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HYDROGEOCHEMICAL STUDIES AT A LANDFILL IN DELAWARE

by

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Introduction

The movement of contaminated ground water from waste disposal sites has become a major problem in many parts of the world. Disposal of liquid and solid wastes in landfills creates an environment where organic and inorganic compounds present in the waste or those generated in the landfill are subject to movement in the hydrologic regime. The problems are more pronounced in humid and temperate climates because infiltration of rainfall is high to moderate and it is difficult if not impossible to isolate waste disposal sites from the underlying aquifers for long periods of time. In these areas landfills become anaerobic and organic materials decay largely through fermentation process, thus creating many intermediate organic compounds that affect the ground-water chemistry differently than those originally buried.

The degree to which leachate should be contained, removed and treated, or allowed to move at a controlled rate through natural materials is a basic question that must be considered in making management decisions. In addition to understanding the hydrogeology of an area, and the physical processes, such as dilution, dispersion, and filtration, an understanding of the biological and geochemical processes is necessary to describe and predict the movement of contaminants. The principal chemical reactions and processes that occur in the ground water at disposal sites include biological decay, precipitation and dissolution of minerals and other inorganic compounds, sorption of chemical constituents, leaching of sediments, ion exchange, generation and diffusion of gases, and movement of dissolved species.

The purposes of this paper are to review a ground-water contamination problem at a landfill; examine and interpret hydrologic and data available from 1973 to 1981; describe the hydrogeologic processes and chemical reactions that have affected the ground-water chemistry; and discuss the results in terms of long-range planning and management of contaminated aquifers. The landfill studied is the Army Creek landfill, previously known as the Llangollen landfill, in New Castle County, Delaware. Complete chemical analyses for water sampled from the landfill, from immediately downgradient, and from supply well fields within a mile of the landfill have been published earlier (Baedecker and Back, 1979a). Considerable data have been collected by New Castle County and the State of Delaware since 1972 (unpublished files).

The chemical constituents discussed here in detail are Cl, because it is considered a conservative parameter, and pH, oxygen, alkalinity, NH_4, NO_3, Fe, Mn, CH_4, organic carbon, and volatile organics, because these species are sensitive to oxidation-reduction reactions. The mixing of native ground water that is highly oxygenated and leachate that is anaerobic has a significant impact on the water chemistry. Variations in concentrations of chemical species downgradient of the landfill are controlled by changes in leachate composition, changes in the flow path of the leachate, physical attenuation processes, and chemical reactions.

Statement of Problem

The Army Creek landfill, New Castle County, Delaware, covers about 24 hectares and contains more than one and a half million cubic meters of refuse. The refuse was deposited during 1960-1968 in an abandoned quarry from which 6 to 9 meters of sand and gravel had been removed. The excavation continued until either the water table or a red clay zone was encountered. Many types of waste were accepted including solid and liquid industrial wastes and municipal refuse. During the 1960's major well fields were developed in a confined aquifer 900 to 1,200 meters south and east of the landfill. Pumpage from the well fields lowered water levels and increased the downward movement of water from the landfill to the aquifer.

In 1970 the landfill received a final cover of sandy material and the property was purchased by the county for a park. Two years later a water quality problem was detected in a nearby domestic well. It has been concluded that the absence of or the removal of the red clay layer in places permitted leachate to migrate into the underlying aquifer (Apgar, 1974). The leachate, highly contaminated in both organic and inorganic compounds, was not adequately diluted or purified by filtration before it entered the aquifer. By 1972 it was confirmed that leachate had spread extensively through the confined aquifer and was moving south toward major supply wells.

Description of Site

The Army Creek landfill lies in the Atlantic Coastal Plain. It is partially unsaturated and partially below the water table. The surficial sands of Pleistocene age (Jordan, 1970), Columbia Formation, are not thick enough in the immediate area to be developed for supply purposes. Underlying the Columbia Formation sand is the Cretaceous Potomac Formation which overlies Precambrian rocks. The Potomac Formation consists of silt and clay interbedded with quartz sand and some gravel (Pickett, 1970). The upper sand of the Potomac Formation thickens to the southeast and forms one of the most productive confined aquifers in the state (Figure 2). The major well fields developed in the Potomac sand south and east of the landfill are capable of producing 25 x 10^3 m^3/day of water. Pumpage from the well fields lowered water levels and increased the rate of water movement through the aquifer and increased the downward movement of water from the landfill to the Potomac sand.

To limit the spread of contaminants after the problem was recognized, a coordinated effort was undertaken to reduce pumping rates from supply wells and to initiate a program of recovery well pumping between the landfill and the supply wells (Figure 2). Pumping of the contaminant recovery wells caused a local cone of depression which reduced contaminant movement toward the supply wells. The recovery well program was begun in 1973 and expanded in 1974 to the 10 wells which operate today, although not all recovery wells have been operating continuously. The recovery wells discharge into Army Creek which flows into the Delaware River.

The direction of ground-water flow in the Potomac aquifer has been altered significantly over the past several decades. Elevation of the potentiometric surface in the 1950's before significant development of the aquifer was about 6 meters above sea level and the flow direction was toward Delaware Bay to the southeast. In the 1960's after well fields were developed for public water supply and industrial use the direction of ground-water flow was to the south and east (Figure 3a) The supply wells produce water from the confined Potomac sand aquifer from depths of 45 to 60 meters. After the recovery well system was in operation the flow direction of leachate was reversed locally away from the supply wells (Figure 3b). Most of the recovery wells are screened over 12 to 25 meter intervals and are completed 25 to 43 meters below land surface. The flow pattern indicates that water upgradient from the landfill moves through and beneath the landfill where it encounters leachate and is then discharged in part by the recovery wells downgradient from the landfill. Part of the discharge from the recovery wells is also native ground water from south and east of the landfill.

Continued pumping for water supply purposes has permitted contaminants to move south of the recovery well system (Figure 3c). Also, closing of the recovery wells periodically for maintenance allows the contaminant plume to spread. Hydrologic and chemical data indicate that leachate does not migrate at a continuous rate from the landfill, but rather moves in pulses. The amount of leachate generated at any one site depends on the amount of recharge to the landfill. It is estimated that 70% of the landfill leachate originates as infiltrating percolation on the site and the remaining 30% results from lateral inflow where the refuse is below the water table. These estimates are based on an evaluation of aquifer transmissivity, measurements of the hydraulic gradient in the aquifer adjacent to the landfill and, estimates of rainfall entering the landfill. During periods of low precipitation, the water table declines and less leachate is generated. Another factor that affects the rate of leachate movement in the aquifer is variation in the rate of pumpage from wells. Greater withdrawal rates reduce water levels and create greater vertical hydraulic gradients from the landfill to the underlying aquifer. The steeper gradients result in more leachate movement into the aquifer and more rapid movement towards the wells.

In 1980, the Amoco chemical plant closed and its well field located 900 meters southeast of the landfill was shut down a year later. Since then and to the present (1982), the direction of ground-water flow is southward (Figure 3d).

Three major well fields, Artesian Water Company, Amoco Chemical Corporation, and the County's contaminant recovery system (Figure 3) account for all of the pumpage in the area. Total pumpage rates in the immediate vicinity of the landfill have ranged from a high of 20×10^3 m^3/day in 1974 to a low of 12×10^3 m^3/day in 1981 (Figure 4). Amoco's pumpage rate has gradually declined from 5.3×10^3 m^3/day in 1971 to 0.8×10^3 m^3/day in 1981, while Artesian's rate averaged a maximum of 12.5×10^3 m^3/day in 1972 and reached its lowest level of 5.3×10^3 m^3/day in 1976. The contaminant recovery well system was in operation by late 1973 and operated at maximum capacity in 1974 at a withdrawal rate of $9.5 \times 10^3\ m^3$/day. Since then the pumpage rate of the recovery wells has declined to an average of $3.8 \times 10^3\ m^3$/day in 1981 because the wells are operating less efficiently and some have been closed permanently.

The location of the wells and their pumpage rates have influenced the extent of plume migration and concentrations of chemical constituents within the plume as shown by the 50 mg/l isochlor maps for the landfill area (Figure 5). The leachate plume migrated significantly farther downgradient in 1974 than in 1973. The effect of the recovery wells in controlling the leachate plume was observed by 1975 and in 1976 when the extent of plume migration was significantly diminished. However, the plume again extended downgradient in 1977 after the pumpage rate of the recovery well system fell below that of the public water supply wells (Figure 4). Although for the past 5 years the position of the 50 mg/l isochlor has changed little, a delicate balance exists between the location of the plume and the relative pumpage rates of the Artesian Water Company and contaminant recovery well fields.

The distribution of Cl concentration in the major leachate plume south of the landfill showed the most striking change prior to 1977 (Figure 6). From 1973 to 1976 the concentration of Cl at the recovery site 29 (shown in Figure 1) decreased from 380 to 50 mg/l. Farther downgradient at sites 33, 25, and 52 the Cl concentrations also declined during this time period but to a lesser extent. The decline in chloride concentrations was caused largely by operation of the recovery well system, which operated most efficiently from 1974 to 1977. Concentrations of chloride in the water standing in the refuse have declined significantly as a result of leaching and this may in part account for the decline downgradient. In

1977, Cl concentrations increased at all sites and since then have remained relatively constant between 25 and 80 mg/l. Pumpage from Artesian Water Company well fields has exceeded pumpage from the contaminant recovery well system since 1977.

Alternatives to operation of a recovery well system to control the generation and movement of leachate have been considered by County and State officials for returning the aquifer to full use. Leachate production can be halted only by preventing water from entering the landfill or by removing the refuse. Methods which have been evaluated to curtail generation of leachate include covering the landfill with a synthetic surface and isolating the leachate by the installation of a barrier or draining ditches. Unfortunately, these solutions are costly and unlikely to completely eliminate the problem of leachate migration to the aquifer. Removal of the refuse and incinerating it or disposing of it at another site, in addition to being costly, is difficult politically and would be environmentally disruptive. The cost of isolating the existing refuse from contact with water was estimated to be in the same range as the cost of moving the landfill. These estimates ranged from 12 to 16 million dollars in 1977 (Apgar, 1975). Installation and operation of the recovery well system, monitoring ground-water quality, and feasibility studies to date have cost about 4 million dollars. Surface grading and runoff control could be used to limit infiltration, although compaction of the refuse and subsidence of cover material are perpetual problems. The recovery wells are currently being relocated on the landfill which may remove contaminants more efficiently and in the process waste less uncontaminated ground water. The latter remedial measures were estimated at 2 to 3 million dollars in 1977.

GEOCHEMICAL ASPECTS

Sampling Techniques

Water samples were collected on the landfill with a metal bailer from 1973-1976 and by a peristaltic pump from 1976 to 1981. Monitor wells were sampled with a submersible pump (Figure 1). Recovery and supply wells were sampled at spigots while the wells were pumping. Vandalism and the closing of some recovery wells has made it difficult to sample the same wells through the period of study. Wells were pumped or bailed before sampling to remove water standing in the well casing.

Temperature, pH, alkalinity, and dissolved oxygen were measured in the field. A sample was filtered in the field through a 0.45 μ filter for analyses of major anions and cations. Samples for iron and manganese analyses were filtered through a 0.1 μ filter to remove colloidal oxidized species. Analyses of methane and organic compounds were made on unfiltered samples. It proved to be difficult to obtain reproducible dissolved organic carbon data because of the high biological activity in leachate contaminated water. For this study organic samples were either chilled and analyzed immediately or preserved by the addition of $HgCl_2$ or Ag and chilled until analyzed.

Dissolved Oxygen, pH, and Alkalinity

The concentration of dissolved oxygen ranges from 9.0 mg/l (near saturation) in uncontaminated zones to completely anaerobic water in and near the landfill. The native ground water is highly oxygenated, however, water moving through the landfill has all its oxygen removed by respiratory processes. The available oxidizable material in the landfill far exceeds the amount of oxygen in the recharge water. Data from 1977 and 1981 show two major plumes of leachate moving south of the landfill (Figure 7). Between the two reducing plumes, is a more highly oxygenated area which has expanded over the 4 year period. Less contaminated water moves in the aquifer beneath the narrow central portion of the landfill, probably because the refuse source is smaller here. Also, the aquifer may be thinner or less permeable in this area. Water level data indicate that the oxygenated area may be recharged locally, however, the data are not unequivocal. The extent of the anaerobic zone southeast of the landfill has diminished in 1981 as compared to 1977 as a result of the closing of the chemical plant well field in 1980.

Large amounts of oxygen are removed from the native ground water by the oxidation of organic matter and dissolution of metals. In fact, more molecular oxygen is needed in contaminated water to account for the amount of dissolved iron and total inorganic carbon ($CO_3^=$, HCO_3^-, H_2CO_3) in solution than is available in native ground water. Water in the landfill and in the partially confined aquifer immediately downgradient are in contact with atmospheric oxygen which can be utilized for oxidative processes. An additional source of oxygen is from organic matter which is both oxidized and reduced by anaerobic fermentative processes to produce carbon dioxide and reduced organic species, such as methane.

The pH of uncontaminated water in the area is between 5.0 to 5.5 which is typical for a poorly buffered water in clay and sand layers that lack calcareous material and have been extensively weathered. In contrast, water from the anaerobic zone has a pH between 6.5 and 6.9. Within this zone the pH at any one site has changed little from 1977-1981; the average change in pH is 0.09 pH units for five locations for which data are available. The major controls on pH in anaerobic leachate are (1) degradation of organic matter producing large amounts of CO_2, which forms carbonic acid and lowers the pH, (2) production of ammonia and methane and reduction of Fe and Mn, all of which consume hydrogen raising the pH and (3) exchange of hydrogen on clays, which may lower or raise the pH. Downgradient from the anaerobic zone the pH values of contaminated water range from 6.8 to 5.2. Within this transition zone the average change in pH at each site is 0.26 for the same 4 year period. The pH varies more in the transition zone because it reflects the subtleties of mixing of the contaminated water with native ground water.

Alkalinity measurement of water in this pH range is largely a measurement of bicarbonate. Although, at some sites on the landfill, organic acids contribute to the total alkalinity, downgradient this contribution is minimal (Baedecker and Back, 1979a). Alkalinity concentrations reflect oxygen concentrations because the major source of bicarbonate is CO_2 from respiratory processes rather than dissolution of calcareous material. Thus, oxygen is consumed in the landfill and bicarbonate concentrations are high; as oxygen concentrations increase away from the landfill, bicarbonate concentrations decrease. The changes that are observed in concentrations of oxygen and bicarbonate, due to mixing and chemical reactions, are discussed in more detail later.

Uncontaminated oxygenated water (> 6 mg/l O_2) has bicarbonate concentrations of less than 10 mg/l. Most of the total inorganic carbon (CO_3, HCO_3, and H_2CO_3) is in the form of carbonic acid (including aqueous CO_2) as reflected in the low pH of the water. Transitional or partially oxygenated water (0.3 to 6.0 mg/l O_2) has bicarbonate concentrations between 12 and 75 mg/l, whereas anoxic water has bicarbonate concentrations of > 100 mg/l. With a few exceptions alkalinity concentrations changed little from 1977 to 1981. The largest change was a decrease in alkalinity at site S-1 on the landfill, a site which has consistently produced the most concentrated leachate. Previous results showed that a large portion of the alkalinity at S-1 was from organic acid anions rather than free bicarbonate. More recently, the contribution from organic acids has greatly decreased, and this may in part account for the decrease in alkalinity over the 4 year period from 4450 mg/l to 1570 mg/l.

Major Constituents

The average concentrations as percentage of milliequivalents/liter and standard deviation of major inorganic constituents are shown in Figure 8 for the three water types based on dissolved oxygen concentrations. Native ground water unaffected by leachate is shown at group A as a calcium-magnesium type with chloride as the major anion. Sulfate concentrations are quite low in both the leachate and natural water. Rainfall is the major source of chloride in the native ground water; rainfall and oxidation of iron sulfide are the main sources of sulfate. Concentrations of all constituents are quite low in the natural water which has a total dissolved solids (TDS) of 50 to 90 mg/l. This mixed cation type of water, in which no cation contributes more than 50% of the total cations, is characteristic of much water in recharge areas of the Atlantic Coastal Plain.

Group D, the anaerobic zone, includes those samples from the landfill and the recovery wells immediately downgradient. This water is a sodium bicarbonate type and the TDS ranges from 250 to 2000 mg/l (1981). From 1977 to 1981 the TDS at S-1 showed the most significant change from 6400 mg/l in 1977 to 2000 mg/l in 1981. This is consistent with other data which indicate that the concentrations of constituents in the leachate have decreased at this location. Other sites within this zone have TDS values which are lower from 1977 to 1981 by about 16%. Concentrations of other constituents such as ammonia iron, manganese, organic compounds, and methane are high in this water type. The high values of bicarbonate, methane and ammonia result from degradation of organic matter by fermentation. A major source of cations may be their exchange from clays by ammonia generated in the leachate. The high concentrations of iron and manganese most likely result from their mobilization when water, which has a reducing potential due to the presence of organic material, comes in contact either with metals in the refuse or with oxidized manganese-bearing minerals and ferric oxide cements in the sand and clay.

Water in the transition zone (B and C) shows the affects of mixing of the two water types A and D. Typce C water is closer to the landfill and Type D water is downgradient farther away from the landfill. The change in water chemistry downgradient from the anaerobic zone results largely from mixing of leachate with native ground water, with only minor changes from chemical reactions. The TDS values in this zone range from 50 to 160 mg/l in 1981 and are about 30% lower than those measured in 1977.

Organic Compounds

Organic carbon concentrations in the landfill ranged from 77 to 260 mg/l in 1981. A marked decline was observed at landfill site S-1 from 3700 mg/l in 1977 to 260 mg/l in 1981. Organic carbon concentrations decrease rapidly downgradient from the landfill to low values of < 0.1 mg/l in uncontaminated water (Table 1). Organic carbon concentrations vary more with time and sampling procedures than do concentrations of inorganic constituents. A major control on organic compounds present in solution at any time and place is their solubility. Much of the organic matter is oxidized as the leachate migrates, however, some compounds are adsorbed on clays. Sorption is expected to be greater if sediments in contact with the water have a high organic content and if the compounds sorbed have low solubilities and polar functional groups (Griffin and Chian, 1979; Means and others, 1980).

Although the clays are weathered and the organic material is low, some lignitic silts were observed at the site in Potomac Formation cuttings when the wells were installed. Many of the organic compounds in the water are polar, including organic acids and chlorinated compounds which may be expected to sorb on sediments. Because organic acids are highly reactive they disappear rapidly downgradient. By contrast the chlorinated hydrocarbons are more refractory and may persist for a long period of time.

Volatile organics were identified in the water samples by purging the water with inert gas, trapping the compounds on a Tenax column, and eluting them into a gas chromatography-mass spectrometry system (Pereira and Hughes, 1980). The compounds with confirmed identification, that is, analyzed with standards run under the same conditions, are listed in Table 1. The column labelled total is the sum of all compounds identified, including those for which identification is tentative. Aromatic hydrocarbons are the most prevalent of the compounds definitely identified. The same compounds are not present throughout the landfill as shown by comparison of analyses from sites A-4 and S-1, which do not show the same suites of compounds. The total concentration of volatiles decreases rapidly away from the landfill and recovery wells, but does not drop much below 10 μg/l. In an earlier study of organics in the landfill area by DeWalle and Chian (1980), S-1 reportedly had a much higher concentration of volatile organics (982,000 μg/l) compared to recent values (840 μg/l). Although it is difficult to compare analyses from different laboratories, it appears that concentrations of volatiles have decreased significantly from 1977, when samples were collected for the study by DeWalle and Chian, to 1981 when samples were collected for the present study. Another factor that may have affected the concentration of organics is lowering of the water table at site S-1, which was 16 feet below land surface in June 1981 as compared to previous water depths of 12 feet. Thus, less of the refuse was saturated in 1981. Data show that the organic carbon content and concentration of specific organic compounds has decreased greatly in the landfill leachate and the water downgradient over a 4-year period.

High concentrations of methane on the landfill result from microbial degradation under anoxic conditions. Methane concentrations have decreased from 22 mg/l in 1977 to 14 mg/l in 1981 from water collected at site A-4 in the landfill. However, at site S-1, the newest part of the landfill, methane concentrations have increased from 10 mg/l in 1977 to > 20 mg/l in 1981. This difference may indicate that the newer part of the landfill near S-1 may have reached the state of high methane production at a later time than the zone near A-4. Nicholson and others (1982) have shown that the gas initially produced in landfills is predominantly CO_2 whereas at later stages the predominant gas is CH_4. Expressed in partial pressures, methane concentration at A-4 is about 0.52 atmospheres, at 16°C, which means it is approximately 52% of the total gases in solution and is probably near maximum concentration. Concentrations of methane decrease rapidly downgradient and are below the limit of detection in the supply wells. However, methane has continued to move downgradient and is present in water containing as much as 1.7 mg/l oxygen.

Chemical Mass Balance

Although most of the leachate is removed downgradient by the recovery wells, some contaminated water travels beyond the recovery well system and it is the behavior and fate of this water with its constituents that is considered in more detail. The contaminants are attenuated by dilution, by chemical reactions and by physical processes as the leachate moves downgradient. The extent of attenuation by dilution was calculated using Cl as a conservative parameter as the contaminated water high in Cl mixes with native ground water low in Cl. The flowpath of contaminants, based on the distribution of chemical species, is from the landfill to well 29, 29 to 33, 33 to 25, and 25 to 52 (Figure 1). Site A-4 was used as the leachate end member because its water chemistry has been relatively consistent over a five-year period and because in recent years the wells have been destroyed on the eastern part of the landfill. Chemical analyses show that as the water moves downgradient, the concentrations of Cl, total inorganic carbon expressed as ΣCO_2, CH_4, NH_4, and pH decrease, concentrations of O_2 increase, and concentrations of Fe, Mn and NO_3 show variations. Chemistry of the native ground water, which is the other end member, is based on the analyses of water from uncontaminated supply wells. The ratios of the mixing components were determined by assuming Cl concentrations along the path are controlled only by mixing of contaminated water with native ground water. For other constituents, deviations of observed concentrations from those calculated by using the mixing ratios for Cl, represent an enrichment or depletion of species due to chemical reactions or processes. It must be assumed that the concentrations of constituents have been constant along the flowpath during the flow time that has been estimated at two years for water from the landfill to reach the outermost well.

This discussion is limited to species of which the abundances are related to the presence of organic matter and that are sensitive to the availability of oxygen and therefore subject to oxidation-reduction processes. To construct a model to explain the sources and sinks of constituents, limitations were placed on the possible reactions which are given in Table 2. For example, sources of Fe and Mn were limited to natural oxide coatings, Fe_2O_3

or MnO_2, however, another source is the material deposited within the landfill. In the model, Mn was precipitated as MnO_2 and Fe was precipitated either as $Fe(OH)_3$ or $FeCO_3$ depending on solubility values at each site. NO_3 was reduced to N_2 although it can be reduced to either N_2O or NH_4 under certain conditions. Because nitrification does not occur in the anaerobic water, NH_4 was removed by cation exchange on clays. Organic matter of the composition, C_2H_6O was oxidized to CO_2; and organic matter containing nitrogen, represented in a general formula by $C_8NH_{19}O_8$, was oxidized to CO_2, reduced to NH_4, and partially reduced to C_2H_6O. Methane was formed by the hydrogenation of CO_2. Although the stoichiometry assigned to organic matter is not unequivocal, it is consistent with reactions known to occur in anaerobic environments. After the mixing ratios were determined on the basis of Cl concentrations, the amounts of reactants and products in the reactions were calculated using in part the computer program BALANCE (Parkhurst and others, 1982). Although electrons were balanced, the concentrations of H and O were not calculated because they are components of water. The amount of oxygen consumed was calculated as the difference between that predicted by mixing and that observed in the final water.

The results of the chemical mass balance (Figure 9) show that from the landfill (A-4) to the recovery well (29) iron and manganese dissolved, organic matter was oxidized and reduced, oxygen was consumed, ammonia was adsorbed, and nitrate was reduced. The dissolution of Fe_2O_3 and MnO_2 by reactions 1 and 2 (Table 2) and reduction of NO_3 by reaction 5 produced 0.32 mmoles/L ΣCO_2 of which 0.06 mmoles/L were used to form CH_4. The limit on the amount of organic matter oxidized by reaction 6 was the amount of oxygen that needed to be removed from solution, whereas the amount of organic matter used by reaction 7 was controlled by the amount of CO_2 needed at site 29 in addition to what was produced by the reactions discussed above. These reactions produced another 2.87 mmoles/L CO_2. A small portion, 0.06 mmoles/L, of the hydrogen produced was used to form CH_4 which leaves 1.8 mmoles/L H_2. Because H_2 was not found in the gases it was probably removed from solution by organic reactions such as $C_nH_{2n} + H_2$ C_nH_{2n+2} or by the formation of additional methane which was outgassed. In the above reaction where $n = 2$, ethylene would be hydrogenated to ethane; both of these compounds were identified in the leachate. However, it is equally probable that methane was formed and subsequently outgassed. On the landfill significant quantities of methane can escape and oxygen can be replenished, before the leachate reaches the confined aquifer. This also means that more organic matter can be oxidized than is indicated in the model as long as the products outgas. The nitrogen in the organic matter was reduced forming ammonia. Most of the ammonia remained in solution and the excess of the mass balance was exchanged on clays.

The reactions that occur in the next sequential step between 29 and 33 are significantly different from those discussed above. Ammonia and oxygen are removed by ion exchange and oxidative processes, respectively. Iron precipitates as $FeCO_3$, Mn as MnO_2, and CO_2 and CH_4 outgas. It is necessary to oxidize only 0.04 mmoles/L organic matter to explain the water chemistry, however, these reactions are difficult to quantify and as discussed above it is possible that more organic matter is oxidized and reduced and the end products (CO_2 and CH_4) outgas. Because the confining layer is thin close to the landfill, and the partial pressures of CO_2 and CH_4 are high, outgassing is a possible mechanism [illegible] of the aquifer. Iron precipitates as either siderite or amorphous iron oxide based on thermodynamic saturation data calculated by the chemical equilibria computer program WATEQF (Plummer and others, 1978). The saturation index [log (ion activity product/ equilibrium constant)] is 0.97 for siderite and 1.43 for amorphous iron oxide. However, siderite is a more stable species than amorphous iron oxide at these conditions with a pH of 6.6, calculated Eh of approximately 0.2 volts, ΣCO_2 concentration of 10^{-2}m, and Fe concentration of 10^{-4}m.

Farther downgradient from 33 to 35 and 25 to 52 (Figure 9) the water chemistry is controlled largely by mixing. In contrast to the sites upgradient, little ammonia was exchanged, less oxygen was removed and little solution or precipitation of metals occurred. The amounts of Fe and Mn transferred (0.001 mmoles/l) are low and close to the limits of precision of the determinations. Small amounts of organic matter were oxidized and 0.2 to 0.4 mmoles/l of CO_2 outgassed. It is unlikely that outgassing of CO_2 would occur through a confining layer of this thickness, greater than 30 meters, even though the PCO_2's of water, 0.05 atm at site 25 and 0.04 atm of 52, are greater than PCO_2 of the atmosphere. Also, the model shows that methane was generated between sites 25 and 52, which is not possible in the presence of oxygen. A possible explanation is that CO_2 and CH_4 concentrations predicted by mixing are not valid at these sites and that gases are present in solution from an earlier reducing front that extended downgradient. Alternatively, a micro-reducing environment may exist that permits gases to be generated in the aquifer.

The mass balance calculations suggest that between the landfill and the first recovery well large amounts of organic matter undergo fermentative reactions as Fe and Mn are solubilizing. Fe and Mn are higher at the recovery site than the landfill because (1) the landfill materials have been leached of these metals since the material was emplaced, or (2) the leachate comes in contact with more oxide coatings as it moves downgradient. The leachate that moves beyond the recovery well is subject to oxidative processes as it mixes with native ground water. Iron and manganese precipitate; concentrations of nitrate increase because it is not subject to reduction. Farther downgradient, with the exception of oxygen removal and ΣCO_2 outgassing small quantities of constituents are involved in these reactions.

Conclusions

Plumes of leachate have migrated dowugradient from Army Creek landfill. The recovery-well system installed between the landfill and major downgradient water-supply wells has successfully intercepted and removed most of the contaminants. At the Army Creek landfill the attenuation of contaminants depends on the following processes: (1) operation of the recovery well system that removes contaminants and reverses the flow locally, (2) dilution of leachate with native ground water, (3) mixing of anaerobic leachate with oxygenated water that facilitates the decomposition of organic matter and precipitation of metals, and (4) interaction of contaminants with clays and other aquifer materials.

Measurements of the major chemical constituents made on water samples immediately downgradient from the landfill show that most constituents have decreased in concentration from 1973 when the recovery system was put in operation. However, the leachate remains anaerobic and large amounts of gas are being generated in the landfill. With the exception of site S-1, the source concentrations of constituents have changed little with time. At site A-4, within the landfill, the pH, alkalinity, Cl, NH_4, and CH_4 measurements were surprisingly constant for the past four years. Although the major inorganic constituents have changed little, the organic carbon content and the number of organic compounds identified in the leachate have greatly decreased. This may be misleading because organic contamination may be a threat even after the aquifer is returned to pre-landfill conditions for the major constituents. The refractory nature of many organic compounds and their tendency to remain coated on aquifer materials may cause a contamination problem for long periods of time. Hydrologic and chemical data during an eight-year period indicate that the major changes which occur beyond the anoxic-oxic boundary are controlled by physical processes rather than chemical reactions. Thus, the extent of leachate movement within the aquifer is determined by factors that influence ground-water velocity including the rates of pumping recovery and supply wells. Concentrations of constituents in the leachate are determined by the nature of the waste and the amount of recharge water that passes through the landfill, in addition to the factors that control ground-water velocity.

Although zones that have water with different chemical compositions develop in the presence of organic matter by reduction-oxidation processes, the boundaries and extent of these zones are controlled by competing rates of reaction and hydrologic transport (Baedecker and Back, 1979b). The fronts of these zones are transient because of the wide range in ground-water velocities and the dispersive character of the aquifer materials. If the flow is extremely slow in the aquifer relative to reaction rates, the plume will be attenuated more rapidly and the boundaries between zones may be unidentifiable. However, if the ground-water flow is fast relative to reaction rates the zones will [illegible] farther downgradient and their boundaries will be more distinct.

The reactions discussed do not remain constant with time. Early diagenesis of landfill materials would produce high concentrations of ΣCO_2, NO_3 and SO_4. During later stages, degradation of organic matter proceeds until available sources of oxygen are consumed and the landfill becomes anaerobic. The main products formed are ΣCO_2, NH_4, H_2S, CH_4, Fe, Mn are partially reduced organic matter. The generation of sulfide may occur earlier than methane or may be suppressed if methanogenic bacteria dominate. As the plume migrates through the aquifer these processes change. Although CH_4 and NH_4 are not formed in the presence of oxygen, they may remain in small concentrations after the water is partially oxygenated whereas Fe and Mn will precipitate. Also, many organics, especially the chlorinated compounds, are insensitive to the presence of oxygen.

The recovery well system has effectively retarded the movement of contaminants in the Potomac sand aquifer from Army Creek landfill. However, to achieve this result, pumpage of water for supply purposes has been curtailed and a signficant amount of uncontaminated ground water is wasted by pumping the recovery wells. When the recovery wells are operating efficiently, the rates of withdrawal from recovery wells approximate withdrawals for water supply. Continued heavy pumping has lowered the head in the aquifer 50 feet since the mid-1960's. As a result salt water intrusion is a threat to the eastern portion of the aquifer (Sundstrom, 1974). At this landfill it is necessary to continue operation of the contaminant recovery wells. However, they can be operated more efficiently close to the landfill so that the more remote wells can be abandoned and less uncontaminated water will be wasted.

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Using the aquifer alone to dilute and attenuate contaminants is an alternative but it involves risks when the downgradient water is used for potable supply purposes. In other areas where downgradient water uses are not sensitive to low concentrations of contaminants or treatment can be provided then the aquifer could be tested as a possible attenuating medium.

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Acknowledgements

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ORIGINAL
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List of Figures

Figure 1. Location of wells sampled. Sites numbered are referred to in text.

Figure 2. Cross Section of landfill area (from Apgar, 1975).

Figure 3. Schematics of the direction of ground-water flow a) before the recovery wells were in operation, b) after the recovery wells were in operation, c) after continued pumping for several years, and d) after Amoco well field closed. Dashed arrows show movement of contaminants in c and d.

Figure 4. Pumpage (cubic meters per day) vs. time in the immediate vicinity of the landfill.

Figure 5. Lines of equal Cl concentration (50 mg/l) for the years 1973, 1974, 1975, 1976, 1977 and 1981.

Figure 6. Average abundances of Cl in ground water from 1973 to 1981 for Sites 29, 33, 25 and 52.

Figure 7. Distribution of dissolved oxygen (mg/l) in ground water. Lines of equal concentration drawn for 0.0, 3.0, 6.0 mg/l.

Figure 8. Inorganic chemical composition of ground water for (A) the native ground water, high in oxygen; (B and C) transition zone, low in oxygen; and (D) the anoxic zone. Average concentrations and standard deviation in percentage of total milliequivalents per liter for cations and anions (modified from Baedecker and Back, 1979).

Figure 9. Chemical mass balance along flowpath at landfill. Concentrations of reactants and products in mmoles/l.

TABLE 1. DISSOLVED ORGANIC CARBON AND VOLATILE ORGANICS IN GROUND WATER FROM THE LANDFILL.

	DOC	VOLATILES		METHYLENE CHLORIDE	BENZENE	TOLUENE	ETHYL BENZENE	CHLORO-BENZENE	TRICHLORO-ETHENE	ETHANE* DIOIC ACID
	MG/L	TOTAL UG/L	NO. OF COMPOUNDS	UG/L						
LANDFILL										
S-1	260	843.5	26	--	76.8	3.0	35.0	--	--	224.7
A-4	77	843.0	34	3.7	140.0	0.7	92.8	16.1	--	207.7
MONITOR/ RECOVER										
69	13	242.4	21	1.8	6.9	0.1	0.4	19.5	--	--
33	3.4	29.8	18	--	2.2	--	--	1.3*	0.2	3.1
25	2.7	26.7	13	--	2.3	--	--	1.6*	--	--
52	1.0	15.4	11	2.4	0.4	--	--	--	0.2*	--
SUPPLY										
G-3	0.1	18.4	7	7.2	--	--	--	--	--	--
AWC-7	0.1	8.9	10	--	--	--	--	--	--	--

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Table 2: Chemical Reactions Used in Model

① $Fe_2O_3 + 2H^+ + CH_2O = 2Fe^{++} + 2H_2O + CO_2$

② $2MnO_2 + 4H^+ + CH_2O = 2Mn^{++} + 3H_2O + CO_2$

③ $Fe^{++} + 2HCO_3^- = FeCO_3 + H_2CO_3$

④ $4Fe^{++} + O_2 + 10H_2O = 4Fe(OH)_3 + 8H^+$

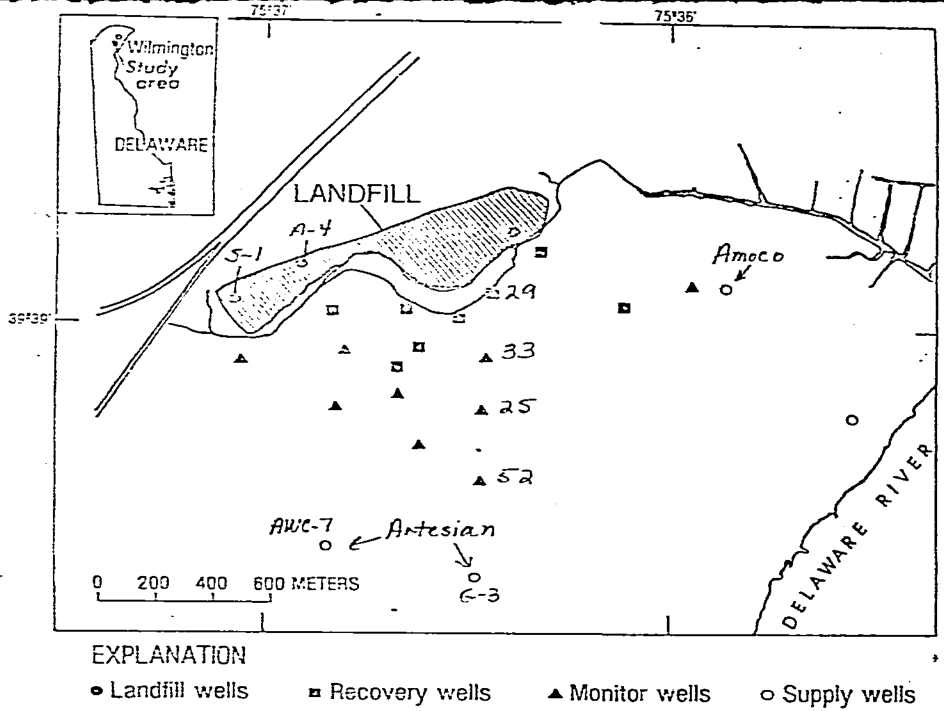
⑤ $4NO_3^- + 5CH_2O \rightarrow 5CO_2 + 3H_2O + 4OH^- + 2N_2$

⑥ $C_2H_6O + 3O_2 \rightarrow 2CO_2 + 3H_2O$

⑦ $C_8NH_{17}O_8 + 2H_2O \rightarrow NH_3 + 2C_2H_6O + 4CO_2 + 3H_2$

⑧ $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

⑨ Cation-clay + NH_4^+ = NH_4-clay + cation$^+$



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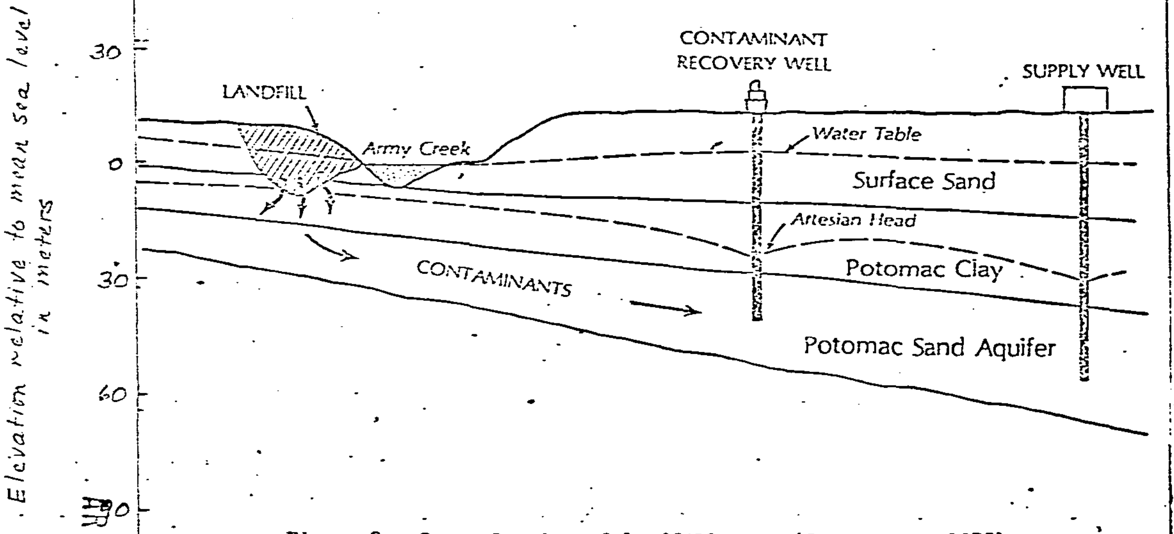

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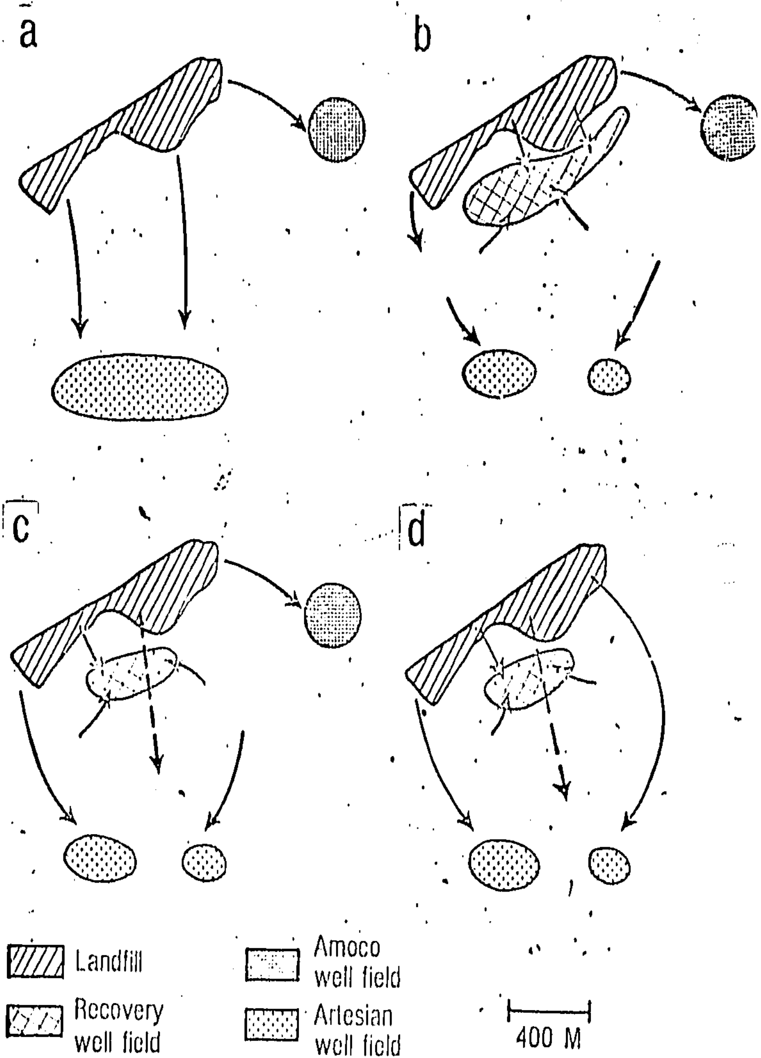

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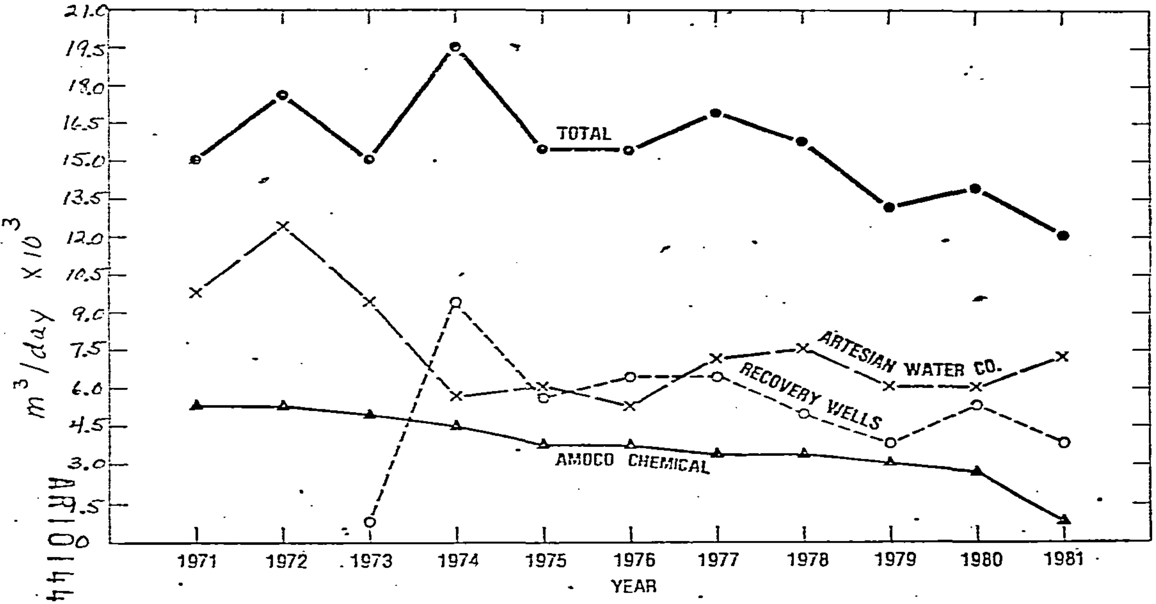

Figure 4. Pumpage (cubic meters per day) vs. time in the immediate vicinity of the landfill.

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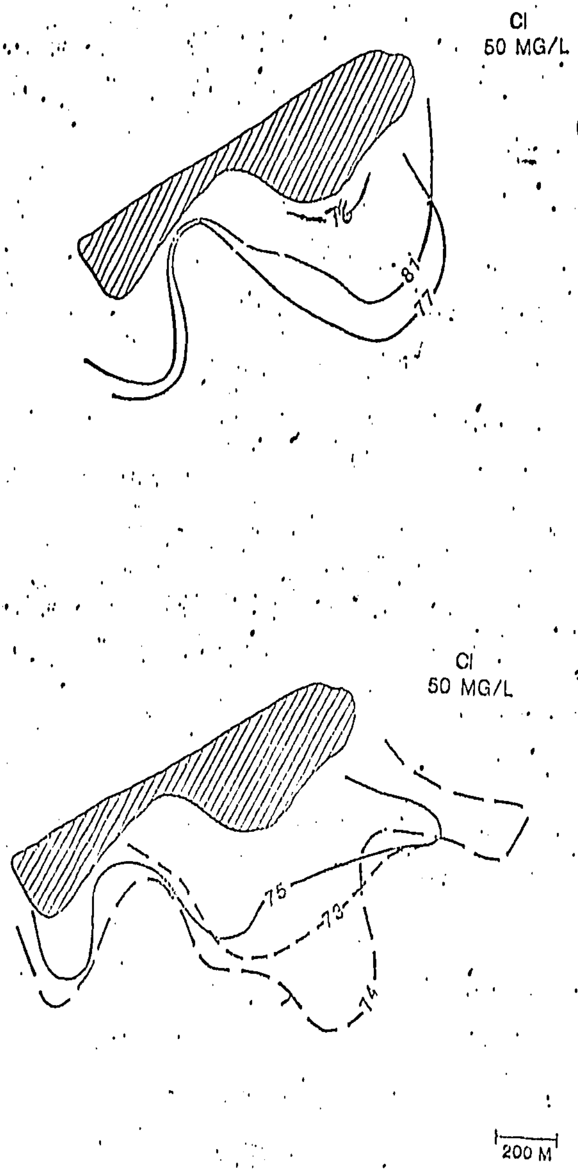

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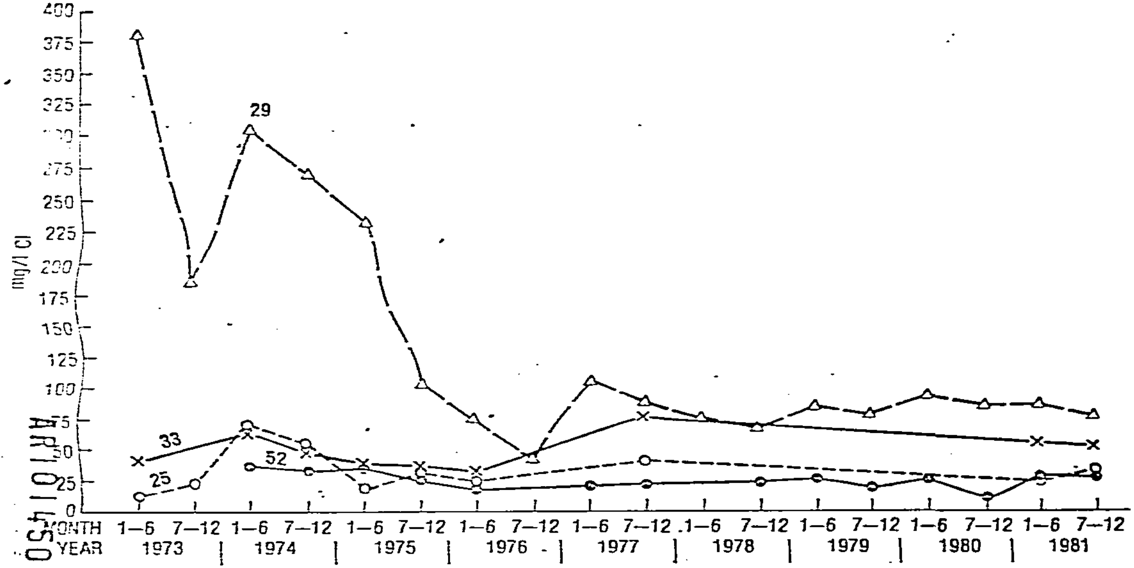

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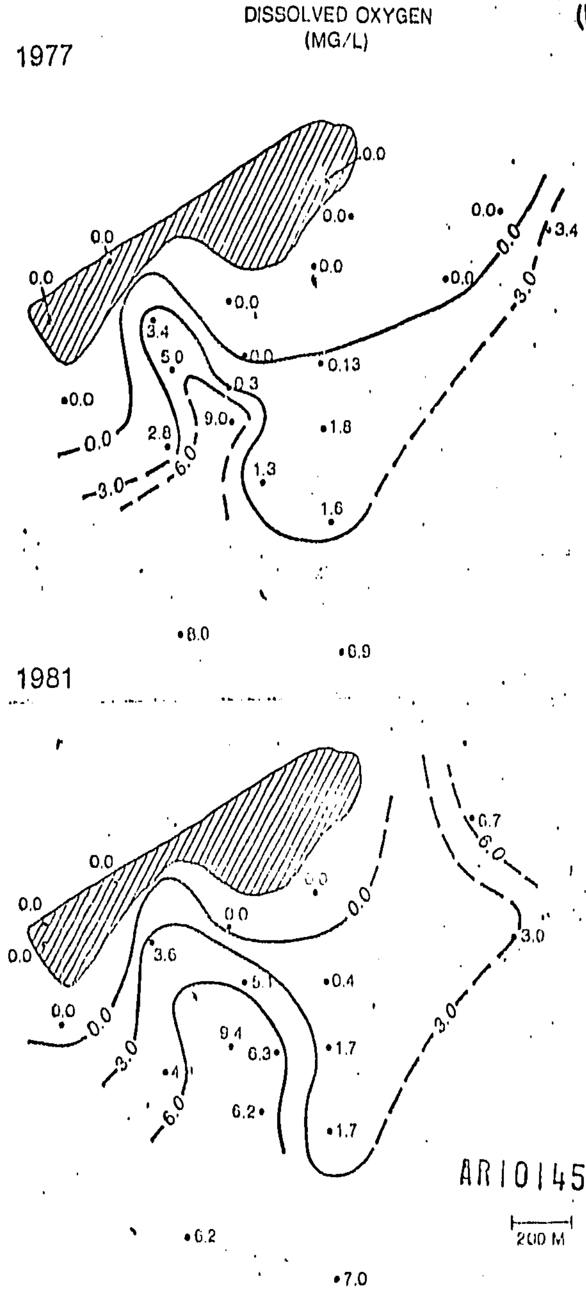

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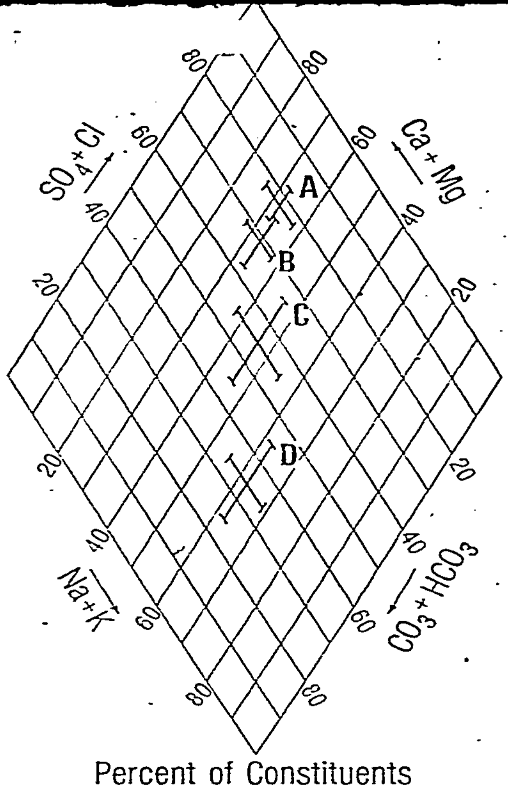

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	Water at A-4		After Dil 1/			Water at 29	
ΣCO_2	26.59		6.95			10.12	
CH_4	0.575		0.192	$+0.274\ Fe_2O_3$		0.256	
NO_3	0.029		0.054	$+0.02\ MnO_2$		0.027	
NH_4	8.150	$\xrightarrow[\text{78.1\% NGW 2/}]{\text{21.9\% A-4}}$	1.788	$-0.261\ O_2$	=	2.445	$+1.28\ C_2H_6O$
Fe	0.269		0.062	$+0.695\ C_5NH_{11}O_3$		0.609	$+0.014\ N_2$
Mn	0.002		0.0005	$+0.315\ CH_2O$		0.020	
O_2	0.0		0.261	$-0.028\ NH_4$-I-Ex 3/		0.0	
Cl	4.027		2.20			2.20	

	Water at 29		After Dil.			Water at 33	
ΣCO_2	10.12		6.41			4.45	
CH_4	0.256		0.147			0.034	$+0.35\ FeCO_3$
NO_3	0.027		0.042	$-1.266\ NH_4$-I-Ex		0.003	$+0.01\ MnCO_3$
NH_4	2.445	$\xrightarrow[\text{42.6\% NGW}]{\text{57.4\% 29}}$	1.402	$-0.130\ O_2$	=	0.136	$+0.020\ N_2$
Fe	0.609		0.351	$+0.043\ C_2H_6O$		0.0009	$+2.07\ CO_2\uparrow$
Mn	0.020		0.012			0.0015	$+0.113\ CH_4\uparrow$
O_2	0.0		0.143			0.013	
Cl	2.20		1.38			1.38	

1/ af

c. 33 to 25

	Water at 33		After Dil			Water at 25	
ΣCO_2	4.45		3.44			3.28	
CH_4	0.034		0.023	$+0.0006\ MnO_2$		0.007	
NO_3	0.003		0.023	$-0.077\ NH_4$-I-Ex		0.003	$-0.0012\ Fe(OH)_3$
NH_4	0.136	$\xrightarrow[\text{33.3\% NGW}]{\text{66.7\% 33}}$	0.091	$-0.067\ O_2$	=	0.014	$+0.010\ N_2$
Fe	0.001		0.0016	$+0.021\ C_2H_6O$		0.0004	$+0.016\ CH_4\uparrow$
Mn	0.0015		0.0011	$+0.025\ CH_2O$		0.0017	$+0.23\ CO_2\uparrow$
O_2	0.013		0.120			0.053	
Cl	1.38		1.02			1.02	

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d. 25 to 52

	Water at 25		After Dil			Water at 52	
ΣCO_2	3.28		2.49			2.23	
CH_4	0.007		0.004	$-0.008\ NH_4$-I-Ex		0.038	$+0.001$ [illegible]
NO_3	0.003		0.028	$-0.172\ O_2$		0.021	$+0.0009\ MnO_2$
NH_4	0.014	$\xrightarrow[\text{42.3\% NGW}]{\text{57.7\% 25}}$	0.008	$+0.057\ C_2H_6O$	=	0.00	$+0.35\ CO_2\uparrow$
Fe	0.0004		0.0015	$+0.009\ CH_2O$		0.0009	$+0.004\ N_2$
Mn	0.0017		0.0011			0.0002	
O_2	0.053		0.172			0.053	
Cl	1.02		0.65			0.65	

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1/ After dilution
2/ NGW = Native Ground Water
3/ I-Ex = [illegible] Exchange

Figure 9. Chemical mass balance along flowpath at landfill. Concentrations of reactants and products in mmoles/l.