Absorbance (um)							
	210	220	230	240	250	270	300	350
Fresh ground water	0.410	0.285	0.225	0.168	0.141	0.125	0.091	0.062
Aerated ground water	0.540	0.341	0.219	0.155	0.130	0.115	0.075	0.036
Heated ground water	0.339	0.224	0.160	0.125	0.105	0.092	0.061	0.002

Table 14. Index of ground water quality

Sample	E_{250}/E_{220}			
	fresh	aerated	heated	stored
Landfill ground water	0.494	0.381	0.468	0.149
Downstream ground water	0.382	0.381	0.407	0.148
Upstream ground water	0.110	0.093	0.083	0.014

Study of bitumen, humic acids and hydrocarbons from the bottom mud of the ground water

A small quantity of bitumen was extracted from each of the mud samples. The concentration of the bitumen in the samples studied ranged from 16 to 62 parts per 100,000 grams of dried mud. The bitumen extracted from the bottom mud of the landfill ground water contained 12.83% of the total organic matter while the downstream mud contained 7.83%, and the upstream mud, 7.50%.

Bitumen consists of the total organic solvent extractable organic compounds,and chromatography was conducted to separate these compounds into single components. All chromatographic data is shown in Table 15. The data was presented as a percentage of bitmen recovered from the silica gel. Most of the hydrocarbons were found in the bottom mud from upstream and downstream. While in the landfill mud, large amounts of long chain asphaltic compounds were obtained with only small amounts of hydrocarbons.

Studies of the column leachate showed that the proportion of the n-heptane, benzene, and methanol fractions of the landfill bottom mud were very similar to those of the leachate sample(Fig.14). Both samples contained high contents of asphaltic compounds(methanol fraction) with a small percentage of hydrocarbons. The heptane and benzene fractions which contained the low molecular weight aliphatic and aromatic hydrocarbons comprised approximately 55% of the chromatographic fraction of bitumen in both upstream and downstream bottom mud. These data suggest that the hydrocarbons

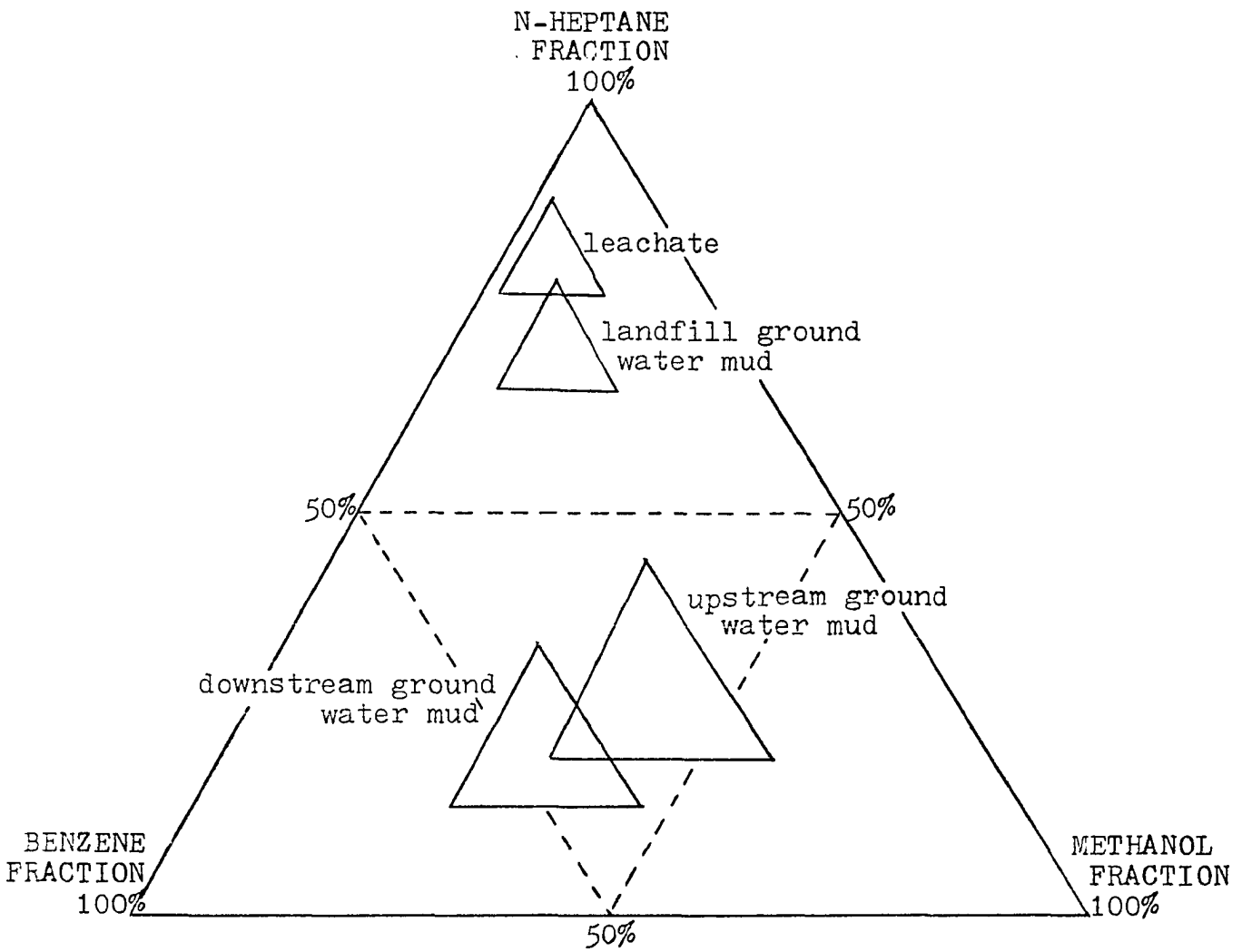


Fig. 14. The proportions of chromatographic fractions of the column leachate and three different ground water mud soils

Table 15. Extraction of bitumen, humic acids and hydrocarbons from the bottom muds of ground waters

Sample	bitumen % in soil	ratio of bitumen/O.M. in soil	humic acid % in soil after bitumen extraction	chromatographic analyses of bitumen		
				n-heptane fraction	benzene fraction	methanol fraction
Landfill mud soil	0.620	12.83	0.049	17.23	6.42	65.87
Downstream mud soil	0.018	7.53	0.150	30.46	24.72	13.18
Upstream mud soil	0.016	7.50	0.173	21.11	32.91	20.49

found in these areas were indigenous hydrocarbons derived from the organisms in the ground water mud soils.

The characteristic infra-red absorption bands arising from various type of organic compounds are presented in Fig.15 , 16 and 17. The spectra of the n-heptane fraction have similar patterns for all three of the different samples. All the samples have common peaks at 2960 cm^{-1}, 2920 cm^{-1} and 2850 cm^{-1} which are characteristic of aliphatic C-H groups. A peak at 1460 cm^{-1} is characteristic

of aliphatic C-H groups. A peak at 1460 cm^{-1} is characteristic of CH_2/CH_3 deformation. A peak at 1360 cm^{-1} is characteristic of both the COO^- and aliphatic C-H groups. A peak at 1100 cm^{-1} is characteristic of C-O stretching(polysacharide, cellulose) and a peak at 710 cm^{-1} is characteristic of CH deformation(hetro-cyclic aromatic compounds).[92]
samples, the intensity of the peaks at 1730 cm^{-1}, 1370 cm^{-1} and 1240 cm^{-1} of all functional groups was reduced in the landfill samples whereas the broad peak at 3420 cm^{-1} became more pronounced.

The absorption pattern in the methanol fraction for the three different samples produced similar absorption bands. The strongest band was evident in the region of 3400 cm^{-1} suggesting the presence of hydrogen banded O-H groups. The appearence of a new band at 1620 cm^{-1} indicated an alkene structure was present in the landfill sample.

The infra-red spectra study showed that the n-heptane and



Fig. 15. Infra-red spectra of n-heptane chromatographic fractions from the column leachate and ground water mud. Lt: Column leachate; L: Landfill mud D: Downstream mud; U: upstream mud.

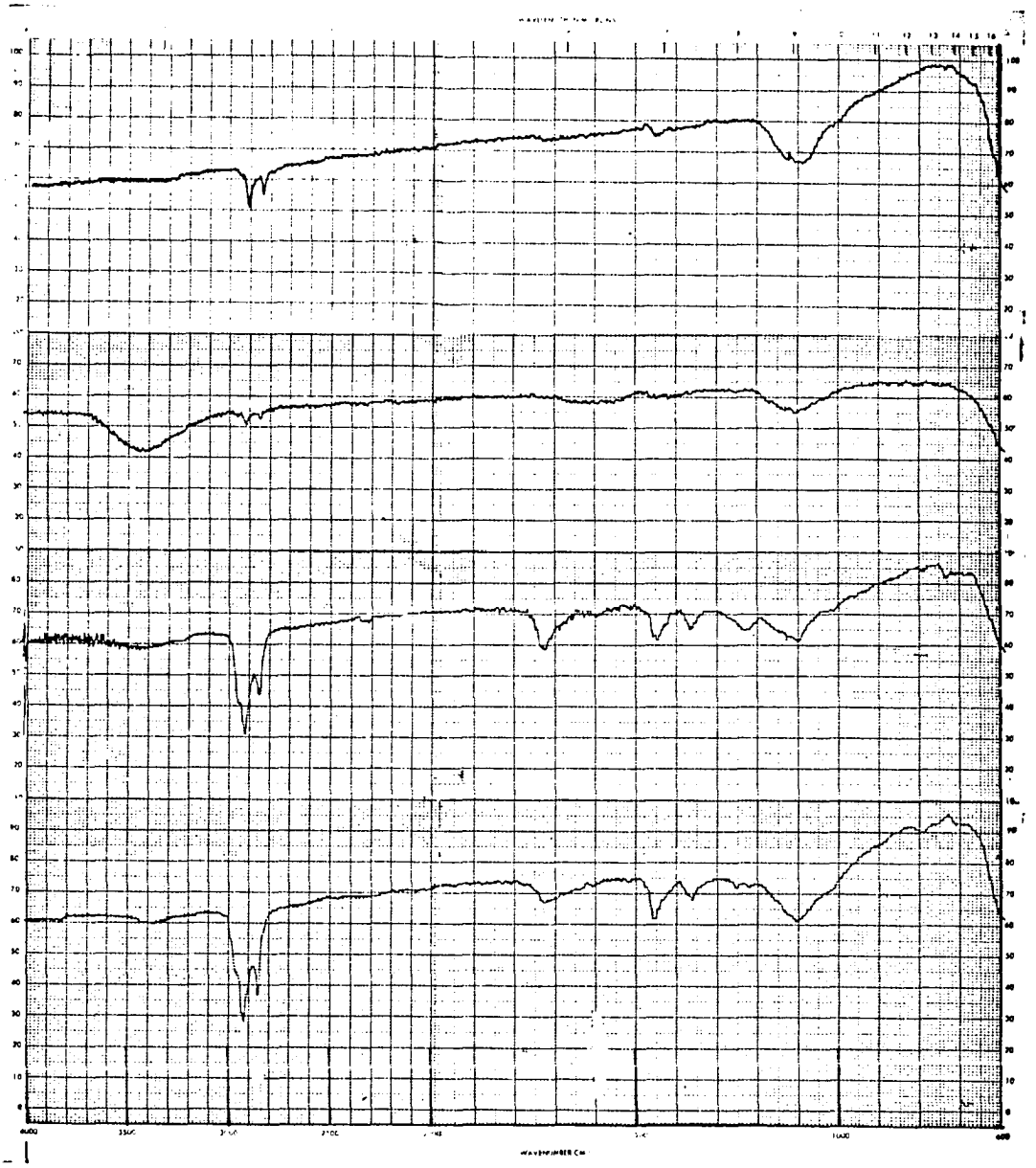


Fig 16. Infra-red spectra of benzene chromatographic fractions from the column leachate and ground water muds.

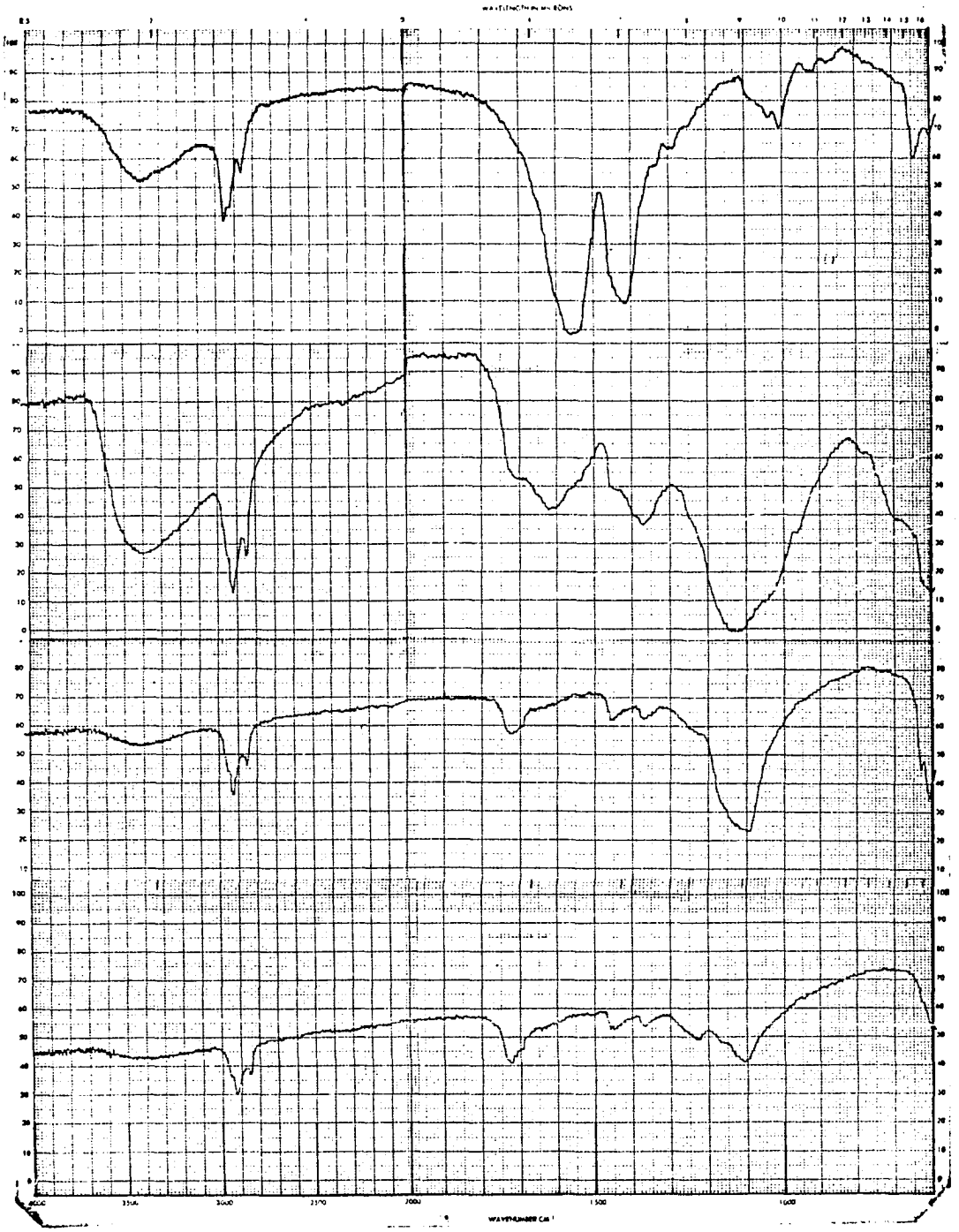


Fig. 17. Infra-red spectra of methanol chromatographic fractions from the column leachate and ground water muds.

methanol fractions of the chromatographic separation in the leachate have different absorption patterns from those of the ground water muds. These different patterns might indicate a complex mixture of organic compounds in the leachate unlike that found in the ground water mud extracts.

NMR spectrometer analyses were also carried out to provide additional information concerning the nature of the functional groups present in the compounds. The absorption spectra of all fractions extracted from the leachate sample and the ground water mud are present in Fig. 18, and the chemical shift of the peaks at different regions are shown in Tables 16 and 17.

In the heptane fraction of the upstream and downstream extracted samples, two single peaks at δ 0.9 and δ 1.3, with TMS(tetramethylsidane) as reference, were observed. The chemical shift of the peaks at these regions were considered to be alkane groups of saturated acyclic hydrocarbons.[92] Double peaks at δ 1.1 and δ 1.3 which were only found in the landfill sample, might be caused by $CH\text{-}CH_3$ while a strong peak at δ 4.6 is caused by olefinic structure. New peaks at δ 1.5 and δ 2.19 appeared in leachate sample indicating the presence of R_3CH and RCOCH groups. The proton position in the methanol fraction, shown in Table 18 and Fig. 14, has a common peak at δ 1.3. The additional peaks at δ 1.7($C\text{-}CH_3$), δ 2.19(RCOCH), δ 4.6 and δ 4.8(C=CH) were observed in the leachate sample. The study of the characteristic chemical shifts of tne proton position

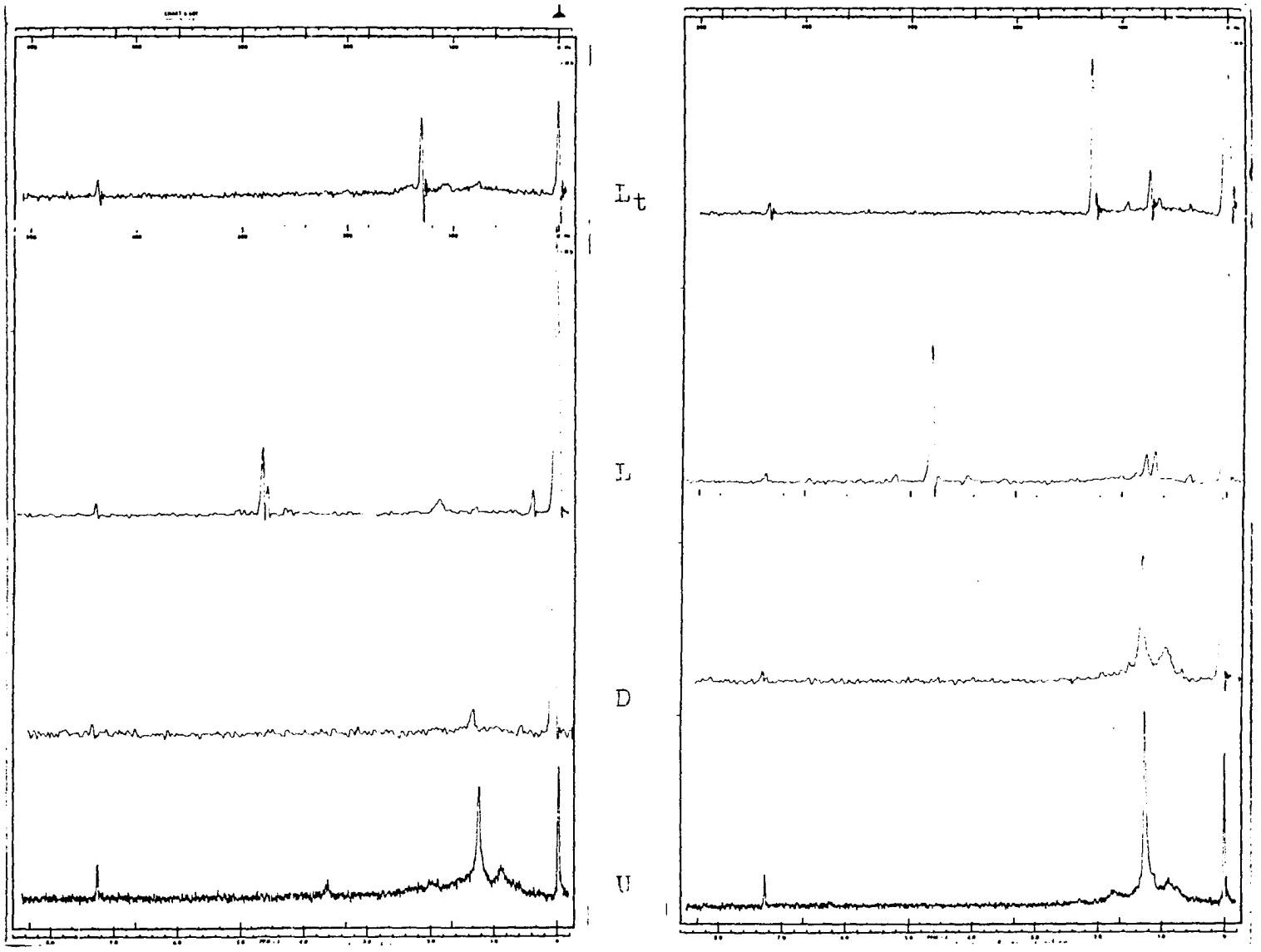


Fig. 18. NMR spectra of chromatographic fractions from the column leachate and ground water muds.

Table 16. NMR spectrograms of the n-heptane chromatographic fraction of column leachate and ground water mud soil.

Sample	Chemical shift ppm					
	0.9	1.1	1.3	1.5	2.19	4.6
Column leachate	X	X	0	0	0	X
Landfill mud	X	0	0	X	X	X
Downstream mud	0	X	0	X	X	X
Upstream mud	X	X	0	X	X	0
	RCH		R_2CH_2	R_3CH	RCOCH	C=CH

Table 17. NMR spectrograms of the methanol chromatographic fractions of column leachate and ground water mud soils.

Sample	Chemical shift ppm								
	0.4	0.9	1.3	1.7	1.8	2.19	3.4	4.6	4.8
Column leachate	X	X	0	0	X	0	X	0	0
Landfill mud	0	X	0	X	0	X	X	X	X
Downstream mud	X	X	0	X	X	X	X	X	X
Upstream mud	X	0	0	X	X	X	0	X	X
	Cyclo propane	RCH_3	R_2CH_2	$C{=}CCH_3$	$C{=}CH_3$	RCOCH	OCH	C=CH	C=CH

in the ground water mud and in the leachate revealed a significant difference in the structures of organic molecules present.[93]

Humic acid was obtained from the bitumen extracted residue of the bottom mud soil. The percentage by weight of humic acid in the landfill sample averaged 0.049% of the extracted residue of the air-dried mud, while in the downstream sample, it was 0.15% and in upstream sample, 0.17%. Thus, it seems that the high content of humic acid was associated with the high concentration of aromatic hydrocarbons.

Infra-red spectra of the humic acid showed a marked difference from the spectra of all fractions of the bitumen(Fig. 19). The distinct bands were at 1620 cm^{-1}, 865 cm^{-1} and 840 cm^{-1} indicating predominantly aromatic structures of humic acid residues.[94]

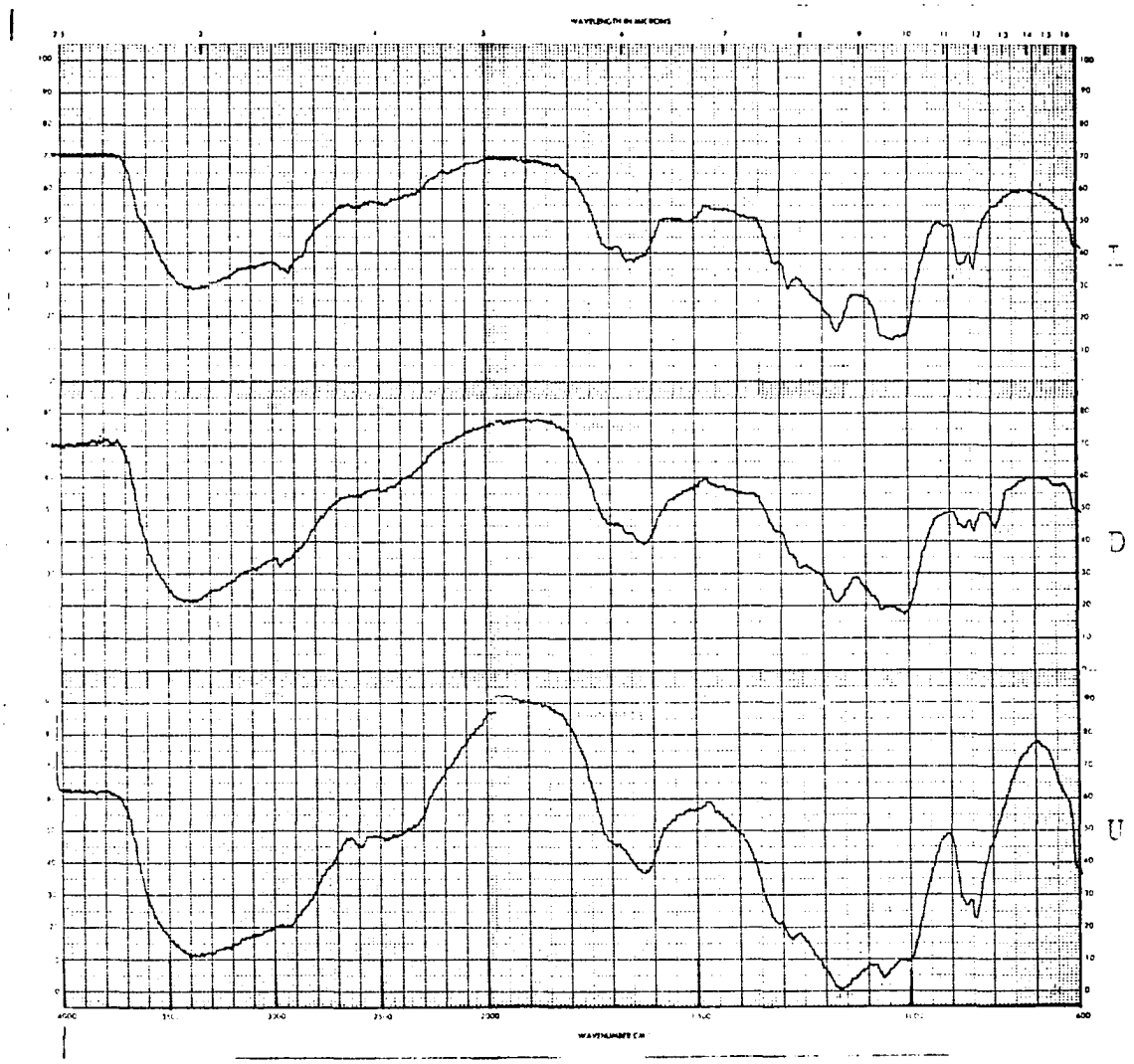


Fig. 19. Infra-red spectra of humic acids extracted from the mud soils of ground water.

V SUMMARY AND CONCLUSION

A study of the laboratory column leachate, ground water and mud soil with emphasis on chemical, bacteriological and mineralogical aspects was conducted in order to become acqainted with the numerous problems associated with ground water pollution from the disposal of solid waste. The investigation of leaching behaviour was carried out using a laboratory leaching column. The ground water studies were from the area of the Norman sanitary landfill where three sampling wells were selected. One well was approximately 0.7 miles upstream from the landfill, one underlying the landfill and the third was one mile downstream from the landfill.

The study of ground water quality showed that contamination was occurring under the Norman sanitary landfill. The components of alkalinity, chromium, nitrate, silica, carbon dioxide, orthophosphate, meta-phosphate and total hardness increased one to two times in concentration as the ground water passed through the fill. The components of BOD, COD, copper, total iron, tannin and lignin increased three to six times in concentration in the fill well. The components of ammonia nitrogen, chloride, ferrous iron, manganese, phenol and sulfate increased more than ten times in concentration as the ground water enters the landfill. All of the above contributed to the contamination of the ground water.

Investigation of the chemical parameters in ground water showed that chloride was the best indicator of inorganic parameter and phenol was the best indicator of organic parameters.

The second experiment using a laboratory column showed that the leachate contained large amounts of organic and inorganic components which was capable of polluting ground water. An estimation of the contribution of leachate materials to ground water showed that the most significant leaching parameters on ground water quality were the following constituents in decreasing order:

$$\text{chloride} > \text{alkalinity} > \begin{matrix}\text{total}\\ \text{dissolved}\\ \text{solids}\end{matrix} > \begin{matrix}\text{total}\\ \text{hardness}\end{matrix} > \text{sulfate}$$

The ultraviolet absorption technique was conducted to study the feasibility of an indicator test of ground water quality. A consistently high absorption in the spectra regions of 350-250 um was found in the landfill ground water. This could be attributed to the large amounts of dissolved organic matter in the ground water. The relatively low absorption in downstream ground water exhibited a marked decrease in the content of dissolved organic matter by the mechanism of dilution, soil adsorption and anaerobic stabilization.

The ratio of E_{250}/E_{220} was indicative of the index of water quality. However, this technique needs further development in order to understand the ultraviolet absorption characteristics of ground

water associated with organic matter and the estimation of organic pollution.

The study of the sulfur cycle showed that the organic sulfur-bearing proteins were broken down and transformed into inorganic sulfur compounds. The principal form of sulfur in the column leachate and in the ground water was dissolved sulfate. The sulfate-reducing bacteria utilized this sulfate to produce hydrogen sulfide and accumulated in the mud surface. The extremely high concentration of sulfide sulfur in the mud soil and the great population of sulfate-reducing bacteria indicated that serious pollution was present in the landfill area.

The ecosystem studies indicated that the cation-exchange capacities in the bottom mud of the ground water were quite high, ranging from 63 to 123 meq/100g. The organic matter level and the extractable iron content which were higher in the landfill mud than other muds suggested that the deposition of organic matter associated with iron was occurring at this site.

The relatively high level of phosphorus and nitrogen in the downstream mud were presumably due to the heavy fertilization.

Clay minerals found in the landfill bottom mud were montmorillonite, vermiculite and illite. Kaolinite was not found to exist in this area. Dolomite found in the landfill mud was a carbonate mineral which has the ability to hold copper and manganese. It was suggested that the high concentration of manganese enhanced the transformation of calcite into dolomite.

Clay minerals found in the upstream and downstream muds were quite similar. Involved were montmorillonite, vermiculite, illite and kaolinite. Calcite, found at these sites, was a carbonate mineral and provided carbonate content to these areas.

Flavobacterium and Micrococcus were isolated from the upstream ground water mud, and Clostridium from both landfill and downstream muds. Beggiatoa and Thiobacillus were not detected in the area studied.

Desulfovibrio, sulfate-reducing bacteria, existed in both the columr. leachate and the ground water muds. Large amounts of organic matter and sulfate leached from the refuse into the landfill ground water enhanced the growth of this bacteria and stimulated its activity to produce hydrogen sulfide.

The investigations of hydrocarbons showed that most of the aliphatic and aromatic hydrocarbons were found in the bottom muds from upstream and downstream. These compounds were predominantly derived from biological degradation by the organisms in the ground water, while in the landfill bottom mud, large amounts of asphaltic compounds with a small percentage of aliphatic and aromatic hydrocarbons were obtained. Studies of the column leachate showed that the proportion of n-heptane, benzene and methanol fractions were very similar to those of the landfill, and suggested that the long chain asphaltic compounds in the landfill ground water mud came from the deposition, migration and diffusion of the landfill leachate.

Humic acid is the most stable constituent of the organic matter. Studies of humic acid from the bitumen extracted residues of the ground water muds showed that the high content of humic acid was associated with the high concentration of aromatic hydrocarbons.

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