Hydrogeological Processes and Chemical Reactions at a Landfill

by Mary Jo Baedecker and William Back

ABSTRACT

Chemical and isotopic analyses were made of water from wells in and downdgradient from a landfill to determine chemical and isotopic effects of generation and migration of leachate on ground water. The distribution and wide concentration range of oxygen and methane permit the delineation of an anaerobic zone, a regional oxygenated zone and an intermediate zone. The ratio of reduced nitrogen to nitrate indicates location of reducing fronts as the leachate migrates. The pH of the native ground water is low (<5.0) primarily because of the low pH of rainfall and the lack of calcareous or other soluble minerals in the aquifer material. The pH is higher (~6.6) in the leachate because of generation of carbon dioxide, ammonia, and methane. The native ground water has a low TDS (80 mg/l) while the leachate has an average TDS of 2800 mg/l and is primarily a NaHCO₃ type water. Sulfate concentrations are extremely low and H₂S was not detected.

We suggest that a major source of cations may be their exchange from the clays by the ammonium generated in the leachate. High concentrations of Fe and Mn are attributed to a source in the refuse but more important to reduction of oxide cements and coatings resulting from degradation of organic matter. The main source of bicarbonate is from organic degradation with minimal CO₂ from the soil zone. At one landfill site 52% of the total alkalinity is attributed to organic compounds, mainly organic acid anions. The δ¹³C of bicarbonate in the leachate is exceedingly heavy (+18.40%/o) which results from fractionation during the formation of methane. The 10 per mil deuterium enrichment of water may be due to decomposition of deuterium-enriched compounds and bacterial processes that preferentially consume the lighter hydrogen isotope.

INTRODUCTION

It has been recognized that many inorganic chemical reactions are controlled largely by the presence of organic compounds. Disposal of liquid and solid waste materials in landfills creates such an environment where organic compounds are an important part of the geochemical system. The principal reactions and processes that may occur are biological decay, precipitation and dissolution of inorganic constituents, sorption of chemical constituents, leaching of sediments, ion exchange, generation and diffusion of gases and movement of dissolved materials.

The purpose of this study is to understand the chemical reactions that occur in a highly reducing environment and their effect on the ground-water chemistry. A landfill provides a suitable environment in which to study the interrelation of organic compounds and inorganic reactions because the extremely high concentration of organic compounds in leachate makes it possible to identify the reactions.

Decomposition of organic materials in ground water is largely through biological activity. Under anaerobic conditions many intermediate organic compounds are formed that affect the ground-water chemistry more profoundly than do the unaltered compounds originally deposited. Effects of microbial degradation on organic compounds, using glucose as an example, are demonstrated in a simplified scheme in Figure 1. Complete oxidation of glucose yields CO₂ and H₂O, whereas absence of free oxygen permits fermentation reactions that produce a variety of end products. Glucose, for example, can dissipilate by a series of enzymatic reactions.

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Discussion open until March 1, 1980.
MICROBIAL DEGRADATION

Respiration
\[ C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \]
\[ C_6H_{12}O_6 + 4O_2 \rightarrow 3(COOH)O_2 + 3H_2O \]

Fermentation
\[ C_6H_{12}O_6 \rightarrow 2CH_3COCOOH + 2H_2 \]
\[ H_2O \]
\[ CH_3COCOOH + HCOOH \]

Acetic acid
\[ CH_4 + CO_2 \leftarrow \]
\[ CO_2 + H_2 \]
\[ 4H_2O \]
\[ \rightarrow CH_4 + 2H_2O \]

Fig. 1. Simplified reaction sequence for decomposition of glucose under oxidizing and anoxic conditions. H_2A = any hydrogen donor, i.e., hydrogen gas, fatty acids, alcohols.

to yield pyruvic acid which subsequently can be used as a substrate to form acetic and formic acids. Other organic compounds such as fatty acids, amino acids, and carbohydrates degrade by similar reactions and upon complete dissimilation yield as end products CO_2, CH_4, NH_3, and in some cases H_2S and H_2 (Langmuir, 1972). Hydrogen is seldom detected in environments of anaerobic decay, especially if fatty acids are produced. Any hydrogen gas formed will be utilized immediately by methane producers (Toerien and Hartringh, 1969). Although controls on these reactions are not well understood, oxygen deficiency and the type and availability of organic material are probably the most important controls on biological activity in subsurface environments.

Nitrogen- and carbon-containing compounds are of particular importance in understanding the geochemical system. One of the major problems is to determine the role and fate of CO_2 and HCO_3~ and to evaluate the relative significance of their several sources such as soil gas, solution of calcareous material, and CO_2 produced by organic decomposition.

HYDROLOGIC SETTING

The Army Creek landfill near Wilmington, Delaware covers about 60 acres and consists essentially of solid and liquid industrial waste and municipal refuse. These wastes were deposited during 1960 to 1968 in an abandoned quarry from which twenty to thirty feet of Tertiary sand and gravel (Columbia Group, Pleistocene by Jordan, 1976) had been removed. The sand was removed from beneath the water table with a drag line and in some places red clay of the underlying Potomac Group was probably removed (Apgar, 1975, 1976). Poorly compacted refuse was put into standing water and loss of the clay layer of tighter permeability permitted migration of leachate into the aquifer.

Approximately 3,500 ft (1,066 m) south and east of the landfill two major well fields were developed in the 1960's to produce water from the Potomac formation from depths of 150 to 200 ft (46 to 61 m). In 1973, discovery that leachate from the landfill was moving into the aquifer led to installation of a series of recovery wells to pump contaminants and to reverse the flow direction of leachate away from supply wells. These recovery wells discharge the landfill effluent, and cause large quantities of oxygenated ground water to mix with leachate. This mixing has significant consequences on the chemical character of the ground water and is a major control on the types of reactions occurring.

The direction of ground-water flow and location of wells sampled in this study are shown in Figures 2 and 3. Wells on the landfill are 25 to 30 ft (7 to 9 m) deep and the recovery and monitor wells are about 100 ft (30 m) deep. Elevation of the natural potentiometric surface before develop-
determine organic-acid concentrations water samples were acidified with sulfuric acid, then steam distilled to remove the low-molecular weight acids which were then titrated with a base. Specific organic acids from the landfill water were determined on the distillate by conversion to p-bromophenacyl esters and subsequent detection by gas chromatography. Amino acids were analyzed colorimetrically by the ninhydrin method. All other analyses were made by standard methods and procedures.

GEOCHEMICAL ASPECTS

Oxygen, Nitrogen Species and Redox

In this study the concentration of dissolved oxygen ranged widely from near saturation (8.4 mg/l) in water from supply wells to anoxic water on the landfill. This wide range of oxygen concentration permits delineation of three zones, an anaerobic zone, the regional oxygenated zone and a broad intermediate transition zone (Figure 4). Within the transition zone oxygen values range from a few tenths to 5.0 mg/l with highest concentrations in wells downgradient from the narrowest part of the landfill and in the easternmost well (PW-3).

A nitrogen index, which is the ratio of organic and ammonia nitrogen to nitrite and nitrate nitrogen was used to delineate redox zones (Figure 5). A low number (0.01) indicates absence of ammonia whereas a large number (>100) caused by greater concentration of ammonia and N-containing organic compounds indicates more

Fig. 3. Location of wells sampled. Wells FW-4, MV and NC are upgradient of the landfill and were considered back-ground wells. They are within a mile of the landfill in the direction of the arrow.

Fig. 4. Distribution of dissolved oxygen in ground water within the regional oxygenated zone, an anaerobic zone and a transition zone.

EXPERIMENTAL

Dissolved oxygen was determined in the field by the Alsterberg azide modification of the Winkler method. Organic nitrogen was determined by the Kjeldahl method; ammonia by distillation and subsequent detection with Nessler reagent; and dissolved organic carbon by the combustion method. Gases were collected and measured by the method of Fisher (see Pearson and others, 1978). Complete alkalinity titration curves were made because in some samples organic-acid anions contributed significantly to the alkalinity and the inflection point ranged between a pH of 3.0 and 4.9. To
landfill (A-4 and S-5). These wells in the older part of the landfill are representative of leachate migrating in the eastern reducing plume. Water samples from the landfill had small quantities of nitrate (<0.2 mg/l as N) and its source is probably from recharge water upgradient (3 mg/l as N) or rain water that directly infiltrates the landfill. Use of nitrate concentrations alone to indicate areas of contamination in ground water is misleading in a reducing environment because nitrate is biologically reduced to ammonia or denitrified to N₂ or N₂O. The concentrations of organic N and NH₄ are high (120 and 160 mg/l as N, respectively). The concentration of amino acids is low (<10 mg/l as N) because in an environment dominated by methanogenic bacteria free amino acids are converted to other organic acids, NH₄ and CO₂. Nitrification does not occur in the anaerobic zone because nitrifying bacteria require some oxygen and are intolerant of high concentrations of organic carbon. The ammonia moves downgradient where it is mixed with oxygenated water or is attenuated by sorption on clays.

The nitrogen index plotted against pH (Figure 7) shows that the supply wells have oxygenated water with low pH values from 4.6 to 5.2 which is consistent with an area that lacks natural calcareous material. Dissolved Fe and Mn are either not detected or present in small amounts (<0.02 mg/l) in the oxygenated water. However, water from the anaerobic zone has higher pH values, 6.3 to 6.8, and mean Fe and Mn concentrations of 86.8 and 1.7 mg/l, respectively. The high concentrations of iron and manganese most likely result from the refuse or from their mobilization when water, which has a reducing potential from the oxidation of organic material, comes in contact with ferric oxide.
Table 1. Chemical Analysis of Water from Army Creek Landfill (mg/l)

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<th>Mg</th>
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N.D. = not detected  
N.A. = not analyzed

¹ Organic acid anions calculated as acetic acid contribute 52% of the total alkalinity at S-1 and less than 13% at all other sites.

Cements in the sands and clays and with oxidized manganese-bearing minerals. The reduction and release of Fe from clay surfaces has been suggested earlier on the basis of field evidence and by column experiments (Cartwright and others, 1976). Water in the transition zone shows the effects of mixing the two water types. The significantly higher pH in the anaerobic zone is somewhat surprising because large amounts of CO₂ generated from degradation of organic matter should lower pH. However, the pH is increased by the generation of ammonium ion and by fermentation reactions which consume hydrogen and CO₂ during the formation of methane.

**Major Inorganic Ion**

Chemical analyses for the landfill and downgradient water are given in Table 1. The mean and standard deviation of relative concentrations (percentage of meq/l) of major inorganic constituents are shown (Figure 8) for four water types based on the nitrogen index. Native ground water unaffected by leachate is shown at group A as a calcium-magnesium type with chloride as the

![Nitrogen Index Group](https://example.com/nitrogen-index-group)

**Percent of Constituents**

![Percent of Constituents](https://example.com/percent-of-constituents)

**Fig. 8. Inorganic chemical composition of ground water from four redox environments based on the nitrogen index.** Percentage of mean concentration of each group is plotted and the standard deviation is indicated by length of the lines.
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 oxidization 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 about 80 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. The feldspars in the Potomac formation have been kaolinized (Owens, 1969) and the feldspars, chiefly microcline, in the overlying Tertiary sediments show evidence of extensive weathering and alteration (Owens and Minard, 1975). No calcareous material occurs in these sediments, and the saturation indices [Saturation Index = log (Ion Activity Product/Equilibrium Constant)] for calcite and dolomite are about −5 and −9 which indicates the water is greatly undersaturated with respect to these carbonates. Within the area of study Ca, Na, and K in ground water unaffected by leachate are derived originally from the feldspars. In addition, alteration of ferro-magnesium silicates (hornblende, pyroxene, and epidote) contribute Fe, Mg, and Mn.

Chemical types and concentrations of major inorganic constituents of groups B and C (Figure 8) are intermediate between groups A and D and result from mixing of these two end-member types of water. Group D, with the highest nitrogen index includes those samples from the landfill and the recovery wells immediately downgradient. This water is a sodium bicarbonate type and the TDS of the leachate ranges from 800 to 6,400 mg/l. The saturation indices for samples of the leachate are 0.67 for calcite and 1.24 for dolomite, which shows supersaturation with respect to these minerals; three other samples in this group (D) immediately downgradient are slightly undersaturated. The highest TDS of samples collected downgradient from the landfill is about 450 mg/l. This increase in TDS from that of native ground water and the shift toward Na bicarbonate type water is primarily a result of simple mixing with leachate. Ionic ratios using chloride as a conservative parameter show that concentrations of Na, K, Ca, and Mg in downgradient wells result from mixing of leachate with native ground water rather than from additional dissolution.

The origin of the major cations in the leachate remains an unanswered question with the possible sources being (1) chemical sources in the refuse, (2) alteration of silicate minerals, and (3) desorption from clays. If the cations are coming from inorganic compounds in the refuse, anions of Cl and SO₄ would perhaps be higher; if the cations originate from silicates the dissolved silica should be higher than the ~9 mg/l observed, which differs only slightly from natural concentrations of silica. The red clays of the Potomac formation are primarily kaolinite with illite and some vermiculite and montmorillonite (Pickett, 1970). These clay minerals often have sorbed cations which could be readily exchanged with the ammonium generated in the leachate. Therefore, clays in the material used for daily cover of the trash may be an important source of Na, K, Ca, and Mg.

**Carbon Species**

Dissolved organic carbon is high in the landfill leachate (up to 3,700 mg/l); however, its concentration decreases rapidly downgradient (<20 mg/l) as organic compounds are degraded and the leachate is diluted. The dissolved organic carbon does not have a systematic distribution and, therefore, was not used to define reaction zones.

We separated and identified by gas chromatography eight low molecular weight organic acids from one site on the landfill (S-1). They were straight-chained and 2-methyl branched acids ranging from 2 to 8 carbon atoms per molecule (Table 2) with a total concentration of 470 mg/l. The total alkalinity, including anions of organic acids, was 4,450 mg/l at this site which means the acids comprise at least 11% of the alkalinity. This value represents the minimum contribution because some acids may not have been detected owing to problems of incomplete separation and recovery during analysis. In a separate experiment leachate water was acidified, distilled, and the distillate then back titrated to determine the concentration of volatile organic compounds, including organic

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</table>

¹ Separated by distillation and identified by gas chromatography as p-bromophenacyl esters by comparison with known standards.
acids, that react with hydrogen ions. The back-
titration alkalinity was approximately 2,330 mg/l
which indicates that organic compounds comprise
as much as 52% of the total alkalinity.

Analyses of the hydrocarbon gases show that
the concentration of methane ranges from less than
0.1 mg/l (the detection limit) to 22 mg/l (Figure 9).
The highest concentrations are on the landfill and
the distribution shows a systematic downgradient
decrease similar to the nitrogen index. Only a few
metabolic pathways are documented which lead to
production of methane (Wolfe, 1971). The most
likely mechanisms for its generation on a landfill
are the conversion of acetate to methane and
CO₂ and the direct hydrogenation of CO₂ to
methane (Figure 1). Large amounts of CO₂ and CH₄
are produced in the landfill beneath the water
table; however, hydrogen is not detected in these
waters because it is utilized by the methane-
producing bacteria probably as rapidly as it is
formed. Only a small amount of bicarbonate
(10 mg/l) is in the natural ground water while the
bicarbonate in the landfill water is more than
950 mg/l. Therefore, the main input of CO₂ is
from inorganic degradation in the landfill with a
minimal contribution of CO₂ from the soil zone
(Figure 10). Some of the CO₂ is retained as
bicarbonate, part is microbially converted to CH₄,
and the rest is lost by outgassing. Part of the
generated methane diffuses upward and escapes
directly or is oxidized to CO₂ and that remaining
migrates with the leachate.

The unsaturated hydrocarbon, ethylene, was
detected also but its distribution (Figure 9) is
quite different from that of methane. With one
exception it was found only on the west side near
the newer part of the landfill, and this restricted
occurrence suggests that it was deposited or
generated within that part of the landfill and
migrated. Its detection in several downgradient
wells may indicate ethylene is conservative and
perhaps will be useful as a tracer in chemical
transport modeling. Ethylene in Well 53 may be
from a smaller landfill in that area where liquid
chemicals were deposited. Also, the saturated
hydrocarbon, ethane, was detected only at the sites
where ethylene occurs and was probably formed
by the hydrogenation of ethylene. It is apparent
that ethylene and ethane originated from organic
material by processes different from those bacterial
processes responsible for the generation of methane.

Isotopes

Several studies have shown that the carbon
isotopic composition of CO₂ and CH₄ is controlled,
in part, by biological decay processes (Nissenbaum
et al., 1972; Games and Hayes, 1974, 1976;
Baedecker and Fisher, 1977). In biological processes
the lighter isotope, ¹³C, is preferentially utilized
which results in the remaining carbon being enriched
in the heavier, ¹²C, isotope. Isotopic ratios are
expressed in terms of δ¹³C where

\[ \text{δ}^{13}\text{C per mil} = \frac{\text{¹³C/¹²C sample} - \text{¹³C/¹²C standard}}{\text{¹³C/¹²C standard}} \times 1000 \]

A more positive δ¹³C value indicates enrichment in
¹³C and conversely, a more negative value indicates
depletion in the ¹²C isotope.

The δ¹³C of inorganic carbon dissolved in
natural ground water for this area is about -25 per
mil which indicates that the main source of CO₂ is
from vegetation and oxidation of organic matter in
soils and reflects the absence of calcareous material

![Fig. 10. Schematic of the origin and fate of carbon compounds in ground water under anoxic conditions.](image-url)
for dissolution. δ¹³C values of inorganic carbon in the landfill water are +10.30‰ in the most recently filled part (S-1); +15.30‰ in the middle portion (A-4); and +18.40‰ in the oldest part (S-5).

The inorganic carbon pool is most highly enriched in the ¹³C at site S-5 because the fill has been emplaced for a longer period of time which has allowed the decomposition reactions to go nearer to completion and produce more methane. It is probable that as the reactions continue in the newer portion of the landfill, δ¹³C values for inorganic carbon will eventually approach the δ¹³C values in the older part. Several recovery wells (27, 28, 29, RW-5, RW-6) downgradient of the landfill have enriched δ¹³C values ranging from +7.1 to −10.5‰ which indicates mixing with a substantial amount of leachate.

The percentage of leachate in downgradient wells was calculated using Cl as a conservative constituent assuming that water high in Cl from the landfill mixes with native water low in Cl. A hypothetical mixing line can be drawn using as end members the landfill wells (A-4 and S-5) for 100 percent leachate and from supply wells (AWC-7, FW-4, MV, NC) for 0 percent leachate. A plot of percent leachate against both ¹³C values and HCO₃ concentrations of water from recovery and monitor wells shows that water with a higher percentage of leachate (Sites 27, 28 and 29) is depleted in inorganic carbon and enriched in the ¹³C isotope (Figure 11). If mixing were the only process involved, the data would fall on the mixing line. Possible reactions that could cause this depletion are (1) precipitation of calcite, (2) formation of methane by hydrogenation of CO₂, and (3) outgassing. The first reaction can be eliminated from consideration because the contaminated water downgradient from the landfill has saturation indices of −1 to −4 which indicates it is greatly undersaturated with respect to calcite; however, the latter two processes may explain both the loss of HCO₃ and the heavier δ¹³C values.

Deuterium and oxygen-18 measurements of ground water were made to determine if chemical and biological reactions of constituents dissolved in leachate significantly affect the isotopic composition of water. Previous work by Fritz, Matthes, and Brown (1976) showed a marked enrichment in both deuterium and oxygen-18 in leachate relative to the surrounding ground water. Isotope measurements in this present study showed enrichment in deuterium (−36.44‰) (parts per thousand difference of D/H relative to Vienna, Standard Mean Ocean Water (V-SMOW)) in landfill leachate compared with −44.65‰ for downgradient supply wells. However, oxygen isotope values of −7.68‰ and −7.75‰ for the leachate and surrounding water, respectively, do not differ significantly. Deuterium enrichment may be due to decomposition of materials in the landfill with a different isotopic composition or from bacterial processes that preferentially consume the lighter hydrogen isotope.

CONCLUSION

Pumping the recovery wells causes leachate to mix with highly oxygenated native water, and the resulting oxygenation of the leachate is one of the important controls on the chemical character of the water. The availability of oxygen and the formation and existence of certain types of organic material have a major influence on biological activity in the subsurface environment. Distribution of the nitrogen species, such as that indicated by the ratio of reduced nitrogen (organic N and NH₃) to nitrate can be used to locate reducing plumes as the leachate migrates through the aquifer. The natural water has an extremely low pH, while water with an increasing percentage of leachate in the landfill area has a higher pH, probably as a result of the generation of CO₂, NH₃ and CH₄.

Sources for the major cations in the natural water are rainfall and alteration of silicate minerals. Sources of cations in the contaminated water are possibly from refuse and from the alteration of silicate minerals, but more probably from clays by exchange with the large amount of ammonium generated. Possible sources of high concentrations of Fe and Mn in the landfill water are the

![Fig. 11. Relationship of percentage leachate δ¹³C values, and concentration of HCO₃. Mixing line based on Cl concentrations in water from supply wells for 0% leachate and Wells A-4 and S-5 for 100% leachate. Numbered wells are discussed in text.](image-url)
buried trash and reduction of Fe oxides and natural oxide coatings by reaction with organic compounds. Organic acid anions contribute significantly to, and at one site control, the alkalinity concentration. The extremely heavy $^{13}$C of inorganic carbon in the leachate results from generation of isotopically light methane and perhaps to a lesser extent by outgassing of CO$_2$, thereby leaving a residual pool of heavier carbon. Although we do not understand the process that causes enrichment of deuterium in the landfill, the enrichment appears to be a valid indicator of contamination and may result from decomposition of carbohydrates and bacterial processes that preferentially consume the light hydrogen isotope. Isotopic data and chemical analyses indicate that processes other than simple mixing are important in the distribution of some species in water downgradient of the landfill. These preliminary results on the use of isotopes as indicators of pollution are encouraging and merit further investigation.

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