Spatial and Temporal Variations of Synthetic Organic Compounds in the Contaminant Plume Emanating from the KL Landfill

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SPATIAL AND TEMPORAL VARIATIONS OF SYNTHETIC ORGANIC COMPOUNDS IN THE CONTAMINANT PLUME EMANATING FROM THE KL LANDFILL

by

Lynn Diane Broede

A Thesis
Submitted to the Faculty of The Graduate College in partial fulfillment of the requirements for the Degree of Master of Science Department of Geology

Western Michigan University Kalamazoo, Michigan December 1990
SPATIAL AND TEMPORAL VARIATIONS OF SYNTHETIC ORGANIC COMPOUNDS IN THE CONTAMINANT PLUME EMANATING FROM THE KL LANDFILL

Lynn Diane Broede, M.S.
Western Michigan University, 1990

Thirty-one synthetic organic compounds have been detected in samples collected from the KL Landfill contaminant plume from March, 1980 to March, 1986. Two groups of organic compounds have been delineated based on their occurrence, concentrations, and persistence throughout the 7-year monitoring period.

Changes in plume geometry and concentration have been studied relative to time, and concentration variations have been related to selected inorganic plume parameters, distance from the landfill, and precipitation. The spatial and temporal distribution of the organic compounds are attributed to biodegradation, three biotransformation sequences, physical properties of the organics and other factors. Three abbreviated anaerobic biotransformation sequences are indicated: (1) 1,1,1-trichloroethane → chloroethane, (2) carbon tetrachloride → methylene chloride, and (3) tetrachloroethene → vinyl chloride.
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Lynn Diane Broede
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Western Michigan University, 1990

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CHAPTER I

INTRODUCTION

Organic Chemical Contamination of Groundwater and Description of the Study

Contamination of groundwater supplies by synthetic organic chemicals is a growing problem in the United States. The use of synthetic organic chemicals has grown at a rapid rate since World War II. More than 3,000,000 organic compounds are known to exist and more than 40,000 are currently being manufactured (Cherry, Gillham, & Barker, 1984). The majority of the organic compounds currently in use have not been rigorously tested to determine their toxicities and may be hazardous or potentially hazardous to humans in parts per billion (ppb or ug/L) or parts per trillion concentrations in groundwater (Cherry, et al., 1984). Generally, these organic chemicals are introduced into the environment through agricultural practices, sewage disposal, waste disposal, leakage from buried containers, leakage from liquid waste storage ponds, and accidental spills from trucks (Freeze & Cherry, 1979).

The relatively limited supply of information on the chemical and biochemical behavior of organic compounds
within aquifer systems becomes a serious problem when assessing future changes in groundwater quality impacted by organic chemicals. In general, organic chemicals are relatively mobile and stable in groundwater systems, and volatile organic solvents in unsaturated soils may remain in place for tens of years (National Academy of Sciences, 1984). Many or most of the chemical reactions involving organic compounds within aquifers and the unsaturated zone are controlled by microorganisms (Cherry, et al., 1984).

In terms of environmental contamination, the major concern is focused on those organic substances that are relatively soluble, nonvolatile, and refractory, meaning they are not immediately degraded by bacteria, but may persist for several years and gradually degrade in the future. Some of the factors controlling the distribution of organic chemicals in contaminated groundwater zones are: (a) groundwater flow rates, (b) contaminant attenuation rates, (c) vertical distribution within the aquifer flow system, (d) interactions with inorganic chemicals, (e) interactions with the physical environment, (f) biodegradation (where organic chemicals are degraded completely to CO₂), and (g) biotransformation (where organic chemicals are biotransformed into one another via reductive dehalogenation) (e.g., Fogel, Taddeo, & Fogel, 1986; Marrin & Thompson, 1987; Molz, Mercer, & Wilson,

The KL Landfill site in Kalamazoo County, Michigan is an acceptable field location to study the behavior of synthetic organic chemicals in groundwater. The spatial and temporal distribution of the 31 synthetic organic chemicals that have been detected within the leachate plume were monitored beginning in 1975 to 1986 by the Michigan Department of Natural Resources and the Kalamazoo County Health Department. Additional monitoring was conducted by the U.S. Environmental Protection Agency from 1987 to 1988. The groundwater samples used in this study were analyzed for these organic chemicals quarterly, bi-annually, and at other times from March, 1980 to March, 1986.

The specific factors that will be addressed in this study are: (a) changes in plume geometry and concentrations of organic chemicals in the groundwater over the 7-year monitoring interval; (b) the behavior of each organic chemical detected within the aquifer relative to the other organic chemicals present; (c) the relationship between the organic chemicals and selected inorganic chemicals and parameters such as chloride, pH, and redox potential; (d) the effects of precipitation on the synthetic organic chemical concentration levels within
the landfill leachate plume; (e) the physical properties of the organic chemicals relative to their occurrence and distribution within the flow system; (f) biodegradation and biotransformation and their effects on the concentration levels, distributions with time, and plume geometries of the synthetic organic chemicals; and (g) the effects of aquifer characteristics such as the glacial stratigraphy.

Location

The KL Avenue Landfill is located in a semi-rural to residential area of Oshtemo Township in Kalamazoo County, Michigan (Figure 1). It is approximately 7 miles west of the city of Kalamazoo in west-central Kalamazoo County, Section 21, T.2 S., R. 12 W. (Figures 2 & 3).

The landfill is approximately 1/2 mile east of the intersection of KL Avenue and South 4th Street and 1/2 mile south of the junction of Almena Drive and West Main Street (Figure 4). In relation to the surface water features of the area, the landfill is about 300 feet southwest of Bonnie Castle Lake and about 1 mile east of Dustin Lake.
Figure 1. Location of Oshtemo Township, Kalamazoo County, Michigan (Adapted from Passero, 1981).
Figure 2. Street Map of Oshtemo Township Showing the Location of the KL Landfill (Adapted from Passero, 1981).
Figure 3. Location of the KL Avenue Landfill in Section 21, Oshtemo Township (Adapted from Passero, 1981).
Figure 4. Map of the KL Avenue Landfill Site Showing Locations of the Domestic, Monitor, and Test Wells (Adapted from Passero, 1981).
Landfill History

The KL Landfill site initially served as the local garbage dump for Oshtemo Township. The pit was developed in the early 1960s and covered 20 acres at the southwest corner of the site. It was intended for residents to dispose of their household waste. At this time, management of the site was minimal (Passero, 1981).

In 1967 Kalamazoo County entered into a sanitary landfill agreement with Oshtemo Township to purchase the dump site and 66 acres of surrounding lands (Figure 5). In May, 1968, the site became the municipal landfill for Kalamazoo County. Although owned and managed by the Kalamazoo County Board of Public Works, the landfill was operated on a daily basis by a private company. The landfill occupies 87.40 acres of land, 57.31 acres of which were filled with waste (Figure 5), (Passero, 1981).

The landfill received both industrial and commercial waste with an average volume of about 500,000 yd³/year. The types of material handled included general refuse (from streets, construction, demolition; and ashes), garbage, industrial waste, liquid waste, and rubbish. The landfill was originally expected to meet the county’s solid waste disposal needs for 15-20 years. However, the available land was being filled and completed much faster.
Figure 5. Acreage and Ownership of the KL Avenue Landfill (Adapted from Passero, 1981).

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than expected. In December, 1970 a new contractor was hired and the trench-area method of landfilling was initiated to increase the life of the landfill. After using the trench method of disposal for 2 1/2 years, it was determined that the site would not be able to accept waste for any more than 10 years. This led to a Solid Waste Management Plan for Kalamazoo County proposed by the Kalamazoo County Metropolitan Planning Commission, which recommended an expansion of the landfill to accommodate the solid waste disposal needs of the county through the year 1990 (Passero, 1981).

In April of 1979, after the landfill had been in operation for 11 years, volatile organic chemicals were detected in 10 local domestic wells. The KL Landfill was the suspected source of the contamination and the Michigan Department of Natural Resources ordered the landfill closed on May 4, 1979. Any well that contained over 1 ug/L of any volatile organic compound was considered unfit for human use. These wells were capped immediately and an alternative water supply was proposed for the local residents (Passero, 1981).

In November, 1979 and March, 1980, 11 deep wells were drilled. Ten of the wells were drilled for residences with contaminated wells, and one was drilled for a future property owner planning to build in the area of
contamination. As a final measure to minimize the effects of the known groundwater contamination, Kalamazoo County installed a new water main that extended to the residents near the landfill. A closeout plan was designed by Wilkins and Wheaton Testing Laboratory, Inc. of Kalamazoo, Michigan in February of 1980. The plan called for a reduction in the permeability of the material covering the filled area, thereby reducing infiltration of precipitation and surface water into the refuse (Passero, 1981).

The proposal outlined a method of applying granular bentonite to the surface of the filled area. Bentonite was chosen because it will expand with increasing moisture content, decreasing the permeability of the cover material as well as reducing the development of cracks in the cover. Bentonite also permits exchange of gases between the landfill and the atmosphere. However, since domestic or residential waste is not the dominant type of refuse buried at the site, the amount of gas generation would be minimal. The partial bentonite cap was disked into the soil cover at an application rate of 1/2 lb/sq ft in 1980. It was later determined that this final cover had a wide range of permeabilities from $10^{-2}$ cm/s to $10^{-6}$ cm/s with an average permeability of $10^{-4}$ cm/s (Carey, in preparation).
Topography and Drainage

The landfill was constructed on several small hills and includes portions of three major closed depressions (Figure 6). Elevations increase to the west and northwest away from the landfill site. Further to the northwest, the morainal topography descends rather abruptly onto the Alamo Plain where elevations range from 700 to 800 feet. The southern margin of the study area is adjacent to the northwestern end of a large depression. Further to the southwest, the moraine descends more gradually onto an outwash plain at elevations ranging from 850 to 900 feet (Passero, 1981).

The knob and kettle topography of the moraine is dominated by low hills surrounded by closed depressions, that range in area from a few acres to over 1,000 acres. The irregular, rolling surface of the moraine ranges in elevation from approximately 900 feet above mean sea level to slightly over 1,000 feet above mean sea level. Local relief ranges from a few tens of feet to slightly more than 150 feet. In the vicinity of South 4th Street, surface elevations are generally higher, ranging from 975 feet to 990 feet above mean sea level, which is 20 to 40 feet above the hills surrounding the landfill.
Figure 6. Topographic Map of Kalamazoo County, Michigan. (The contour interval is 50 feet and indicates the elevation of the land above sea level).
Surface drainage is generally toward the closed depressions which may contain lakes and wetlands or may remain dry except during periods of high precipitation. To the east, the site slopes into a closed low area that includes Bonnie Castle Lake. West of South 4th Street, the land surface descends fairly abruptly to Dustin-Mud Lake at an altitude of about 850 feet, as much as 110 feet lower than the surface of the KL Landfill.

Runoff and Erosion

The surface of the landfill is relatively unstable due to the refuse. Settlement of the decaying refuse, frost, and other factors have resulted in areas of standing water and periodic alteration of drainage patterns over the filled areas. Fertilizer was applied in two applications to increase the vegetative cover on the landfill (Knoy, 1983), and bentonite was applied to reduce infiltration and erosion. Site inspections conducted after the site closure plan revealed that several leachate outbreaks or seeps existed at the site and that minor erosion was occurring on all faces of the landfill (Passero, 1981). Steep slopes on the northeast section of the landfill exhibit extensive erosion of the landfill cover. Sediment is being deposited in a small pond adjacent to the landfill as a result of this erosion. In
addition, where leachate springs have been observed in several areas of the landfill, vegetation appears to be reduced, indicating the potentially toxic nature of the leachate (Knoy, 1983).

Climate

The KL Landfill is about 35 miles east of Lake Michigan. Lake Michigan has considerable influence on the climate of Kalamazoo County, an effect often referred to as the "lake effect." The "lake effect," coupled with the prevailing westerly winds, tends to reduce extremes in the seasonal temperature fluctuations. Kalamazoo County is characterized by strong seasonal variations. Winters are characterized by short cold periods with maximum daytime temperatures remaining below freezing on about half of the days in January. Temperatures range from 27°F in February to 74°F in July. The average annual temperature for the area is 49.7°F (Allen, Miller, & Wood, 1972).

From 1940 to 1969 annual precipitation ranged from about 21 inches to over 43 inches; the mean annual precipitation level for Kalamazoo County is 34.27 inches. Table 1 lists the average monthly means of temperature and precipitation for the county. The most recent average monthly precipitation values obtained from the Kalamazoo Regional Psychiatric Hospital ranging from January, 1980
Table 1
Average Monthly Temperatures and Precipitation Levels for Kalamazoo County, Michigan

<table>
<thead>
<tr>
<th>Month</th>
<th>Precipitation (in.)</th>
<th>Temperature (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>January</td>
<td>2.16</td>
<td>24.7</td>
</tr>
<tr>
<td>February</td>
<td>1.75</td>
<td>26.8</td>
</tr>
<tr>
<td>March</td>
<td>2.62</td>
<td>35.5</td>
</tr>
<tr>
<td>April</td>
<td>3.45</td>
<td>48.7</td>
</tr>
<tr>
<td>May</td>
<td>3.54</td>
<td>59.3</td>
</tr>
<tr>
<td>June</td>
<td>3.76</td>
<td>69.2</td>
</tr>
<tr>
<td>July</td>
<td>3.37</td>
<td>72.9</td>
</tr>
<tr>
<td>August</td>
<td>2.78</td>
<td>71.7</td>
</tr>
<tr>
<td>September</td>
<td>2.95</td>
<td>64.4</td>
</tr>
<tr>
<td>October</td>
<td>3.00</td>
<td>53.8</td>
</tr>
<tr>
<td>November</td>
<td>2.65</td>
<td>40.0</td>
</tr>
<tr>
<td>December</td>
<td>2.24</td>
<td>28.8</td>
</tr>
</tbody>
</table>


to March, 1986 for Kalamazoo County are shown in Table 2. Climatic records have been collected at the Kalamazoo Regional Psychiatric Hospital since 1867, and are considered to be representative of conditions in the Kalamazoo area.
Table 2
Quarterly-Averaged, Average Monthly Precipitation Levels Recorded at the Kalamazoo Regional Psychiatric Hospital, Kalamazoo County, Michigan (1980-1986)

<table>
<thead>
<tr>
<th>Date</th>
<th>Average (in.)</th>
<th>Date</th>
<th>Average (in.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/80</td>
<td>2.43</td>
<td>3/83</td>
<td>3.31</td>
</tr>
<tr>
<td>6/80</td>
<td>6.98</td>
<td>9/83</td>
<td>7.75</td>
</tr>
<tr>
<td>9/80</td>
<td>3.00</td>
<td>10/83</td>
<td>1.92</td>
</tr>
<tr>
<td>12/80</td>
<td>1.68</td>
<td>3/84</td>
<td>3.79</td>
</tr>
<tr>
<td>3/81</td>
<td>Trace</td>
<td>6/84</td>
<td>0.69</td>
</tr>
<tr>
<td>6/81</td>
<td>3.63</td>
<td>9/84</td>
<td>6.37</td>
</tr>
<tr>
<td>9/81</td>
<td>5.50</td>
<td>3/85</td>
<td>3.42</td>
</tr>
<tr>
<td>12/81</td>
<td>1.20</td>
<td>9/85</td>
<td>3.23</td>
</tr>
<tr>
<td>3/82</td>
<td>4.28</td>
<td>3/86</td>
<td>1.08</td>
</tr>
<tr>
<td>9/82</td>
<td>1.29</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The greatest 24-hour rainfall was 5.20 inches recorded in 1914. The heaviest snowfall measured for a single day was 16.0 inches recorded on December 23, 1907 (Allen et al., 1972). The average seasonal snowfall is 69.7 inches; however, snowfall at the landfill site is slightly higher due to its location in the upland portion.
of the county, on the Kalamazoo Moraine (Passero, 1981).

Soils

Soils found in the vicinity of the KL Landfill were initially mapped and described in the Kalamazoo County Soil Survey (Austin, 1979). The most abundant soils in the landfill area are three phases of the Coloma series and the Spinks-Coloma phase (Figure 7). These soils, CoC, CoB, CoD and StE, are characterized by rapid permeabilities and low available water capacities. Of these, CoC, CoD, and StE are rated unsuitable for the development of landfill facilities. The soil located on the landfill proper is classified as a udipsamment (Ua), or disturbed soil. The other area soils include the Oshtemo and Houghton series.

The most extensive soil found in the area of the landfill is the Coloma loamy sand (CoC), with slopes ranging from 6-12%. This loamy sand is a rolling, somewhat well-drained soil commonly found on upland ridges and the sides of hills. Soil areas are generally irregular in shape and are long and narrow, ranging in size from 10-200 acres. The subsurface layer is a 7-inch thick dark brown loamy sand followed by a 44-inch thick light to medium yellowish-brown sand banded with a darker loamy sand. Surface runoff is rated as medium (Austin, 1979).
Figure 7. Soils Map of the KI Avenue Landfill Area (Adapted from Austin, 1979).
Figure 7—Continued

**SOIL LEGEND**

- **CoB**: COLOMA LOAMY SAND, 0-6% slopes
- **CoC**: COLOMA LOAMY SAND, 6-12% slopes
- **CoD**: COLOMA LOAMY SAND, 12-18% slopes
- **OsB**: OSHTEMO SANDY LOAM, 1-6% slopes
- **OsC**: OSHTEMO SANDY LOAM, 6-12% slopes
- **OsD**: OSHTEMO SANDY LOAM, 12-18% slopes
- **OsE**: OSHTEMO SANDY LOAM, 18-35% slopes
- **SpB**: SPINKS LOAMY SAND, 0-6% slopes
- **SpC**: SPINKS LOAMY SAND, 6-12% slopes
- **SpD**: SPINKS LOAMY SAND, 12-18% slopes
- **SpD**: SPINKS-COLOMA LOAMY SANDS, 18-35% slopes
- **Hs**: HOUGHTON AND SEBEWA SOILS, ponded
- **Ua**: UDIPSAMMENTS, level to steep
The second most common soil type is the Coloma loamy sand (CoB) with slopes ranging from 0-6%. It is a nearly level to undulating soil that is also somewhat well-drained and located on uplands and small ridges. The soil covers areas that are irregular in shape and range from 10 to 120 acres. The 10-inch thick surface layer is a dark brown loamy sand with a 32-inch thick subsurface layer of light to medium yellowish-brown sand. The deepest horizon, a yellowish-brown sand with bands of brown loamy sand, extends to a depth of 66 inches. Surface runoff is slow or medium and the soil’s major problems are susceptibility to dryness, soil blowing, and slope instability when excavated (Austin, 1979).

The Coloma loamy sand (CoD) with a slope from 12 to 18% is a hilly and somewhat well-drained soil found on upland ridges and slopes. The surface exposure is irregular, to long and narrow, ranging from 10 to 100 acres. The surface layer is a 6-inch thick dark brown loamy sand underlain by 35 inches of a light to medium yellowish-brown loamy sand. Surface runoff is medium and the soil is highly susceptible to erosion and dryness. The principal limitation is that steep slopes may cave in during excavations.

The Spinks-Coloma loamy sands (StE) have slopes ranging between 18-38%. This phase is characterized by
steep, well-drained and somewhat well-drained soils located on sandy ridges and escarpments. Soil areas are usually long and narrow ranging in size from 5 to 60 acres. The Spinks soil comprises 35-45% of the area, as does the Coloma soil. The Spinks soil is found in the lowland portions of the site, whereas the Coloma soil is found in the steeper areas. In certain areas of the map where the two soils are intricately mixed, and have not been distinguished, the unit is described as Spinks-Coloma (StE). Typically, the Spinks soil has a 5-inch thick surface layer of dark brown loamy sand, a 6-inch thick horizon of dark yellowish-brown loamy sand, and an 86-inch thick basal horizon composed of a yellowish-brown sand with bands of loamy sand. As part of this unit, the Coloma soil consists of 5 inches of dark brown sand followed by 28 inches of a light to medium yellowish-brown loamy sand. The greatest limitation of this soil is its steep slopes and rapid surface runoff.

The udipsamments (Ua) are generally level to steep, moderately well-drained to well-drained soils that have been disturbed. The soil surface exposures are usually irregular in shape and range in area from 5 to 30 acres. This unit includes sanitary landfills, flood plains, and lowlands that have been filled with various types of natural and manmade debris. The fill material is 1 foot
to several feet thick and is commonly covered with a sandy or loamy material. Permeability and the available water capacity are variable, and the degree of runoff depends on the slope.

The Oshtemo sandy loam (OsC) has between 6-12% slopes, is a rolling well-drained soil, and is usually found in upland areas. Soil exposures are irregular in shape and cover from 10 to 110 acres. The soil is predominantly composed of a sandy loam, but contains a 29-inch subsoil composed of loamy sand, overlying a sandy loam with a dark yellowish-brown sand base. Surface runoff is medium and slope is a major limitation.

The Oshtemo sandy loam (OsB) has slopes of 1-6%. It is a nearly level to undulating well-drained soil found on sandy upland plains. Soil areas are irregular in shape covering from 110 to 180 acres. The soil consists of about 19 inches of sandy loam with a 50-inch subsoil. The subsoil is divided from top to bottom into a sandy loam, a loamy sand, and a sand with bands of loamy sand. Surface runoff is slow to medium.

The Oshtemo sandy loams, OsC and OsB, have moderately rapid permeabilities with moderate available water capacities. These soils are rated as well-suited to the development of landfills. The most severe limitation is the tendency of the soil to cave during excavations. Two
minor soil problems are their susceptibility to erosion and midsummer dryness.

The Houghton and Sebewa soils (Hs), the Spinks loamy sand (SpB), and the Oshtemo sandy loam (OsE) are only found in small portions of the area.

The Houghton and Sebewa soils (Hs) are nearly level, extremely poorly drained soils that are found in flat depressed areas subject to frequent flooding. The Houghton soil is predominantly composed of brown to black muck, while the Sebewa soil is predominantly a black to gray loam. The principal limitation is the shallow water table at or near the surface.

The Spinks loamy sand (SpB) has 0-6% slopes and is a nearly level to undulating well-drained soil. It is found atop sandy uplands that range in area from 0 to 100 acres. Permeability is rapid, runoff is slow, and the available water capacity is low.

The Oshtemo sandy loam (OsE) has slopes ranging between 18-35%. The soil is a steep, well-drained soil found on sandy uplands and ridges, that range in area from 5 to 40 acres. It ranges in composition from a sandy loam near the surface to a sand at the base. Permeability is moderately rapid, surface runoff is rapid, and available water capacity is moderate.
CHAPTER II

GEOLOGY

Bedrock Geology

Kalamazoo County is located on the southwestern flank of the Michigan structural basin (Figures 8 & 9). The Paleozoic bedrock dips slightly to the northeast. Oshtemo Township is located in the northwestern portion of Kalamazoo County. In the southeastern quarter of the township, the bedrock surface is characterized by a ridge that reaches an elevation of more than 850 feet in Section 35 (Figure 10). The ridge is broken by a northwest-trending valley in the east-central portion of the township, Sections 1 and 12 (Passero, 1981). Shale, siltstone, and limestone members of the Mississippian Coldwater Formation underlie the glacial drift throughout Kalamazoo County except for the northeast corner (Figure 10). In the northeastern corner of the county, the Marshall Sandstone overlies the Coldwater Shale; however, the contact has not been well delineated (Ibrahim, 1970). The Coldwater Shale is relatively impermeable and forms an effective barrier to the downward migration of water in the glacial drift (Passero, 1981). The Coldwater Shale is
Figure 8. Geologic Map of Michigan Showing the Location of Kalamazoo County on the Southwestern Flank of the Michigan Structural Basin, and the Geographic Distribution of the Bedrock Units Across the Lower Peninsula of Michigan (Adapted from Martin, 1955).
Figure 9. Geologic Cross-section A-A' Through the Michigan Basin Illustrating the Layering of the Bedrock Units (Adapted from Martin, 1955).
Figure 10. Map of the Bedrock Surface Elevation (Adapted from Ibrahim, 1970).

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a usable source of groundwater in Kalamazoo County from only a few wells. However, the Marshall Sandstone is highly fractured and permeable and is used for residential wells in northeastern Kalamazoo County and elsewhere in Michigan (Ibrahim, 1970).

The Coldwater Shale is underlain by a thick shale sequence (550 feet) that is divided into two units known as the Ellsworth and Antrim Shales (Figure 11). These units directly underlie the drift in portions of Van Buren, Berrien, Cass, and St. Joseph counties. The Coldwater, Ellsworth, and Antrim Shales are all considered to be aquicludes in Kalamazoo County. A number of oil fields have been developed in the upper few feet of the Traverse Limestone which underlies these units (Passero, 1981).

**Regional Bedrock Topography**

The bedrock topography map of Kalamazoo County shows a prevailing westward slope (Figure 10), and a complex bedrock drainage system. The principal valleys drained, generally, trend east-west or north-south. These buried bedrock valleys were identified on Bouger gravity maps by Ibrahim (1970). The buried bedrock channels relate to a pre-Pleistocene drainage system. The channels were
Figure 11. Stratigraphic Column for Michigan Ranging From the Pleistocene Glacial Deposits Through the Devonian Dundee Limestone (Adapted from the Michigan Geological Survey).
subsequently modified by glaciers and glacial melt waters and are partially or completely filled with glacial and glaciofluvial sediments. Their surface expressions, with the exception of the Kalamazoo River Valley, are completely obliterated (Ibrahim, 1970).

The present bedrock topography in the Southern Peninsula of Michigan was produced mainly by the combined effects of preglacial erosion and ice sculpturing when the latest Wisconsinan ice sheet moved through the area, as well as by post-glacial erosional modification.

Bedrock Topography of Oshtemo Township

The elevation of the bedrock surface in Oshtemo Township ranges from less than 300 feet to over 850 feet above mean sea level (Figure 12). A prominent bedrock valley trends from southwest to northeast from sections 18 and 19 through sections 3 and 4 (Figure 12). An interpreted tributary of this major valley system extends southeastward to the southwest 1/4 of Section 22 and passes beneath, and to the west of, the KL Landfill site. This buried channel was delineated by well records and by earth resistivity surveys (Passero, 1981). The time of formation of this southeastward tributary and its relationship to the ice front had a profound effect on the type of glacial deposits left behind to fill it (Ibrahim,
Figure 12. Bedrock Topography Map of Oshtemo Township (Adapted from Passero, 1981).
Regional Pleistocene Geology

The glacial drift in Kalamazoo County was deposited during the Pleistocene Epoch. Wisconsinan deposits are the youngest and best preserved. Drilling records revealed the presence of a soil profile containing tree logs, brush stems, and muck or peat, which indicates Illinoian glaciation, but whether the Nebraskan and Kansan deposits have been preserved in Kalamazoo County is uncertain (Ibrahim, 1970).

Late Wisconsinan glaciation was characterized by the advance of the Michigan, Saginaw, and Erie lobes (Figure 13), into the Lake Michigan, Lake Huron, and Lake Erie basins (Mazola, 1962).

During the Wisconsinan recession of the ice sheet, the present moraines were deposited in concentrated groups. The general pattern of deposition is characterized by groups of several closely spaced moraines followed by a few moraines that are more widely spaced. The depositional pattern appears to be cyclic across the Midwest (Leverett & Taylor, 1915).

The Kalamazoo moraine and its accompanying outwash plain to the southeast, were deposited during a relatively stationary phase that occurred as the Lake Michigan Lobe
Figure 13. Illustration of the Advancing Ice Sheet and its Three Ice Lobes that Followed the Lake Michigan, Lake Huron, and Lake Erie Basins (Adapted from Leverett & Taylor, 1915).

retreated from the southeast to the northwest across the area. The moraine trends from the southwest to the northeast across the northwest corner of Kalamazoo County and is composed of two well-defined ridges separated by a narrow, yet nearly continuous, outwash apron (Figure 14). The width of each ridge varies between 1 and 4 miles (Ibrahim, 1970). It is during these periods of ice-margin equilibrium that the melt-water streams emanating from the ice sheets transport massive quantities of glacial debris to be deposited as outwash adjacent to and on the moraines. Typically, the surface is characterized by pits
Figure 14. Map of the Glacial Geology and Depositional Structures in Kalamazoo County, Michigan (Adapted from Schmaltz, 1978). (The Square Indicates the Location of the KL Landfill).
or depressions. These kettles and kettle lakes are also found in the morainal areas (Schmaltz, 1978). For example, near the KL Landfill, two such lakes are located on the Kalamazoo Moraine. These are now Bonnie Castle Lake and Dustin Lake.

As the Valparaiso Moraine was being formed, large volumes of glacial meltwater were forced to flow to the southwest between the Kalamazoo Moraine and the developing Valparaiso Moraine. This drainage pattern, referred to as the Kankakee torrent, drained all three ice lobes in southern Michigan. Meltwater created a drainageway from the Otsego-Plainwell area through Paw Paw to Dowagiac. It left a low relief plain with some minor lakes and streams locally divided into two units known as the Alamo and Gunn Plains (Figure 14) (Schmaltz, 1978).

Local Pleistocene Geology

Kalamazoo County bedrock is generally covered with drift ranging in thickness from less than 50 feet in areas along the Kalamazoo River Valley to more than 600 feet in the upland areas south and west of Kalamazoo (Figure 15). The KL Landfill is located within the "inner" crest of the Kalamazoo Moraine (Figure 16) above a north-trending bedrock ridge where the glacial drift is approximately 500 feet thick (Figure 17). The thickest drift deposits are
Figure 15. Map of Drift Thickness and Locations of the Main Buried Bedrock Channel Systems in Kalamazoo County, Michigan (Adapted from Smith, 1975 & Ibrahim, 1970).
Figure 16. Glacial Landforms of Kalamazoo County, Michigan (Adapted from Schmaltz, 1978). (Square Indicates the Location of the KL Landfill).
Figure 17. Thickness of Glacial Drift in Oshtemo Township, Kalamazoo County, Michigan (Adapted from Passero, 1981).
located where the Kalamazoo Moraine overlies bedrock valleys (Ibrahim, 1970).

Oscillation of the Lake Michigan Lobe resulted in the deposition of interbedded till and outwash deposits sometimes containing buried blocks of ice. In addition, the ice-contact material at the front of the ice was dissected by meltwater streams that eroded through the ridges at the margins of the till. The cyclic yet sporadic advances and retreats of the ice front, coupled with the breaks made by meltwater streams, resulted in discontinuous lenses of ice contact material being interbedded both laterally and vertically with the water-laid outwash sand and gravel deposits (Figure 18). Oshtemo Township contains 100 to 600 feet of vertically and laterally heterogeneous glacial materials forming a complex three dimensional package of till, outwash, glacial lake beds, and stream deposits with variable physical properties (Passero, 1981).

The texture of the glacial deposits, between the KL Landfill and Dustin Lake, were determined from 20 samples obtained from cable tool and rotary drilling of wells M-3A, 745 South 4th Street, and 632-34 South 4th Street. These samples were predominantly sand. Clay ranged from only 0-4%, 0-10%, and 0-24% clay, respectively, and gravel ranged from 3-18%, 13-38%, and 3-25%, respectively. Those
Figure 18. Geographic Distribution and Composition of the Glacial Sediments in Kalamazoo County, Michigan (Adapted from Shah, 1974).
analyses tended to correlate closely with the gamma ray logs for these wells. These data suggest that the glacial deposits here are predominantly coarse-grained, and that the fines are composed predominantly of silt as opposed to clay (Passero, 1981). Eight distinct glacial units (Figures 19 & 20) have been identified and traced by their physical characteristics as recorded by gamma ray logs, drillers' records, split-spoon samples, and well-cuttings (Passero, 1981). The units delineated in the area west of the KL Landfill from top to bottom are as follows:

1. Unit 1 is a till that is composed predominantly of silt with some clay and varying amounts of sand and gravel (Figure 21). It is exposed in areas of greater topographic relief; however, as in topographically low areas where monitor well M7 and M8 are located, the unit is missing. Thus, this unit is rather discontinuous over portions of the landfill area (Figure 22). The thickness of the unit ranges from 0 in M8 to about 30 feet in M-3A.

2. Unit 2 is an outwash deposit composed essentially of sand with greater quantities of gravel and minor, variable amounts of clay. This deposit varies in thickness from 20 feet in the well at 9060-62 West KL Avenue to 58 feet in the well at 8880 West KL Avenue.

3. Unit 3 is a till unit with some gravel and sand. This unit is also relatively discontinuous, and is
Figure 19. Geologic Map Indicating the Locations of the Cross-sections: A-A', B-B', C-C', and D-D' Across the KL Avenue Landfill Area in Oshtemo Township.
Figure 20. Geologic Cross-section A-A' Illustrating the Composition of the Glacial Deposits and the Delineation of the Upper Unconfined Aquifer (Unit 4) and the Lower Confined Aquifer (Unit 6).
CROSS-SECTION LEGEND

CLAY or SILT

SAND

GRAVEL

SANDY CLAY or SILT

GRAVELLY CLAY or SILT

CLAYEY SAND

GRAVELLY SAND

SANDY GRAVEL

SANDY CLAYEY GRAVEL

CLAYEY SANDY GRAVEL

SANDY GRAVELLY CLAY or SILT

GRAVELLY SANDY CLAY or SILT

CLAYEY GRAVELLY SAND

GRAVELLY CLAYEY SAND

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Figure 21. Geologic Cross-section B-B'.

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Figure 22. Geologic Cross-section C-C'.

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completely absent from the wells located at 9305 West KL Avenue. This unit ranges in thickness from 13 feet in M-3A, near the western edge of the landfill proper, to more than 60 feet in the well at 9060 West KL Avenue as the deposit thickens west of the landfill.

4. Unit 4a is a thick zone ranging from 30 to 145 feet. It is a glacial outwash unit, composed of sand and gravel, serving as the upper unconfined aquifer. It also contains a till unit with a discontinuous lake clay unit that ranges between 5 and 23 feet. This unit is regarded as a single continuous hydrologic entity.

Unit 4b is a bed of lake clay composed of silt and clay with less than 9% fine to medium sand. The unit is 5 feet thick at a well at 8880 West KL Avenue and thickens toward the KL Landfill. In well M-3A the deposit reaches a maximum thickness of about 10 feet.

Unit 4c is an outwash deposit that is separated from the shallow unconfined aquifer in the vicinity of South 4th Street. However, adjacent to the landfill, the unit is part of the aquifer unit.

5. Unit 5 is a till composed predominantly of clay and silt with some gravel and boulders, and nominal amounts of sand (Figure 23). It ranges in thickness from approximately 37 to 178 feet. The till is thick and continuous on the west side of the landfill site, but
Figure 23. Geologic Cross-section D-D'.

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thins to the east, as the outwash deposit becomes thicker. At monitor well M-3A the lower half of the well is outwash and the upper half is till.

In addition, a reddish-zone was penetrated in four of the wells drilled into Unit 5 west of the filled area. It was first observed in the well at 632-34 South 4th Street, but was later observed in the wells at 8900 West KL Avenue and at 745 South 4th Street. This is the aforementioned buried soil zone found on the Illinoian glacial deposits and stream deposits, formed during the Sangamon Interglacial. Since the wells penetrate this zone at different elevations, it would appear to reflect the topographic surface of the pre-Wisconsinan deposits. Due to the presence of sand and gravel immediately beneath the reddish-zone, and the presence of a lake clay at this depth in monitor well M3, it is believed that the soil zone also formed on a pre-Wisconsinan-post-Illinoian stream valley. This interpretation is supported by gamma-ray logs and electrical resistivity surveys.

6. Unit 6 is an outwash deposit essentially composed of sand and gravel with minor amounts of interspersed clay. This unit overlies bedrock at 9024-26 West KL Avenue where it is 10 feet thick. It reaches a maximum thickness of at least 30 feet in the well at 8794 West KL Avenue. Since this unit is in contact with bedrock in the
only well to penetrate bedrock, the thickness is probably controlled by the bedrock topography. This sand and gravel outwash deposit comprises the lower aquifer in the area.

Directly above the bedrock surface, in some locations, is the presence of an almost continuous layer of dense plastic blue clay that contains no evidence of varving or stratification. It does possess lenses of sand and gravel and includes blocks of the Coldwater Shale bedrock. This deposit is generally thicker in locations of low bedrock topography. For example, in some bedrock valleys this clay deposit may reach a maximum thickness of 50 feet. Even in places where the clay is relatively thick there is no gradual change from clay to till. The fact that the clay layer is notably thicker in bedrock depressions suggests that it may have been deposited under stagnant ice conditions by turbid ice-dammed and semi-stagnant water. The clay could also be an outwash deposit formed during a long interval of still stand conditions in the initial phase of Wisconsinan glaciation. In this case, the clay may be eroded rock flour produced during the early glacial advance (Ibrahim, 1970).

Incomplete well data beyond the area adjacent to the KL Landfill suggest that the upper till is relatively widespread, but locally discontinuous, whereas the outwash
sands and gravels of the shallow aquifer are continuous over a broad area. Information for the deeper units is lacking outside the area between the KL Landfill and South 4th Street, because the majority of the wells in this general area are not drilled deeper than the shallow aquifer or exceed depths of approximately 150 feet (Passero, 1981).
CHAPTER III

HYDROLOGY

Regional Surface Water

The configuration of the water table in Kalamazoo County reflects the movement of groundwater from topographically high areas to lowland areas. Discharge areas such as lakes, ponds, streams, and marshes are characterized by a water table at or near the land surface. Precipitation as well as groundwater supports the surface water system, and natural losses occur by evaporation, transpiration, and stream-flow out of the county. Additional losses are brought about by the influence of human activities on surface water supplies resulting in evaporation, consumption during manufacturing processes or exportation of water out of the area (Allen et al., 1972).

There are approximately 356 lakes and ponds in Kalamazoo County ranging in size from less than 1 acre to 2,050 acres. About 3% or 11,700 acres of the total area of Kalamazoo County is covered by lakes, while 3 to 5% of the total county area is covered by marshes. In addition, Kalamazoo County is dissected by 44 miles of main channel
streams and 321 miles of tributary streams (Figure 24) (Harrison, 1978).

Although the surface water resources of Kalamazoo County are extensive, little if any surface water is used directly for human consumption, due to the poor quality of the water. In accordance with Michigan water quality standards, the majority of the surface waters in this area contain significant levels of suspended and dissolved solids as well as coliform bacteria, while some locations also contain high levels of PCB's, sulfate, and chloride. A large portion of the surface water contamination is due to past waste disposal practices of the paper industry, pharmaceutical production, waste water treatment, and the manufacture of transportation equipment. However, the Kalamazoo Water Department does have several artificial groundwater recharge areas, where surface water is ponded and allowed to infiltrate enhancing the usable groundwater reserves. Several million gallons of water a year are withdrawn in Kalamazoo by industry for process and cooling water, and in rural areas by farmers for livestock and crop irrigation (Harrison, 1978).

Local Surface Water

The two dominant surface water features in the vicinity of the KL Landfill are Bonnie Castle Lake to the
Figure 24. Surface Water in Kalamazoo County, Michigan (After Allen et al., 1972).
northeast and Dustin Lake to the west. A recent study (Hobin, in preparation) of lake levels, static water levels, lake depths, and water quality data related the lakes to the groundwater flow system. Although the exact depth of Bonnie Castle Lake and Dustin Lake are not known, accumulated data suggest that Bonnie Castle Lake is a perched recharge lake and Dustin Lake is a discharge or flow-through lake. At the southern edge of the landfill property, there are two ponds that receive runoff from the landfill. Their water levels vary seasonally depending on the immediate runoff conditions (Passero, 1981).

Groundwater Flow System

The unconsolidated glacial and stream deposits of Kalamazoo County are predominantly composed of sand and gravel with occasional lenses of fine sand, silt, and clay. These deposits are highly permeable, yield substantial quantities of water to wells, are the main aquifers for the area, and form the only significant groundwater reservoirs (Allen et al., 1972). The majority of Kalamazoo County is underlain by a water-table or unconfined aquifer, which forms the upper aquifer (Figure 25). Rather than being a single interconnected aquifer that exists over a wide area, it is a series of near-surface sand and gravel deposits that are separated by
Figure 25. Map Showing the Locations of the Upper and Lower Aquifers in Kalamazoo County, Michigan (Adapted from Jones & Henry, 1972).
clay-rich deposits (Figure 26). Water infiltrates readily from the land surface downward into the upper aquifer in some areas, but in other areas the surface is covered with a relatively thin, clay-rich glacial layer that slows the downward migration of the water (Straw, 1978). The two main sources of water to the aquifers are precipitation and surface water. Most recharge occurs during seasons of low evapotranspiration such as November through May in Kalamazoo County (Allen et al., 1972).

A major portion of Kalamazoo County is underlain by several lower confined aquifers (Figure 26). In many areas the confining layers, which consist predominantly of fine sand, silt, and clay, are not completely impermeable and contain lenses of well-sorted coarse materials of high permeability such as sand and gravel (Figure 26). These semipermeable confining layers may allow water to be drawn through them during pumping. Recharge of the lower confined aquifers is less direct than for unconfined aquifers, and may occur, in areas where the confining layer or layers are discontinuous. However these confining layers, over the aquifers, keep them more protected from contamination than unconfined aquifers, but since recharge is slower, overdrafts due to pumping are more likely to become a problem. Generally, the unconsolidated deposits in portions of Kalamazoo County
Figure 26. Hydrologic Cross-section Depicting the Generalized Nature of the Aquifer System in Kalamazoo County, Michigan (Adapted from Allen et al., 1972).
may be separated into approximately four units: (1) an upper aquifer, (2) a semi-confining layer or aquitard, (3) a lower aquifer, and (4) a bedrock confining layer (Figure 27) (Straw, 1978).

In Kalamazoo County, the average saturated thickness of the glacial deposits ranges from 0 to more than 140 feet in the upper aquifer and from 0 to 160 feet in the lower aquifer. Due to the variation in sorting and stratification the unconsolidated deposits vary in permeability both vertically and horizontally. Generally the transmissivity of the upper aquifer ranges from less than 20,000 gpd/ft to more than 140,000 gpd/ft. In the vicinity of the KL Landfill, the transmissivity of the upper aquifer is approximately 60,000 gpd/ft (Allen et al., 1972).

Regional Groundwater Flow

The depth to groundwater in Oshtemo Township ranges from less than 5 feet in the northwest corner of the Township beneath the Alamo Plain to more than 120 feet beneath the highest elevations of the moraine. A regional map of the static water levels (Figure 27) recorded for Kalamazoo County illustrates that the water-table surface generally conforms to the regional surface topography.
Figure 27. Water-table Contour Map Showing the Generalized Regional Flow Patterns for Kalamazoo County, Michigan (Adapted from Allen et al., 1972).
The regional groundwater divide follows the north-northeast trend of the crest of the Kalamazoo Moraine. Regional groundwater flow in Oshtemo Township is predominantly to the northwest and southeast away from the divide at a gradient of approximately 20 to 40 feet/mile (Figure 28). The KL Landfill site is located just west of this north-northeasterly trending regional groundwater divide, and flow beneath the landfill is to the west and northwest. Water-table contours decrease in elevation from approximately 900 feet along the crest of the divide to approximately 740 feet beneath the Alamo Plain to the northwest, to approximately 750 feet adjacent to the Kalamazoo River to the northeast, and to about 840 feet beneath the outwash plain to the southwest.

Local Groundwater Flow

Depths to static water level in the vicinity of the KL Landfill range from 23.5 feet in TW3 on the landfill property to 138 feet beneath a north-trending topographic high in the vicinity of the intersection of South 4th Street and West KL Avenue. Generally, the depth to static water level increases west of the KL Landfill and conforms to the topography. Elevations of static water levels on the landfill appear to represent a closed high with a maximum measured elevation of about 888 feet (Figure 29).
Figure 28. Regional Potentiometric Surface and Groundwater Flow Directions in Oshtemo Township (Adapted from Allen et al., 1972).

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Figure 29. Map of Static Water Levels Illustrating the Local Groundwater Flow Patterns as Influenced by the KL Landfill (Adapted from Passero, 1981).
It is possible that the high static water levels recorded at the landfill represent mounding of groundwater beneath the filled area. The mounding beneath the landfill proper is caused by higher permeabilities inducing greater recharge within the fill and cover material as opposed to the surrounding glacial deposits (Figure 30). Depth to groundwater is approximately 25-100 feet beneath the landfill and generally increases radially away from the landfill. Due to this mounding, groundwater appears to be moving away from the landfill in all directions with more minor components of flow to the south, north, and east as well (Passero, 1981).

On the west margin of the landfill, the local groundwater gradient reaches approximately 200 feet/mile. The contours of static water levels to the west of the landfill, however, also show pronounced irregularities paralleling West KL Avenue trending toward Dustin Lake. The average groundwater gradient along this linear zone is approximately 80 feet/mile. This feature has been interpreted to coincide with a buried stream channel that was cut into the surface of the till confining layer (Unit 5) during an interglacial episode. The channel is just north of and almost parallel to KL Avenue. The more permeable deposits left by subsequent glacial activity are thicker along this channel than in the surrounding area.
Figure 30. Diagram Illustrating the Process of Groundwater Mounding at a Landfill Site (Adapted from Freeze & Cherry, 1979).
Since the channel is filled with more permeable deposits, it may serve as a conduit for contaminants as reflected on isoconcentration maps (Passero, 1981).

Constant head and falling head permeability tests or hydraulic conductivity tests were run on 32 disturbed cable tool samples from well M-3A on the western edge of the landfill. Permeabilities in the shallow unconfined aquifer range from $4.1 \times 10^{-2}$ cm/sec to $7.9 \times 10^{-3}$ cm/sec. The average permeability value is $2.0 \times 10^{-2}$ cm/sec. Permeabilities of the underlying till range from $0.9 \times 10^{-6}$ cm/sec to $5.7 \times 10^{-2}$ cm/sec. Porosity is 25-50%.

Using a groundwater gradient west of the site of 80 feet/mile, the maximum flow velocities are estimated to range between 2.84 feet/day to 5.95 feet/day. The estimated maximum velocity of flow in the shallow aquifer west of the landfill is 5.95 feet/day. The average linear velocity to the northwest of the landfill is 1.76 feet/day. Additionally, the specific capacities measured for the shallow wells at 632-34 and 710-12 South 4th Street are consistent with the hydraulic conductivities determined in the lab; however, the specific capacities from these two wells are higher than most in the area. The specific capacities measured from the deep wells indicate that these values are much lower for the deep aquifer than for the shallow aquifer; but it should be
noted that the deep wells were pumped for longer periods of time (Passero, 1981).
CHAPTER IV

WATER QUALITY

Groundwater Monitoring Program

The Environmental Health Division of the Kalamazoo County Health Department and the Michigan Department of Natural Resources staff have been monitoring groundwater quality near the KL Landfill since 1975. Between 1975 and 1979, the county collected groundwater samples from 90 domestic wells. Groundwater contamination was first identified in February of 1976, when the Kalamazoo County Health Department detected odors and taste in four domestic wells adjacent to the site. Five onsite test wells were drilled with hollow stem augers in 1977. Between 1979 and 1980, 9 monitoring wells were drilled resulting in a total of 14 monitoring wells both on and off the landfill site (Figure 31). The test wells were located as monitoring wells, whereas the M series wells were based on health considerations and a preliminary hydrogeologic investigation. The casings of these wells are galvanized steel with stainless steel screens and were equipped with hand-operated, deep-rod pitcher pumps.

70
Figure 31. Map of the Well Locations Sampled at the KL Landfill (Adapted from Passero, 1981).
It should be noted that in order to obtain accurate organic and inorganic chemical data from a leachate plume such as the one at the KL Landfill, extreme care in sampling and analysis must be taken. Proper sampling procedures, for this type of situation should include exclusion of air during sampling, in-line analysis of unstable constituents, collection of samples in \( N_2 \)-flushed containers, cooled sample storage, and rapid analysis (Dodge & Francis, 1986). Contact with air may result in a reduction of the volatile constituents in the sample, and a variety of chemical reactions may also occur within the water sample which could alter the original site concentration levels. Although samples were collected following EPA standard procedures, the criteria of air exclusion and in-line analysis were not met, which is common for general groundwater sampling programs. As a result, and because several useful non-standard parameters were not measured, several assumptions must be made in order to interpret the chemical data obtained from the KL Landfill site (Kehew, Passero, & Rudder, 1988).

All of the wells at the KL Landfill site monitor the upper or shallow aquifer, except monitor well M3-A, which is a deep well. Additionally, 10 deep domestic wells were installed in the area north of West KL Avenue and the area along South 4th Street. The deep wells range in depth from
about 300 to 415 feet. Shortly after the deep wells were installed, extremely low concentrations of various parameters including phenols were detected within the deep domestic wells. However, none of these data will be considered in this study. According to the Kalamazoo County Health Department, the low levels of phenols and other parameters found in the deep wells resulted from the introduction of contaminants from the upper aquifer into the lower aquifer during well drilling. Since these deep wells were purged, they showed non-detectable levels of these various contaminants (Passero, 1981).

Five test wells, 9 monitoring wells, and 20 domestic wells were sampled in the 1980 monitoring program. A total of 156 water samples were collected quarterly in March, June, September, and December and were analyzed for 18 parameters including volatile chlorinated hydrocarbons. In 1981, about 22 shallow private residential wells, 12 deep private residential wells, 4 test wells, and 8 monitoring wells were sampled quarterly, while in 1982 and 1983 these wells were sampled semi-annually in March and September by the county and the Department of Natural Resources. The shallow residential wells sampled are generally less than 200 feet deep (Figure 31). Analysis of the water samples was done by the Michigan Department of Natural Resources and by a private laboratory (Passero,
1984).

In 1984 groundwater samples were collected in March and September, but no samples were collected in December. Additionally, the chemical data obtained in June of that year were extremely limited and of little use in the chemical interpretation. The 1985 groundwater samples were collected in March and September only, and the last set of chemical data used in this study was collected in March of 1986. A total of 19 sets of sampling data was collected from 1980 to 1986. From 1981 to 1986, at least 23 parameters were monitored including inorganics and several volatile organic compounds.

General Laboratory Methods

The U. S. Environmental Protection Agency (USEPA) standard methods used by the private laboratory to detect the various synthetic organic chemicals in the water samples were EPA Purge and Trap Methods 601 and 602 using a Flame Ionization Detector (FID) and Hall Electrolytic Conductivity. The backup method used was EPA Method 624 using a Tracor 590 Gas Chromatograph (GC) coupled with a Finnigan Mass Spectrometer. The GC carrier gas used was helium. The general detection limit for the volatile organics was 1 ug/L except for methylene chloride which had a detection limit of 10 ug/L (Bouma, personal
Initially in 1980, the Michigan Department of Natural Resources decided that the water samples collected would be scanned for certain specific synthetic organic chemicals. It wasn't until March, 1984 that the laboratory was requested to perform complete organic scans of the water samples (Bouma, personal communication, 1990). At this time, the water soluble organic chemicals such as the alcohols, ketones, and ethers were first detected. These non-halogenated non-aromatic compounds had a detection limit of 100 ug/L. Duplicate samples were run when available from the Health Department and the Department of Natural Resources. The cis-1,2-dichloroethene and trans-1,2-dichloroethene were delineated by using a Resteck RX-502.2 Column and mass spectrometry (Bouma, personal communication, 1989).

Organic Chemical Data

The synthetic organic chemicals that were monitored regularly from March, 1980 to March, 1986 are listed with a summary of their concentration ranges for each well in Table 3. Xylenes and ethylbenzene were detected in a few wells from March, 1984 to March, 1986 (Table 4). Both the xylenes and ethylbenzene ranged from non-detectable levels to maximum concentration levels of 220 ug/L.
<table>
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<tr>
<th>Chemical Name</th>
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<th>TV3</th>
<th>TV4</th>
<th>TV6</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
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<td>100-5,750</td>
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<td>27-ND</td>
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<td>2-160</td>
<td>ND</td>
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<td>443</td>
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<td>37-2</td>
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<td>49-HD</td>
<td>6,250-HD</td>
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</table>

* NS - Not sampled.
Table 3

**Organic Chemical Concentrations in Wells Sampled at the KL Landfill, 1980-1986 (ug/L)**

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<th>H6</th>
<th>H1</th>
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<td>ND</td>
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<td>ND</td>
<td>73-ND</td>
<td>* HS</td>
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<th>Chemical Name</th>
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<td>ND</td>
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<td>120-400</td>
<td>650-720</td>
<td>180-780</td>
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<td>ND</td>
<td>2,100-7,500</td>
<td>550-550</td>
<td>ND</td>
<td>37-170</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>2-Propanone (Acetone)</td>
<td>ND</td>
<td>ND</td>
<td>3,300-19,000</td>
<td>3,000-5,400</td>
<td>ND</td>
<td>33-170</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>4-Methyl 2-pentanone</td>
<td>ND</td>
<td>ND</td>
<td>590-7,000</td>
<td>100-2,600</td>
<td>ND</td>
<td>18-300</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Xylene</td>
<td>ND-5</td>
<td>ND-4</td>
<td>10-11</td>
<td>ND</td>
<td>43-220</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>ND</td>
<td>4-7</td>
<td>ND-4</td>
<td>ND-7</td>
<td>ND</td>
<td>27-31</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Ethyl ether</td>
<td>8-9</td>
<td>70-81</td>
<td>86-110</td>
<td>21-97</td>
<td>ND</td>
<td>38-110</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

Table 4
Ranges of Additional Organic Chemical Data Collected at Xel Landfill from March, 1984 - March, 1986

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### Table 4

Ranges of Additional Organic Chemical Data Collected at the KL Landfill From March, 1984 - March, 1986 (ug/L)

<table>
<thead>
<tr>
<th></th>
<th>H4</th>
<th>H5</th>
<th>H6</th>
<th>TW1</th>
<th>TW2</th>
<th>TW3</th>
<th>TW4</th>
<th>TW5</th>
<th>263</th>
<th>710</th>
<th>745</th>
<th>8710</th>
<th>8794</th>
</tr>
</thead>
<tbody>
<tr>
<td>100-1,300</td>
<td>ND</td>
<td>HD-2,400</td>
<td>ND</td>
<td>ND</td>
<td>11-12</td>
<td>ND-9,999</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>60-260</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>100-780</td>
<td>ND</td>
<td>64-290</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND-4,300</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>HD-180</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>100-16,000</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>2,400-30,000</td>
<td>HD</td>
<td>ND</td>
<td>ND-2,100</td>
<td>3,400-9,100</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>150-330</td>
<td>HD</td>
<td>73-500</td>
<td>HD</td>
<td>HD</td>
<td>ND</td>
<td>HD-1,700</td>
<td>HD</td>
<td>ND</td>
<td>HD-180</td>
<td>HD-290</td>
<td>HD</td>
<td>HD</td>
<td>ND</td>
</tr>
<tr>
<td>150-500</td>
<td>HD</td>
<td>ND-37</td>
<td>HD</td>
<td>HD</td>
<td>HD</td>
<td>2,700-4,900</td>
<td>HD-110</td>
<td>HD-120</td>
<td>170-750</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td>100-5,400</td>
<td>HD</td>
<td>33-170</td>
<td>HD</td>
<td>HD</td>
<td>HD</td>
<td>89-10,000</td>
<td>HD-69</td>
<td>HD-1,700</td>
<td>1,600-2,300</td>
<td>HD</td>
<td>HD-41</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td>100-2,600</td>
<td>HD</td>
<td>10-300</td>
<td>HD</td>
<td>HD</td>
<td>ND</td>
<td>1,900-3,000</td>
<td>ND</td>
<td>HD</td>
<td>510-1,300</td>
<td>HD-130</td>
<td>ND</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td>ND</td>
<td>HD</td>
<td>43-220</td>
<td>HD</td>
<td>HD</td>
<td>ND</td>
<td>33-42</td>
<td>ND</td>
<td>ND</td>
<td>HD-26</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td>ND-7</td>
<td>HD</td>
<td>27-31</td>
<td>ND</td>
<td>HD</td>
<td>HD</td>
<td>8-10</td>
<td>ND</td>
<td>HD</td>
<td>ND-220</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td>21-97</td>
<td>HD</td>
<td>38-110</td>
<td>ND</td>
<td>HD</td>
<td>ND</td>
<td>19-3,400</td>
<td>ND</td>
<td>ND</td>
<td>52-180</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td></td>
</tr>
</tbody>
</table>

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Several organics were added to the monitoring program in March, 1984 (Table 4) resulting in a total of 30 synthetic organic parameters being monitored at the site. This additional group of organic chemicals includes several alcohols, ketones, arenes, and an ether. The specific organic chemicals that were added to the program, accompanied by a summary of the monitoring data, are shown in Table 4. Several additional organic chemicals found in the groundwater at the site, but appearing in only a few wells at low or insignificant levels, are as follows: methane, 1,1-dichloroethene, butanol, pentanol, dichlorofluoromethane, and 2-butanol.

One additional set of monitoring data, was acquired during a recent EPA investigation of the KL Landfill site beginning on January 18, 1987. The groundwater samples were collected on January 26, 27, and 28, 1987. A summary of these recent organic chemical data is shown in Table 5. These data were later used to substantiate some of the initial findings and conclusions drawn from the earlier sets of monitoring data.

The EPA split samples with Dames and Moore from M1-M9, and a newly installed deep and shallow monitoring well. These samples were collected and stored according to USEPA specifications and were sent to Hazelton Labs in Madison, Wisconsin for complete organic and inorganic
Table 5
Ranges of Recent Organic Chemical Data Obtained From the KL Landfill on January 26-28, 1987 (ug/L)

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>M1</th>
<th>M3</th>
<th>TW4</th>
<th>M7</th>
<th>M9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene chloride</td>
<td>ND</td>
<td>ND</td>
<td>ND-560</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>1,1-Dichloroethane</td>
<td>ND-8</td>
<td>ND-14</td>
<td>ND-720</td>
<td>ND-43</td>
<td>190-210</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>ND</td>
<td>ND</td>
<td>ND-21</td>
<td>ND-22</td>
<td>120-130</td>
</tr>
<tr>
<td>Chloroethane</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND-22</td>
</tr>
<tr>
<td>trans-1,2-Dichloroethene</td>
<td>ND-7</td>
<td>ND-5</td>
<td>ND</td>
<td>ND-46</td>
<td>ND-8</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND-120</td>
</tr>
<tr>
<td>2-Propanone (Acetone)</td>
<td>ND</td>
<td>6,100-8,700</td>
<td>ND-17,000</td>
<td>ND</td>
<td>2,700-2,800</td>
</tr>
<tr>
<td>2-Butanone</td>
<td>ND</td>
<td>1,300-6,000</td>
<td>ND-2,300</td>
<td>ND</td>
<td>150-530</td>
</tr>
<tr>
<td>4-Methyl-2-pentanone</td>
<td>ND</td>
<td>220-630</td>
<td>ND</td>
<td>ND</td>
<td>230-390</td>
</tr>
<tr>
<td>Benzene</td>
<td>ND</td>
<td>ND</td>
<td>ND-460</td>
<td>ND-6</td>
<td>ND-24</td>
</tr>
<tr>
<td>Toluene</td>
<td>ND</td>
<td>ND</td>
<td>ND-1,100</td>
<td>ND</td>
<td>ND-3</td>
</tr>
</tbody>
</table>
analyses. The samples were collected using a Bennett pump that was decontaminated with potable and distilled water. All bailer decontamination was carried out by doing an Alconox wash, a tap water rinse, a distilled water rinse, an isopropyl alcohol rinse, and a final distilled water rinse (Dames & Moore, 1987).

**Inorganic Chemical Data**

The inorganic parameters that were monitored quarterly over the entire sampling interval from March, 1980 to March, 1986 are: pH, iron, lead, total chromium, chemical oxygen demand (COD), and specific conductance. The pH of the groundwater ranged from a low of 6.0 to a maximum of 9.6. The average pH value of the groundwater in the vicinity of the landfill site was 7.2. The chemical oxygen demand ranged from lows of 8 or 9 mg/L to a high of 4,960 mg/L. The COD ranges per well over the entire monitoring period from March, 1980 to March, 1986 are listed in Table 6. The specific conductance ranged from 260 to 4,320 umhos/cm from well to well between March, 1980 and March, 1986. The specific conductance ranges from 1980 to 1986 per well at the site are shown in Table 7. The chloride levels ranged from 1 to 660 mg/L in each well across the site, and Table 8 lists the chloride concentration ranges found in each well, over the 7-year
Table 6
COD Ranges for Selected Wells at the KL Landfill Site
From March, 1980 to March, 1986

<table>
<thead>
<tr>
<th>Monitor Well # / Well Address</th>
<th>COD Ranges (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>691 S. 4&lt;sup&gt;th&lt;/sup&gt; St.</td>
<td>332 - 1,500</td>
</tr>
<tr>
<td>710 S. 4&lt;sup&gt;th&lt;/sup&gt; St.</td>
<td>83 - 660</td>
</tr>
<tr>
<td>8383 W. Main St.</td>
<td>4 - 23</td>
</tr>
<tr>
<td>8835 Almena Dr.</td>
<td>5 - 21</td>
</tr>
<tr>
<td>M1</td>
<td>68 - 540</td>
</tr>
<tr>
<td>M2</td>
<td>48 - 853</td>
</tr>
<tr>
<td>M3</td>
<td>384 - 2,593</td>
</tr>
<tr>
<td>M4</td>
<td>47 - 1,200</td>
</tr>
<tr>
<td>M5</td>
<td>7 - 85</td>
</tr>
<tr>
<td>M6</td>
<td>5 - 80</td>
</tr>
<tr>
<td>M7</td>
<td>4 - 67</td>
</tr>
<tr>
<td>M8</td>
<td>240 - 810</td>
</tr>
<tr>
<td>TW1</td>
<td>6 - 260</td>
</tr>
<tr>
<td>TW3</td>
<td>5 - 24</td>
</tr>
<tr>
<td>TW4</td>
<td>1,060 - 4,960</td>
</tr>
<tr>
<td>TW6</td>
<td>10 - 680</td>
</tr>
</tbody>
</table>

monitoring interval. Since the first set of organic chemical data used in this study was collected in March of 1980, the total organic carbon (TOC) data acquired from
## Table 7
Specific Conductance Ranges for Selected Wells at the KL Landfill Site From March, 1980 to March, 1986

<table>
<thead>
<tr>
<th>Monitor Well #/Well Address</th>
<th>Specific Conductance Ranges (umhos/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>691 S. 4th St.</td>
<td>1,440 - 1,700</td>
</tr>
<tr>
<td>710 S. 4th St.</td>
<td>500 - 1,080</td>
</tr>
<tr>
<td>920 S. 4th St.</td>
<td>540 - 730</td>
</tr>
<tr>
<td>8710 KL Ave.</td>
<td>370 - 590</td>
</tr>
<tr>
<td>8794 KL Ave.</td>
<td>*NS - 630</td>
</tr>
<tr>
<td>8383 W. Main St.</td>
<td>435 - 510</td>
</tr>
<tr>
<td>8835 Almena Dr.</td>
<td>400 - 505</td>
</tr>
<tr>
<td>M1</td>
<td>410 - 700</td>
</tr>
<tr>
<td>M2</td>
<td>440 - 870</td>
</tr>
<tr>
<td>M3</td>
<td>1,200 - 2,550</td>
</tr>
<tr>
<td>M4</td>
<td>360 - 1,200</td>
</tr>
<tr>
<td>M5</td>
<td>285 - 400</td>
</tr>
<tr>
<td>M6</td>
<td>460 - 1,460</td>
</tr>
<tr>
<td>M7</td>
<td>530 - 890</td>
</tr>
<tr>
<td>M8</td>
<td>945 - 1,820</td>
</tr>
<tr>
<td>TW1</td>
<td>260 - 570</td>
</tr>
<tr>
<td>TW3</td>
<td>240 - 710</td>
</tr>
<tr>
<td>TW4</td>
<td>1,950 - 4,320</td>
</tr>
<tr>
<td>TW6</td>
<td>260 - 660</td>
</tr>
<tr>
<td>Monitor Well #/Well Address</td>
<td>Chloride Ranges (mg/L)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>691 S. 4th St.</td>
<td>111 - 295</td>
</tr>
<tr>
<td>710 S. 4th St.</td>
<td>27 - 150</td>
</tr>
<tr>
<td>920 S. 4th St.</td>
<td>15 - 47</td>
</tr>
<tr>
<td>8710 KL Ave.</td>
<td>9 - 41</td>
</tr>
<tr>
<td>9033 KL Ave.</td>
<td>130 - 265</td>
</tr>
<tr>
<td>9067 KL Ave.</td>
<td>17 - 52</td>
</tr>
<tr>
<td>8383 W. Main St.</td>
<td>3 - 13</td>
</tr>
<tr>
<td>8835 Almena Dr.</td>
<td>ND - 13</td>
</tr>
<tr>
<td>M1</td>
<td>17 - 82</td>
</tr>
<tr>
<td>M2</td>
<td>19 - 64</td>
</tr>
<tr>
<td>M3</td>
<td>73 - 470</td>
</tr>
<tr>
<td>M4</td>
<td>13 - 155</td>
</tr>
<tr>
<td>M5</td>
<td>ND - 10</td>
</tr>
<tr>
<td>M6</td>
<td>8 - 290</td>
</tr>
<tr>
<td>M7</td>
<td>ND - 150</td>
</tr>
<tr>
<td>M8</td>
<td>56 - 470</td>
</tr>
<tr>
<td>TW1</td>
<td>ND - 24</td>
</tr>
<tr>
<td>TW3</td>
<td>8 - 137</td>
</tr>
<tr>
<td>TW4</td>
<td>48 - 660</td>
</tr>
<tr>
<td>TW6</td>
<td>4 - 20</td>
</tr>
</tbody>
</table>
November, 1978 to March, 1980 were essentially unusable in this study.

Surface Water Monitor Program and Data

The two prominent surface water features in the area, Dustin Lake and Bonnie Castle Lake, were also monitored to determine if the KL Landfill had any impact on their water quality. A preliminary series of water quality tests did not indicate a water quality problem in Bonnie Castle Lake. However, in November, 1978 and May, 1979, a more extensive water quality analysis of Bonnie Castle Lake was conducted. Samples were analyzed for sulfate, phenols, TOC, TDS, 8 metals, COD, phosphorus, and nitrate. Phenols were reported to be 5.6 and 2.2 ug/L and was the only parameter that exceeded the 1 ug/L limitation set by the Kalamazoo County Health Department. The phenols test results indicated a potential for contamination in Bonnie Castle Lake. Because the sampling locations were on the far side of the lake away from the KL Landfill, and because samples were not analyzed for volatile hydrocarbons, it is difficult to determine the actual degree of contamination. Dustin Lake water quality analyses indicate that this lake is probably not impacted. However, the chemical analyses of water samples taken from M5 located about 375 feet east of Dustin Lake, have shown
low levels of the phenols. These results indicate that Dustin Lake could possibly receive contaminants from the KL Landfill (Knoy, 1983).
CHAPTER V

CHEMISTRY OF THE LEACHATE PLUME AND DISTRIBUTION OF THE CONTAMINANTS

Movement and Distribution of the Contaminants in the KL Landfill Leachate Plume

The two organic chemicals found at the highest concentration levels in groundwater at the KL Landfill site are the phenols and toluene. The phenols levels were determined by using the Total Phenols Test as specified by the U. S. Environmental Protection Agency (USEPA). The phenols values, therefore, represent a combination of all phenolic compounds as well as the possibility of some compounds that may interfere with the phenols reading (Bouma, personal communication, 1987). The two inorganic chemicals found at the highest detectable concentration levels in the plume are iron and chloride. The three most highly contaminated wells at the landfill site are TW4, M3, and M8.

The contaminant plume is predominantly coincident with a portion of the interpreted buried channel at the site. This buried channel, which is filled with the sand and gravel of the upper aquifer, tends to divert local groundwater flow and the subsequent contaminant migration.
from the landfill in a southwesterly direction (Passero, 1981). The maximum westerly extent of the contaminant plume is M5 about 375 feet east of Dustin Lake. Phenols, iron, lead, and chromium have been detected in M5 (Figure 32).

The inorganic chemical contaminant distribution also indicates a secondary northwesterly flow path (Figure 33). It is not known whether the northwest flow path is the result of another buried channel or whether the contaminant movement in this direction is controlled by the regional hydraulic gradient. The only organic chemical contaminant that followed this northwesterly flow path is the phenols, which were detected from ND-36 ug/L at 25 South 4th Street. However, organic chemical contaminant levels do continually change along flow paths by dispersion, microbial degradation, biotransformation, and complex chemical and physical interactions with aquifer solids (Kehew et al., 1988). These factors could limit the organic chemical migration along the northwesterly flow path. An increase in redox potential along this northwesterly extension of the plume is indicated by an increase in sulfate concentration from 5.0 mg/L at TW4 to 16 mg/L at MW-9 (Kehew et al., 1988). This increase may be due to mixing of contaminated water with fresh, oxygen-rich, uncontaminated water at the periphery.
Figure 32. Isoconcentration Map of the Phenols (March, 1982). (Only Selected Concentrations are Shown).
Figure 33. Isoconcentration Map of Iron (May, 1987) Showing Iron Concentrations in the Wells Sampled (Kehew et al., 1988).
of the plume resulting in aerobic conditions that would rapidly degrade the organic chemicals preventing their movement to the northwest.

Sulfate concentrations do not increase along the southwesterly trend of the plume until a greater distance from the landfill has been attained. The organic chemical contaminants also persist for longer periods of time to the southwest and move further downgradient following the buried channel. It is possible that the wells along this southwesterly flow path are screened closer to the center of mass of the plume and would be less likely to be influenced by mixing with fresh groundwater at the edge of the plume (Kehew et al., 1988). It has been determined in previous laboratory studies that organic chemicals are rapidly degraded aerobically, while anaerobic degradation occurs more slowly (Wilson, Bledsoe, Kampbell, Wilson, Armstrong, & Sammons, 1987). If those wells are screened closer to the center of mass of the plume only anaerobic degradation would be occurring allowing persistence of the organic chemicals within the channel and anoxic conditions further downgradient.

The high organic load leached from the refuse controls the consumption of oxygen and other available electron acceptors in the groundwater at the KL Landfill site. Anaerobic degradation of organic matter is
accomplished by reactions which reduce nitrate, iron, and manganese compounds from the aquifer solids and sulfate. Anoxic conditions are maintained in the leachate plume beneath the landfill and for some distance along the flow path. Detectable H₂S, an indicator of highly reducing conditions, was found only in TW4, whereas wells M8 and M4 were below the 0.5 mg/L detection limit for this parameter. Depression of the redox potential to the level of sulfate reduction at TW4 is indicated by the low concentration of sulfate, the detectable concentration of H₂S, and the high concentrations of ammonium, iron, and manganese, which are produced by redox reactions occurring at redox potentials above that of sulfate reduction (Kehew et al., 1988). Lowering of the redox potential below sulfate reduction is likely, and high dissolved methane concentrations were measured indicating methanogenesis (Fahle, in preparation).

The leachate plume extends at least to a depth of 72.5 ft below static water level in M8; however, the plume most likely extends to the till (Unit 5). During the period of analysis, there was only one monitor well nest between the landfill and South 4th Street. This well nest includes monitor wells M1, M2, and M8, located within the central portion of the contaminant plume. The deepest well is M8, which generally contains the highest
concentrations of contaminants of the three wells at that location (Passero, 1981). Possible reasons why many of the contaminants are found at high concentration levels in M8 include the downward flow direction possibly accentuated by groundwater mounding beneath the filled area. This would force the contaminants down to greater depths closer to the landfill proper. Another possibility is that chlorinated compounds will sink at the source when in excess of their solubility in water (Cline & Viste, 1984). Since there is only one group of nested wells at the landfill site, it is extremely difficult to draw any specific conclusions about the vertical distribution patterns of the individual organic chemicals or the inorganic chemicals. General discussions of the vertical distributions of selected organic chemicals will appear later in this paper.

Classification of the Synthetic Organic Chemicals Detected in the Leachate Plume at the KL Landfill

Thirty-one synthetic organic chemicals have been detected within the contaminated groundwater beneath and to the west of the KL Avenue Landfill (Table 3). The most persistent organic chemicals can be divided into two major groups based on their behavior, persistence, distribution, and physical properties (Table 9).
<table>
<thead>
<tr>
<th>Organic Chemicals</th>
<th>Solubility (ppm)</th>
<th>Density (g/cm³)</th>
<th>Molecular Weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Group 1</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenols</td>
<td>93,000</td>
<td>1.070</td>
<td>94.11</td>
</tr>
<tr>
<td>Benzene</td>
<td>1,780</td>
<td>.879</td>
<td>78.11</td>
</tr>
<tr>
<td>Toluene</td>
<td>535</td>
<td>.867</td>
<td>92.10</td>
</tr>
<tr>
<td>1,1-Dichloroethane</td>
<td>5,100</td>
<td>1.180</td>
<td>98.96</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>8,700</td>
<td>1.250</td>
<td>98.96</td>
</tr>
<tr>
<td><strong>Group 2</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>720</td>
<td>1.350</td>
<td>133.41</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>4,500</td>
<td>1.440</td>
<td>133.41</td>
</tr>
<tr>
<td>Chloroform</td>
<td>8,200</td>
<td>1.489</td>
<td>119.38</td>
</tr>
<tr>
<td>Chloroethane</td>
<td>--</td>
<td>.920</td>
<td>64.50</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>19,400</td>
<td>--</td>
<td>84.93</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>2,700</td>
<td>.912</td>
<td>62.50</td>
</tr>
<tr>
<td>trans-1,2-Dichloroethene</td>
<td>6,300</td>
<td>1.260</td>
<td>96.95</td>
</tr>
<tr>
<td>cis-1,2-Dichloroethene</td>
<td>3,500</td>
<td>1.280</td>
<td>96.95</td>
</tr>
<tr>
<td>1,1-Dichloroethene</td>
<td>8,000</td>
<td>1.218</td>
<td>96.95</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>1,100</td>
<td>1.460</td>
<td>131.50</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>130</td>
<td>1.626</td>
<td>165.83</td>
</tr>
</tbody>
</table>

The first group consists of the phenols, benzene, toluene, 1,1-dichloroethane and 1,2-dichloroethane; these compounds persisted throughout the 7 years of monitoring from 1980 through 1986 in several wells and ranged in concentration from 2 ug/L to 5,750 ug/L. The average concentrations range in the hundreds of micrograms per liter. These five organic compounds have been studied with respect to time, areal distribution, vertical distribution, and distance from the source. Due to their high concentration levels, persistence, and wide distribution across the site, the concentrations could be contoured for a plume analysis. The organic chemical concentrations were also compared with precipitation, chloride, chemical oxygen demand (COD), and the composition of the glacial deposits. Correlation coefficients were derived by applying a simple linear regression analysis to the data.

The second group of organic chemicals consists of chloroform, methylene chloride, 1,1,1-trichloroethane, 1,1,2-trichloroethane, chloroethane, tetrachloroethane, 1,1,2-trichloroethene, cis-1,2-dichloroethene, and trans-1,2-dichloroethene. These organic chemicals were less persistent throughout the 7-year sampling period. Concentrations fluctuated markedly in each well and the numbers and locations of contaminated wells varied.
considerably. The spatial and temporal distributions of these organic chemicals are attributed to biodegradation, biotransformation sequences, and other factors. The chlorinated alkanes and alkenes appear as primary, secondary, tertiary or quaternary biotransformation intermediates within several reductive dehalogenation reaction sequences that occur under anaerobic conditions within the contaminant plume. The three anaerobic biotransformation sequences observed at the KL Landfill site are as follows:

1. $1,1,1$-trichloroethane $\rightarrow [1,1$-dichloroethane]$ \rightarrow [1,2$-dichloroethane]$ \rightarrow$ chloroethane

2. carbon tetrachloride $\rightarrow$ chloroform $\rightarrow$ methylene chloride

3. tetrachloroethene $\rightarrow$ trichloroethene $\rightarrow$ vinyl chloride

Several of these organic contaminants were found in only a few wells, and occurred at lower concentrations, appeared or disappeared in wells within the center of the plume, or appeared in wells located further downgradient from the landfill. They appear to fit this biotransformation model.
Besides these two predominant groups of organic contaminants, several other organic chemicals were detected at the site, such as xylenes and ethylbenzene. Both of these chemicals were detected much later in the monitoring program and will be discussed briefly. Additionally, three other classes of hydrocarbons were not being checked in the groundwater samples until March, 1984 (Bouma, 1990); these chemical classes are the alcohols, ketones, and an ether. However, due to the limited appearance of these chemicals, general trends in concentration and distribution could not be discerned.

Physical Properties

Densities within the persistent Group 1 organic chemicals are lower in relation to the less persistent and more erratic Group 2 organic chemicals. Generally the organic chemicals that undergo biotransformation have densities that are higher by 0.04-0.38 g/cm$^3$ and have molecular weights that are greater by 10 to 70 grams (Table 9). No distinctions between the two groups can be made on the basis of vapor pressure, solubility, log octanol/water partition coefficients or volatilities. Moreover, there are no apparent trends related to the ability of the organic chemicals to undergo photolysis, oxidation or hydrolysis (USEPA, 1983).
Organic Chemical Concentrations Relative to the Composition of the Glacial Deposits

The compositions of the glacial deposits appear to exert little or no influence on the distribution of synthetic organic chemicals at the KL Landfill site. Wells, for example, containing higher levels of silt with smaller amounts of clay generally occur at the periphery of the plume. This fact makes it difficult to determine whether the higher levels of silt or clay influence the chemical concentration levels detected in the individual wells, or whether the location of the wells at the edge of the plume is responsible for the lower concentration levels. Since all of the organic chemicals behave differently, it appears that other factors must be controlling their concentration levels and areal distributions at the landfill site. In addition, analyses show that the majority of the fines are silt composed of silica (Passero, 1981), and little adsorption would occur (Mortland, 1985). Sorption is generally related to the amount of organic carbon found in the deposits (Schwarzenbach & Giger, 1985). At the KL Landfill site, the aquifer materials are predominantly composed of sand, gravel, and silt, with iron oxide and hydroxide coatings (Kehew et al., 1988) and little or no clay and organic carbon, according to 20 samples obtained from cable tool
and rotary drilling and gamma ray log data (Passero, 1981). This would minimize the possibility that significant sorption would occur, resulting in little or no retardation of the organic chemical contaminants. In addition, dissolution of the iron oxide and hydroxide coatings is occurring via reduction by landfill organics, and the dissolved iron is mobilized by ferrous iron-organic complexes and carried out of the landfill (Kehew et al., 1988).

Moreover, the log/octanol water partition coefficients of ethylbenzene (3.15) and toluene (2.69) are two of the highest partition coefficients (Reinhard, Goodman, & Barker, 1984) at the site, and both of these contaminants have been detected at 2,200 and 2,250 feet downgradient of the KL Landfill. This supports the conclusion that this predominantly sandy and gravelly aquifer exhibits poor sorption characteristics. Additionally, tetrachloroethene has a log octanol/water partition coefficient of 2.88 (higher than toluene). Initially it was restricted to the landfill proper, which suggests anaerobic biotransformation resulting in rapid attenuation of this chemical compound or limited transport since release. However, later in the monitoring period during September, 1984, perhaps when bacterial growth was inhibited, the tetrachloroethene reached as far as 710
South 4th Street approximately 2,250 feet downgradient, again indicative of the poor sorption characteristics of the aquifer materials.
CHAPTER VI

STATISTICAL ANALYSIS

Methodology of the Simple Linear Regression Analysis

A series of values were calculated by averaging each of the organic chemicals’ detectable concentration levels during each sampling quarter within the 7-year monitoring interval in all of the wells at the site. All of the organic chemicals except the phenols have their highest detectable concentrations adjacent to the landfill rather than on the landfill proper. Additionally, downgradient wells around the intersection of KL Avenue and South 4th Street and beyond, generally contain low to non-detectable levels of these organic compounds, which would not influence the calculated plume average concentrations significantly. These average organic chemical concentration values or plume averages were correlated with the average precipitation values for the quarter, chloride, and COD levels for each of the sampling quarters. A simple linear regression analysis was performed on each possible pair of these four variables. The specific organic chemicals used in these correlations are the Group 1 organic chemicals (phenols, benzene,
toluene, 1,1-dichloroethane, and 1,2-dichloroethane). Table 10 lists the correlation coefficients determined from the computer generated graphs.

Table 10
Simple Linear Regression Analysis
Using Plume Average Values

<table>
<thead>
<tr>
<th>Organic Chemicals vs.</th>
<th>Average Precipitation per Quarter</th>
<th>Chloride</th>
<th>COD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenols</td>
<td>not significant</td>
<td>.50</td>
<td>.56</td>
</tr>
<tr>
<td>Benzene</td>
<td>.22</td>
<td>.45</td>
<td>.27</td>
</tr>
<tr>
<td>Toluene</td>
<td>-.02</td>
<td>.38</td>
<td>.34</td>
</tr>
<tr>
<td>1,1-dichloroethane</td>
<td>.31</td>
<td>.46</td>
<td>.71</td>
</tr>
<tr>
<td>1,2-dichloroethane</td>
<td>.20</td>
<td>.57</td>
<td>.24</td>
</tr>
<tr>
<td>Chloride</td>
<td>-.10</td>
<td>--</td>
<td>.57</td>
</tr>
<tr>
<td>COD</td>
<td>.20</td>
<td>.57</td>
<td>--</td>
</tr>
</tbody>
</table>

A second simple linear regression analysis was performed on the actual set of organic chemical concentration levels detected in a single well (TW4) directly on the KL Landfill. TW4 was chosen because it is the only TW well containing high concentrations of all five of the Group 1 organic chemicals; the other TW wells generally contain low to non-detectable concentrations of all these organic chemicals except the phenols. All of
the organic chemical concentration levels detected in TW4 during the 7-year monitoring program were correlated with precipitation, chloride, and COD values found in that same well. Once again the Group 1 organic chemicals used in the first linear regression analysis were used at TW4. These correlation coefficients are listed in Table 11.

Table 11
Simple Linear Regression Analysis
Using Data Collected at TW4

<table>
<thead>
<tr>
<th>Organic Chemicals vs.</th>
<th>Average Precipitation per Quarter</th>
<th>Chloride</th>
<th>COD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenols</td>
<td>-.35</td>
<td>.24</td>
<td>-.15</td>
</tr>
<tr>
<td>Benzene</td>
<td>-.06</td>
<td>-.08</td>
<td>.21</td>
</tr>
<tr>
<td>Toluene</td>
<td>.03</td>
<td>.32</td>
<td>.60</td>
</tr>
<tr>
<td>1,1-dichloroethane</td>
<td>.12</td>
<td>.37</td>
<td>.50</td>
</tr>
<tr>
<td>1,2-dichloroethane</td>
<td>.25</td>
<td>.22</td>
<td>-.48</td>
</tr>
<tr>
<td>Chloride</td>
<td>-.26</td>
<td>--</td>
<td>.28</td>
</tr>
<tr>
<td>COD</td>
<td>.02</td>
<td>.28</td>
<td>--</td>
</tr>
</tbody>
</table>

Simple Linear Regression Analysis (1)
Using Calculated Plume Averages

Prior to the statistical analysis, the calculated average concentration values per sampling quarter for the phenols were plotted on graphs versus precipitation and
COD (Figures 34 & 35). Based on these plots there appears to be some correspondence between the phenols concentration levels, precipitation, and COD. The simple linear regression analysis determined the degree of this correlation.

Generally, the plume average concentration values exhibited a higher degree of direct correlation with precipitation, COD, and chloride, than the actual concentration levels recorded in TW4 versus the same three parameters. The degree of the correlation between the organic chemicals relative to the precipitation, COD, and chloride have been listed in Table 12.

**Plume Average Values Versus Precipitation**

The correlation coefficients for the organic chemicals relative to precipitation are low. The coefficients range from a high positive correlation of .31 for 1,1-dichloroethane to a low of -.02 for toluene (the significance level is ± .001). The 1,2-dichloroethane and 1,1-dichloroethane correlation coefficients of .20 and .31 (Figure 36), respectively, indicate a low positive correlation, and a definite but small relationship (Table 12). Thus, variations in concentrations of these organic chemicals, COD, and chloride cannot be explained by precipitation levels.
Figure 34. Average Phenols Concentrations per Quarter for the Plume Relative to March, 1980 Through Precipitation Values Ranging From March, 1980 Through March, 1986.
Figure 35. Average Phenols Concentrations per Quarter for the Plume Relative to Average Quarterly COD From March, 1980 Through March, 1986.
Table 12

Correlation Coefficient Categories Expressing the Degree of the Direct Correlation Values

<table>
<thead>
<tr>
<th>Correlation Coefficient Ranges</th>
<th>Degree of Correlation</th>
<th>Expression of the Relationship</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;.20</td>
<td>Slight</td>
<td>Almost Negligible</td>
</tr>
<tr>
<td>.20 - .40</td>
<td>Low Correlation</td>
<td>Definite But Small</td>
</tr>
<tr>
<td>.40 - .70</td>
<td>Moderate Correlation</td>
<td>Substantial</td>
</tr>
<tr>
<td>.70 - .90</td>
<td>High Correlation</td>
<td>Marked</td>
</tr>
<tr>
<td>.90 - 1.00</td>
<td>Very High Correlation</td>
<td>Very Dependable</td>
</tr>
</tbody>
</table>


The low correlation with precipitation may be partly due to the application of the bentonite cover over the filled area which would limit the immediate effects of precipitation on the chemical concentration levels recorded in the groundwater. The correlation may also be influenced by the vegetative cover used to reduce infiltration, and the variable localities of ponded surface water and runoff drainage patterns on the surface of the landfill, which are continually modified by the changing topography of the filled area.
Figure 36. Scatter Plot Showing the Linear Regression Analysis of 1,1-Dichloroethane Versus Precipitation.

Plume Average Values Versus Chloride

All of the organic chemicals except toluene exhibit a very stable moderate correlation or substantial relationship with chloride ranging from a low correlation coefficient of .45 for benzene (Figure 37) to a high correlation coefficient of .57 for 1,2-dichloroethane (Figure 38). The correlation coefficient determined for toluene was only slightly lower at .38 (Figure 39), which falls within the upper end of the low correlation category, resulting in a definite but small relationship. Generally, this would indicate that the occurrence of organic chemicals at the site has been similar to
Figure 37. Scatter Plot Showing the Linear Regression Analysis of Benzene Versus Chloride.

Figure 38. Scatter Plot Showing the Linear Regression Analysis of 1,2-Dichloroethane Versus Chloride.
chloride.

**Plume Average Values Versus COD**

The correlation coefficients determined for the organic contaminants relative to COD are all positive and significant, ranging from .24 for 1,2-dichloroethane (Figure 40) to .71 for 1,1-dichloroethane (Figure 41). The COD or chemical oxygen demand is a measure of both the biodegradable and non-biodegradable organic components of the groundwater system as expressed as O₂ (Kemmer, 1979). Therefore the COD would be a measure of both the naturally occurring organic matter found within the flow system as well as the synthetic organic chemical compounds present within the groundwater, including any other reducing substances. The phenols are detected at the highest concentration levels across the site and have a correlation coefficient of .56 (Figure 42), toluene appears at the second highest concentration levels recorded at the site with a coefficient of .34 (Figure 43), third is benzene at .27 (Figure 44), and fourth is 1,2-dichloroethane at .24 (Figure 40). If 1,1-dichloroethane is considered, it has the third highest concentration level at the site, but has the highest correlation coefficient of .71 (Figure 41), which is considered to be a definite relationship.
Figure 39. Scatter Plot Showing the Linear Regression Analysis of Toluene Versus Chloride.

Figure 40. Scatter Plot Showing the Linear Regression Analysis of 1,2-Dichloroethane Versus COD.
Figure 41. Scatter Plot Showing the Linear Regression Analysis of 1,1-Dichloroethane Versus COD.

Figure 42. Scatter Plot Showing the Linear Regression Analysis of the Phenols Versus COD.

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Figure 43. Scatter Plot Showing the Linear Regression Analysis of Toluene Versus COD.

Figure 44. Scatter Plot Showing the Linear Regression Analysis of Benzene Versus COD.
Initially graphs were plotted of the phenols concentration levels in individual wells, such as TW4, relative to precipitation (Figure 45). Since TW4 contained some of the highest contaminant levels at the site, it was chosen as the best well to determine if there were any significant dependable correlations between the organic chemical concentration levels in individual wells versus precipitation, COD, and chloride levels.

**Organic Contaminants Versus Precipitation in TW4**

The correlation coefficients resulting from the relationship between precipitation levels and the organic chemicals in TW4 are extremely low. They range from negative values, indicating a low inverse correlation as is the case for the phenols (-.35), benzene (-.06), and chloride (-.26), to a relatively high correlation coefficient of .25 for 1,2-dichloroethane, which is still considered to be low, but indicates a definite but small relationship. These low positive correlations and definite negative correlations once again suggest an inverse relationship between chemical concentrations and precipitation. Increased precipitation may promote a stronger dilutional effect of the chemical concentrations,
Figure 45. Phenols Concentrations per Quarter Recorded in TW4 Relative to Average Quarterly Precipitation Levels Recorded From March, 1980 Through March, 1986.
initially decreasing chemical concentration levels detected in the groundwater, rather than leaching chemicals from the waste and increasing detectable chemical concentration levels.

**Organic Contaminants Versus Chloride in TW4**

All of the organic chemicals have correlation coefficients ranging from a low of .21 for 1,2-dichloroethane to a high of .37 for 1,1-dichloroethane except benzene (-.08). This range of correlation coefficients falls within the low correlation category indicating a definite but small relationship between the two parameters. These data are consistent with the plume average results, indicating that the distribution of the organic chemicals at TW4 has been similar to chloride.

**Organic Contaminants Versus COD in TW4**

In TW4 both the phenols and 1,2-dichloroethane have negative correlation coefficients of -.15 and -.48, respectively. The inverse correlation for the 1,2-dichloroethane is moderate indicating a substantial inverse relationship. An inverse relationship with COD seems rather unusual for organic compounds. The remaining organic chemicals have correlation coefficients ranging from benzene (.21) to toluene (.60). Both 1,1-
dichloroethane (0.50) and toluene (0.60) have correlation coefficients falling within the moderate correlation category indicating a substantial relationship. Toluene has the highest correlation coefficient and appears at the second highest concentration levels at TW4, while 1,1-dichloroethane has the third highest concentration levels at TW4 and has the second highest correlation coefficient, followed by benzene.
CHAPTER VII

DATA SYNTHESIS OF PERSISTENT GROUP 1 ORGANIC CHEMICALS, CHLORIDE, AND OTHER ORGANIC CONTAMINANTS

Phenols

Of all the organic chemicals detected within the contaminant plume at the KL Landfill, the phenols exist at the highest concentration levels ranging into the thousands of micrograms per liter. Because of the wide range of the phenols concentration levels from 4 ug/L to 5,750 ug/L, concentration percentages were calculated to simplify graphs. All of the organic chemicals are represented this way for consistency, ease of comparison, and manageability of the chemicals’ wide ranging data. The highest concentration of each chemical found over the 7-year monitoring interval is used as a reference level for all of the other detected concentrations, of that specific chemical, found at the site. For example, the phenols highest concentration level is 5,750 ug/L detected in 3/81 at M2 which appears as 100% concentration in Figure 48. The locations of the wells used in the concentration graphs at the landfill site are shown in Figure 46.
Figure 46. Map Indicating the Locations of Wells Used in the Construction of Concentration Versus Distance and Time Graphs.
Phenols concentrations generally increased from March, 1980 to December, 1980 (Figure 47), and levels were definitely much higher closer to the landfill (within about 1,000 feet of TW4 located on the western edge of the filled area). In 1981, levels remain high adjacent to the landfill, and levels also began to increase about 1,400 feet away from TW4 (Figure 48). From 1982 to 1983, phenols levels are definitely higher between 1,000 and 1,400 feet away from TW4, but are decreasing adjacent to the landfill (Figure 49). Finally from 1984 to 1986, phenols levels still remained low adjacent to the landfill and increased even further downgradient between 1,200 to 2,200 feet away from the landfill (Figure 50). The phenols generally exhibited a progressive increase in concentration with distance from the landfill, and time, which would be expected.

**Phenols Plume Analysis**

In March, 1980 the phenols plume extended west to about 9060 West KL Avenue, and the area of the plume was 0.16 mi$^2$ (Figure 51). The phenols plume area is defined by wells containing non-detectable levels of this contaminant. Phenols concentrations increased in individual wells by as much as 5,430 ug/L from March, 1980 to March, 1981. By March, 1982 the phenols plume reached
Figure 47. Phenols Concentrations in Selected Wells Versus Distance and Time (1980). (Percent Concentration Relative to M2 (3/81) 5,750 µg/L).
Figure 48. Phenols Concentrations in Selected Wells Versus Distance and Time (1981). (Percent Concentration Relative to M2 (3/81) 5,750 ug/L).
Figure 49. Phenols Concentrations in Selected Wells Versus Distance and Time (1982-1983). (Percent Concentration Relative to M2 (3/81) 5,750 ug/L).
Figure 50. Phenols Concentrations in Selected Wells Versus Distance and Time (1984-1986). (Percent Concentration Relative to M2 (3/81) 5,750 ug/L).
Figure 51. Map Showing the Extent of the Phenols Plume for March, 1980 and March, 1986 (Adapted from Broede & Passero, 1988). (Plumes are Delineated With the 10 ug/L Contours Taken From More Densely Contoured Maps. Concentrations Shown are Maximum Values for 1980 and 1986).
M5, 2,300 feet west of the landfill. The calculated rate of the phenols movement was about 6.3 ft/day, approximating the maximum calculated groundwater flow velocity of 5.95 ft/day (Passero, 1981), and indicating minimal retardation and the possible effects of preferential flow allowing the phenols to reach wells before the average arrival times expected (Mackay, Roberts, & Cherry, 1985). By March, 1984, phenols increased to 77 ug/L in M5 and the plume expanded to 0.21 mi². The phenols plume reached a maximum area of 0.22 mi² in March, 1986 when the concentration in M5 was 23 ug/L. The area of the phenols plume gradually increases over time with expected short term fluctuations (Figure 52).

Phenols Concentrations in Wells Versus Time and Depth

Although the general shape and orientation of the phenols plume tends to be moderately stable, concentrations at specific wells increase and decrease through time rapidly. Wells at the periphery of the plume such as TW3, M5, M7 (Figure 53), 8383 W. Main St., 263 S. 4th St., 920 S. 4th St., and 9067 KL Ave. all contained low to non-detectable levels of the phenols. The high organic concentrations within the plume may limit aerobic degradation to the oxygenated water along the margins of the plume (Wilson, Leach, Henson, & Jones, 1986). In this
Figure 52. Graph Illustrating the General Increase in Area of the Phenols Plume With Time (1980-1986).
Figure 53. Phenols Concentrations Recorded in Wells TW3, M5, and M7 Located on the Periphery of the Plume (1980-1986).
area the unconfined aquifer may contain sufficient dissolved oxygen or other oxidizing agents to cause the rapid aerobic degradation of the phenols (Sutton & Barker, 1985).

Wells M3, M2, M4, and M8 located within the core of the plume contain high concentrations of the phenols and also exhibit the greatest fluctuations in concentration (Figure 54). The screen depths of these wells below their recorded static water levels (Table 13) are as follows: M3 is 5.0 feet below, M2 is 22.0 feet below, M4 is 25.0 feet below, and M8 is 72.5 feet below. When phenols concentrations were plotted with depth, no depth related trend was indicated. There was no consistent increase or decrease in phenols concentrations with depth below static water level (S.W.L.) (Figures 55 & 56).

From 1980 to 1981, high phenols levels were first located within a narrow depth region ranging between 16 and 24 feet below S.W.L. (Figure 55). The maximum phenols concentration (5,750 ug/L) occurred in M2 in 3/81 about 22 ft below S.W.L. represented by 100% concentration in Figure 55. Over time, between March, 1984 and March, 1986, the phenols appeared to expand over a wider range of depths both upward towards the surface in shallow wells, such as M3 and TW6 about 10 ft below S.W.L., and downward to wells of greater depth, such as M8 72.5 ft below S.W.L.
Figure 54. Phenols Concentrations in Wells M2, M4, M3, and M8 (1980-1986).
Figure 55. Phenols Concentrations Versus Depth (1981). (Percent Concentration Relative to M2 (3/81) 5,750 ug/L).
(Figure 56). This expansion may be attributed to the increasing volume of the phenols being detected over a wider area of the landfill site and downgradient.

Table 13

<table>
<thead>
<tr>
<th>Monitor Well #:Well Address</th>
<th>Depth Below S.W.L. (feet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M3</td>
<td>5.0</td>
</tr>
<tr>
<td>TW6</td>
<td>10.4</td>
</tr>
<tr>
<td>TW2</td>
<td>13.0</td>
</tr>
<tr>
<td>TW1</td>
<td>14.0</td>
</tr>
<tr>
<td>TW4</td>
<td>16.0</td>
</tr>
<tr>
<td>M2</td>
<td>22.0</td>
</tr>
<tr>
<td>M4</td>
<td>25.0</td>
</tr>
<tr>
<td>TW3</td>
<td>26.5</td>
</tr>
<tr>
<td>M5</td>
<td>27.4</td>
</tr>
<tr>
<td>8383 W. Main St.</td>
<td>29.0</td>
</tr>
<tr>
<td>710 S. 4th St.</td>
<td>29.0</td>
</tr>
<tr>
<td>M1</td>
<td>30.0</td>
</tr>
<tr>
<td>691 S. 4th St.</td>
<td>30.0</td>
</tr>
<tr>
<td>263 S. 4th St.</td>
<td>35.0</td>
</tr>
<tr>
<td>920 S. 4th St.</td>
<td>45.0</td>
</tr>
<tr>
<td>M8</td>
<td>72.5</td>
</tr>
</tbody>
</table>
Figure 56. Phenols Concentrations Versus Depth (1984-1986). (Percent Concentration Relative to M2 (3/81) 5,750 µg/L).
However, it could also be attributed to the phenols gradual diffusion upward and downward according to the slight vertical hydraulic gradients at the site.

Concentration maxima were recorded in TW6 (10 ft below S.W.L.) with concentrations ranging between 56% (3/84) and 24% (3/86), in M4 (25 ft below S.W.L.) with concentrations ranging between 52% (3/84) and 7% (3/86), and in M8 (72.5 ft below S.W.L.) with concentrations ranging between 56% (3/84) to 24% (3/86) (Figure 56). All three of these wells exhibited gradual declines in phenols concentrations from March, 1984 to March, 1986, unlike the widely variable concentration increases and decreases in M2.

Therefore, it appears that some wells at different depths exhibit gradual declines in phenols concentrations, while others exhibit extreme fluctuations in the phenols concentrations. This suggests that wells screened closer to the air-water interface are not necessarily displaying any greater degree of aerobic degradation relative to the degree of anaerobic degradation occurring in wells of greater depth within the plume. The low redox potential within the plume (Kehew et al., 1988) would allow the organic contaminants to degrade anaerobically. Since methanogenic conditions do exist within the KL Landfill leachate plume (Fahle, in preparation) the phenols may be
metabolized almost completely to CO\textsubscript{2}, which would partly account for the reductions in the phenols concentrations in these wells (Wilson, Leach, Henson, & Jones, 1986). At the KL Landfill site, oxidation of organic carbon to CO\textsubscript{2} is indicated by the areal distribution of the total alkalinity (Kehew et al., 1988) (Figure 57). For example, in TW4 (Figure 58), which is located at the head of the plume, an abrupt decrease in phenols concentration can be observed suggesting that anaerobic degradation is occurring. The subsequent gradual increase in concentration is probably due to the leaching of more phenols from the waste through time.

The remaining wells M1 (Figure 59), 691 S. 4\textsuperscript{th} St., 710 S. 4\textsuperscript{th} St., TW1, and TW6 (Figure 60), further from the landfill and outside the main flow path, also exhibit minor concentration fluctuations that appear to be superimposed on gradual increasing or decreasing phenols concentration trends. Since the phenols data collected from the wells at 691 S. 4\textsuperscript{th} St. and 710 S. 4\textsuperscript{th} St. were incomplete, no graphs were constructed for these two wells. These wells are at various depths, some at the edge of the contaminant plume and some within the core of the plume.
Figure 57. Total Alkalinity Plume (May, 1987), Showing Concentrations Recorded in Wells at the KL Landfill Site (Adapted from Kehew et al., 1988).
Figure 58. Phenols Concentrations Relative to Chloride Levels in TW4 (1980-1986).
Figure 59. Phenols Concentrations in Ml Indicating the Gradual Increasing and Decreasing Trends in Concentration.
Figure 60. Phenols Concentrations in TW6 and TW1 Indicating the Gradual Increasing and Decreasing Trends of the Phenols.
Benzene

Generally, benzene concentrations at the KL Landfill average in the hundreds of micrograms per liter. The highest concentrations of benzene were always detected about 1,000 feet downgradient from the landfill proper (TW4) at M8. The benzene concentration peak at M8 exhibited a steady decline in concentration levels from a high in 1980 (Figure 61) to a minimum in 1986 (Figure 62), between 2 and 4% of the 1980-maximum peak. Benzene levels adjacent to the landfill remained fairly steady at about 20% of the maximum concentration (1,810 ug/L) recorded in M8 from 1980 to 1986. A more subdued concentration peak was consistently detected about 1,050 feet downgradient at M1. The benzene concentrations detected at M1 also steadily declined in concentration levels from 1980 to 1986.

Benzene Plume Analysis

The benzene plume is narrow and is generally limited to an area southwest of the landfill. The area of the plume in March, 1980 was 0.08 mi$^2$ (Figure 63), the maximum areal extent of the plume during the 7-year study period. The minimum area of the plume was 0.03 mi$^2$ in March, 1982, when the plume receded to the nested wells at M8. Benzene
Figure 61. Benzene Concentrations in Selected Wells Versus Distance and Time (1980).
(Percent Concentration Relative to M8 (3/80) 1,180 ug/L).
Figure 62. Average Benzene Concentrations in Selected Wells Versus Distance and Time (1986). (Percent Concentration Relative to M8 (3/80) 1,810 ug/L).
Figure 63. Map of the Benzene Plumes for March, 1980 and March, 1986 (Broede & Passero, 1988). (Plumes are Delineated With the 10 ug/L Contours Taken From More Densely Contoured Maps. Concentrations Shown are Maximum Values for 1980 and 1986).
concentrations were highest in TW4 (420 ug/L) and M8 (1,810 ug/L). Low levels of benzene were also detected in 8383 West Main Street, upgradient of the landfill near Bonnie Castle Lake, in March, 1980. The area of the benzene plume decreased through time, reflecting a decline in benzene concentrations at various wells within the plume. The benzene plume fluctuations are more gradual than was observed for the phenols plume (Figure 64).

**Benzene Concentrations in Wells Versus Time and Depth**

The wells containing the highest levels of benzene are TW4 (Figure 65), M8, M3, and M1. Generally, benzene levels are more stable in wells than the phenols. Concentrations fluctuated over a narrow range from 20 to 100 ug/L in each well from one sampling quarter to the next. Only a few sampling quarters exhibit a 2- to 3-fold increase or decrease in benzene concentrations. In addition, the 2- to 3-fold concentration increases or decreases in each well occur at different times and appear to exhibit no relationships with time, screen depth below static water level, or distance from the landfill.

When benzene concentrations were plotted with depth below static water level, it is evident that benzene concentrations are generally higher at greater depths (Figure 66). The highest benzene concentration (1,810
Figure 64. Graph Illustrating the General Decrease in Area of the Benzene Plume With Time (1980-1986).
Figure 65. Benzene Concentrations Relative to Chloride Levels in TW4 (1980-1986).
Figure 66. Benzene Concentrations Versus Depth (1980). (Percent Concentration Relative to M8 (3/80) 1,810 ug/L).
ug/L) detected in M8 (72.5 ft below S.W.L.) in March, 1980 appears as 100% concentration in Figure 66. The second highest concentration occurs in TW4 (16 ft below S.W.L.) at 23% (3/80) of the maximum concentration, and the third highest concentration of benzene is recorded in M1 (30 ft below S.W.L.) at 16% (3/80) of the maximum concentration.

From 12/80 to 3/84 benzene levels fluctuated rapidly, increasing and decreasing randomly in wells of all depths rather than gradually increasing or decreasing consistently. The only well that exhibited a gradual decrease in benzene concentration was M8 where levels declined from 100% (3/80) to 28% (12/80) to a minimum of 17% (3/85). Between 1984 and 1986 all benzene concentrations decreased with levels remaining highest in M8 (72.5 ft below S.W.L.) from 17-19%, in TW4 (16 ft below S.W.L.) at 16%, and in M3 (5 ft below S.W.L.) at 9% (Figure 67). Therefore, through time the gap between benzene concentration levels in deep wells and shallow wells has been narrowed.

The wells located at the periphery of the plume such as 691, 710, and M4 all contain lower levels of benzene and exhibit smaller concentration fluctuations. This may indicate that aerobic degradation is lowering the benzene levels faster and more steadily on the perimeter of the plume than anaerobic degradation within the core of the
Figure 67. Benzene Concentrations Versus Depth (1984-1985). (Percent Concentration Relative to M8 (3/80) 1,810 ug/L).
plume (Wilson, Bledsoe, Kampbell, Wilson, Armstrong, & Sammons, 1987).

Since benzene tends to exhibit the most stable concentration levels in individual wells, with only minor concentration fluctuations observed, it appears that anaerobic degradation does not reduce benzene concentrations as much as the other petroleum by-products such as toluene, xylene, and ethylbenzene. However, the benzene plume area does gradually decrease over the 7-year monitoring program perhaps indicating that benzene is degraded more rapidly aerobically at the periphery of the plume area. Also, there is always the possibility that the source of the benzene could gradually be decreasing with time.

Toluene

Toluene concentration levels range between benzene and the phenols from the upper hundreds of micrograms per liter to the lower thousands of micrograms per liter. In 1980 toluene, like benzene, reached its maximum concentration in M8 while low levels of toluene were detected adjacent to the landfill (Figure 68). By 1981, toluene levels had increased adjacent to the landfill but decreased markedly in M8. From 1982 to 1983, toluene levels increased about 25% adjacent to the landfill with
Figure 68. Toluene Concentrations in Selected Wells Versus Distance and Time (1980). (Percent Concentration Relative to M8 (3/80) 2,470 ug/L).
a simultaneous increase in toluene concentrations at 710 South 4th Street about 2,250 feet away from TW4 (Figure 69). From 1984 to 1986, toluene decreased slightly adjacent to the landfill, but increased almost 3-fold at 710 South 4th Street (Figure 70). Overall, toluene does not exhibit any consistent trends over time. Initially, toluene levels are higher away from the landfill than adjacent to the landfill. Finally, much later in the monitoring period, levels increase downgradient and decrease on and adjacent to the landfill (Figure 70).

**Toluene Plume Analysis**

Toluene appears consistently in the same wells over the 7-year sampling period. The stability of the plume area may indicate that lesser degrees of aerobic degradation and/or dilution may be occurring at the periphery of the plume. The toluene plume (Figure 71) was extremely narrow initially and covered an area of only 0.03 mi$^2$ in March, 1980. The areal extent of the plume increased rather steadily to 0.09 mi$^2$ in March, 1986, displaying a significant increase in width. Longitudinally, the toluene plume never extended beyond 710 South 4th Street. The general trend of the toluene plume area is increasing steadily with only minor plume fluctuations (Figure 72).
Figure 69. Toluene Concentrations in Selected Wells Versus Distance and Time (1982-1983). (Percent Concentration Relative to M8 (3/80) 2,470 ug/L).
Figure 70. Toluene Concentrations in Selected Wells Versus Distance and Time (1984-1986). (Percent Concentration Relative to M8 (3/80) 2,470 ug/L).
Figure 71. Map of the Toluene Plumes for March, 1980 and March, 1986 (Broede & Passero, 1988). (Plumes Delineated With the 10 ug/L Contours Taken From More Densely Contoured Maps. Concentrations Shown are Maximum Values for 1980 and 1986).
Figure 72. Graph Illustrating the General Increase in Area of the Toluene Plume With Time (1980-1986).
Toluene Concentrations in Wells Versus Time and Depth

The highest toluene levels occurred in 710 S. 4th St., M3, M8, and TW4 (Figure 73). Toluene levels are extremely high in M8 during the first sampling quarter, March, 1980. Toluene levels increased in wells TW4 and M3, adjacent to the landfill, by December, 1981, whereas M8 levels had declined to less than 2% of the value recorded in March, 1980. Generally, toluene concentrations are far more variable than benzene concentrations, but much less variable than the phenols concentrations. Even though 2- or 3-fold toluene concentration changes may occur from one sampling quarter to the next, these abrupt fluctuations occur far less often than for the phenols. This may indicate that toluene is undergoing a greater degree of anaerobic degradation than benzene. When toluene is depleted by biological activity, it has been found to be degraded completely to CO₂ (Wilson, Leach, Henson, & Jones, 1986).

When toluene concentrations were plotted with depth below static water level, it is apparent that toluene levels were initially high at greater depths and increased through time in the shallow wells. The maximum toluene concentration (2,470 ug/L) was detected in M8 (72.5 ft below S.W.L.) in 3/80, the second highest toluene concentration in 3/80 was detected in TW4 (16 ft below...
Figure 73. Toluene Concentrations Relative to Chloride Levels in TW4 (1980-1986).
S.W.L.) at 17% of the maximum concentration, while the rest of the wells, at this time, contained very low to non-detectable levels of toluene.

After the high was reached in M8 (3/80) toluene levels dropped drastically to only 18% in M8 (6/80). Levels then fluctuated less drastically in M8 through 3/86. From 12/80 on, toluene levels in TW4 remained far above the levels detected in M8 (Figure 74). For example, in 3/82 toluene reached a concentration of 44% in TW4 (16 ft below S.W.L.), while concentrations also increased in M3 to 23% (Figure 74).

From 3/84 to 3/86, levels were high in M3 at 25% (3/84), decreasing to 10% (3/86), and were slightly lower in TW4 at 23% (3/84) decreasing to 19% (3/86) (Figure 75). Only wells M3 and M4 exhibited a relatively gradual increase in toluene concentrations followed by a gradual decrease, whereas the rest of the wells fluctuated throughout the 7-year monitoring period.

Chloride

Chloride was used in this study as a nonreactive tracer to compare with the organic chemical concentrations and areal distributions. Chloride behaves conservatively and therefore reflects advection and dispersion without sorption, biological degradation, or biological
Figure 74. Toluene Concentrations Versus Depth (1982-1983). (Percent Concentration Relative to M8 (3/80) 2,470 ug/L).
Figure 75. Toluene Concentrations Versus Depth (1984-1986). (Percent Concentration Relative to M8 (3/80) 2,470 ug/L).
transformation (Patrick & Barker, 1986).

When comparing the chloride concentrations versus distance from the landfill relative to TW4, with benzene, toluene, and the phenols, there are almost no similarities. The only notable similarity is between benzene and chloride. Chloride and benzene concentrations are high at M8 consistently from 1980 to 1986 (Figures 61-62 & Figures 76-77). The chloride concentrations, however, are low in 1980 (Figure 76) and increase to maximum concentrations in 1981 (Figure 77). In 1980, the highest concentrations of chloride are found in M8; however from 1981 to 1986 the highest chloride levels occur adjacent to the landfill. After 1981, the chloride levels steadily decrease in concentration at all well locations through 1986. There is a prominent area of high concentration that occurs throughout the 7-year monitoring period about 2,200 to 2,800 feet downgradient of the site (Figures 76 & 77), located in the area around the intersection of KL Avenue and South 4th Street. These higher concentrations are most likely due to the application of roadsalt at the intersection during the winter months, which increases the levels of chloride detected in the groundwater at these wells.
Figure 76. Chloride Concentrations in Selected Wells Versus Distance and Time (1980). (Percent Concentration Relative to TW4 (6/81) 660 mg/L).
Figure 77. Chloride Concentrations in Selected Wells Versus Distance and Time (1981). (Percent Concentration Relative to TW4 (6/81) 660 mg/L).
Chloride Plume Analysis

In 1980, the chloride plume extended slightly upgradient towards 8383 West Main Street, down to 8424 KL Avenue and South 4th Street, to 9200 KL Avenue. The areal extent of the chloride plume was greatest in March, 1981 at 0.24 mi$^2$ (Figure 78) and in March, 1983 at 0.23 mi$^2$. From March, 1982 through March, 1984 (Figure 79), the plume extended to M5. In March, 1983 the chloride plume was detected in a northwesterly direction at 25 South 4th Street. From March, 1983 to March, 1986 the chloride plume decreased in area to a low of 0.17 mi$^2$ in March, 1986 (Figures 78 & 80). By March, 1986, the plume had receded to the wells in the vicinity of the intersection of KL Avenue and South 4th Street near 9135 KL Avenue, and the width of the chloride plume across the filled area had diminished to low to non-detectable concentrations in the upgradient wells. Thus, the chloride plume area has generally decreased with abrupt plume fluctuations occurring between March, 1980 and March, 1984 (Figure 80).

The general decrease in area of the chloride plume is markedly different from the 1,1-dichloroethane, 1,2-dichloroethane, toluene, and phenols plumes. The chloride plume is similar to the phenols plume in that both appear to have reached M5, the well farthest downgradient of the
Figure 78. Map of the Chloride Plumes for March, 1981 and March, 1986. (Plumes Delineated With the 10 mg/L Contours Taken From More Densely Contoured Maps. Concentrations Shown are Maximum Values for 1981 and 1986).
Figure 79. Isoconcentration Map of Chloride (March, 1984).
Figure 80. Graph Illustrating the General Decrease in Area of the Chloride Plume With Time (1980-1986).
landfill, and in that both were also detected in wells slightly upgradient. Fluctuations in the phenols plume, however, are more extreme and out of phase with the chloride plume fluctuations. The benzene, toluene, 1,1-dichloroethane, and 1,2-dichloroethane plumes, were more narrow than the chloride plume, and did not extend as far downgradient. The only organic chemical that was detected, as far upgradient as chloride, was benzene, also detected in well 8383 West Main Street. When comparing plume area trends, the only similarity is that benzene exhibits a general decrease with time similar to chloride.

**Chloride Concentrations in Wells Versus Time and Depth Compared With the Organic Chemicals**

Chloride concentrations in all wells generally remain steady with only slight fluctuations in concentration. Chloride concentrations generally increased between 1981-1983, then decreased until the end of the study period in March, 1986.

The relationship of chloride concentrations to depth below static water level, resembles most closely the relationship of phenols concentrations to depth. Chloride, however, exists at high concentrations over a wide range of depths both in shallow wells and deep wells throughout the monitoring program (Figure 81); whereas the
Figure 81. Chloride Concentrations Versus Depth (1981). (Percent Concentration Relative to TW4 (6/81) 660 mg/L).
phenols concentrations start out high in the shallow wells, such as M3, TW6, TW4, M2, and M4 in 1981, but begin to appear in deeper wells such as M1 and M8 from 1984 to 1986. The major difference between chloride and the organic compounds is that chloride appears at shallow depths more consistently (Figure 81). The benzene and toluene exhibited low to non-detectable concentrations in shallow wells. For example, benzene only reaches a high of 23% in shallow wells such as M3 and TW4, and toluene reaches a high concentration of 44% in wells such as M3 and TW4, but during most quarters the levels of toluene are much lower than 44%.

Xylenes and Ethylbenzene

The least soluble organic compounds found at the KL Landfill are the arenes which include the xylenes and ethylbenzene. Xylene is considered to be insoluble in water and ethylbenzene has a solubility of only 152 mg/L. The solubilities of toluene and benzene, in water, are 535 mg/L and 1,780-1,800 mg/L, respectively (USEPA, 1983). Ethylbenzene was not detected in the groundwater until March, 1984, and the xylenes were not detected until September, 1984. This delay may be attributed to the low solubilities requiring a longer time to dissolve and be mobilized in the flow system. Additionally, both of these
chemicals have relatively small plumes (Figures 82 & 83) with only one or two downgradient wells containing detectable levels. The small plumes may indicate extensive biodegradation, which would be consuming these chemicals before they could be mobilized, or sorption restricting the chemicals to only certain wells (Patrick & Barker, 1986). According to Schwarzenbach and Westall (1981), the low solubility of the xylenes and high octanol water partition coefficients will result in some sorption of these chemicals to immobile organic matter within an aquifer based upon their hydrophobicity. Losses due to volatilization can occur at the water table (Schwille, 1981); however, once these organics enter the groundwater, within the aquifer, well below the water table, out of contact with the soil gas phase, losses would be negligible. Therefore, the majority of the attenuation resulting in the greatest losses of these chemicals may be attributed to biodegradation (Patrick & Barker, 1986).

In previous laboratory studies, constituents of petroleum products such as benzene, ethylbenzene, and xylenes all appear to require long lag times before significant biological removals will occur anaerobically. Toluene is the only petroleum product that does not have a long lag time. Following that lag time, xylenes undergo the most rapid and extensive biological degradation
Figure 82. Isoconcentration Map of the Xylenes (March, 1986) Showing Concentrations in Selected Wells.
Figure 83. Isoconcentration Map of Ethylbenzene (September, 1984) Showing Concentrations in Selected Wells.
compared with benzene, toluene, and ethylbenzene. Xylenes have also been found to be consumed as a sole source of carbon and energy by bacteria (Wilson, Smith, & Rees, 1986).

Xylenes in well M8 decreased from 220 ug/L in September, 1984 to 60 ug/L in March, 1985 and decreased to a minimum of 43 ug/L by September, 1985 suggesting rapid anaerobic biodegradation. Ethylbenzene levels were generally lower and more stable, suggesting that ethylbenzene was not degraded as rapidly. The most notable decrease in ethylbenzene occurred further from the landfill at 745 South 4th Street. Ethylbenzene decreased from 220 ug/L in September, 1984 to non-detectable levels in March, 1985. This rapid decrease in the concentration of ethylbenzene may be the result of the location of this well further downgradient, where there may be a significant influx of uncontaminated oxygen-rich water, at the edge of the plume, allowing rapid aerobic biodegradation. Only 26 ug/L of xylene was detected nearby at 710 South 4th Street in September, 1984 and decreased to non-detectable levels by the following sampling quarter. The xylene plume is the smallest plume at the KL Landfill and is confined to the filled area and wells near the filled area (Figure 82).
Alcohols, Ketones, and Ethers

Alcohols were first reported in the groundwater samples in March, 1984. 2-Propanol was found at extremely high levels ranging from 2,400 ug/L to 68,000 ug/L between March, 1984 and September, 1985. By March, 1986, however, 2-propanol was non-detectable in all wells. Methyl pentanol was detected in the hundreds of micrograms per liter to the low thousands of micrograms per liter from March, 1984 through March, 1986. Ethanol and methyl propanol did not reach detectable levels until March, 1985. Ethanol was detected, generally, at levels in the hundreds of micrograms per liter, and the methyl propanol was detected in the thousands of micrograms per liter.

Three ketones were reported including 2-butanone, 4-methyl 2-pentanone, and 2-propanone (acetone). All three of these chemicals reached concentrations in the thousands of micrograms per liter. Both the 2-butanone and 4-methyl 2-pentanone were detected from March, 1984 to March, 1986. The 2-propanone was non-detectable across the site by March, 1986.

The only ether detected in the groundwater samples was ethyl ether. It was found in several wells at detectable levels from March, 1984 to March, 1986. Ethyl ether ranged from 9 ug/L to 3,400 ug/L averaging in the
hundreds of micrograms per liter.

The alcohols, ketones, and ether were first detected 4 to 5 years into the monitoring program. Concentrations remained relatively stable in all wells with slight increases and decreases over the detection period. Because of the sparse data, concentrations could not be contoured for a plume analysis or analyzed statistically.

1,1-Dichloroethane and 1,2-Dichloroethane

1,1-Dichloroethane and 1,2-dichloroethane were included in the Group 1 organic chemicals due to their high concentrations, wide distribution across the landfill site, and persistence throughout the 7-year monitoring program. They could, therefore, be contoured for a plume analysis and studied relative to distance from the source of the contamination, and be studied with depth. Both of these chemicals are also secondary biotransformation intermediates and will be discussed further in Chapter VIII.

Concentrations Relative to Distance from the Landfill

Compared with other Group 1 organic chemicals, the concentrations of 1,1-dichloroethane and 1,2-dichloroethane are high. 1,1-dichloroethane ranges from the low hundreds of micrograms per liter to the low
thousands of micrograms per liter, whereas 1,2-dichloroethane reaches concentrations in the low hundreds of micrograms per liter. The highest concentrations of 1,1-dichloroethane and 1,2-dichloroethane were found within 900 feet of TW4.

M8 contains high levels of 1,1-dichloroethane (1,609 ug/L) only in 1980. From 1982 to 1986, low levels of 1,1-dichloroethane (32-160 ug/L) are detectable about 2,300 feet downgradient of TW4 at 710 South 4th Street. The highest 1,1-dichloroethane concentration (3,300 ug/L) was detected in March, 1983 at TW4 (Figure 84).

1,2-Dichloroethane exhibits a secondary peak also in 1980, approximately 1,200 feet downgradient in TW1. From March, 1983 to March, 1986 a low concentration of 1,2-dichloroethane was also detected at 710 South 4th Street. The highest 1,2-dichloroethane concentration (426 ug/L) was detected in TW4 in June, 1980 (Figure 85).

Plume Analyses

In March, 1980 1,1-dichloroethane was detected in only a few wells. However by March, 1981 the plume extended to 691 South 4th Street and was relatively wide (Figure 86). By 1982, the plume had receded to M1 and M2. By 1983, it was at 710 South 4th Street and had reached its
Figure 84. 1,1-Dichloroethane Concentrations in Selected Wells Versus Distance and Time (1982-1983). (Percent Concentration Relative to TW4 (3/83) 3,300 ug/L).
Figure 85. 1,2-Dichloroethane Concentrations in Selected Wells Versus Distance and Time (1980). (Percent Concentration Relative to TW4 (6/80) 426 ug/L).
Figure 86. Map of the 1,1-Dichloroethane and 1,2-Dichlorethane Plumes (March, 1981). (Plumes are Delineated With the 10 ug/L Contours Taken From More Densely Contoured Maps. Concentrations Shown are Maximum Values for 1981).
maximum width. From 1984 to 1986, the plume remained at 710 South 4th Street, but began to decrease in width. Overall, the area of the 1,1-dichloroethane plume gradually increased (Figure 87) with significant areal fluctuations through 1982, but stabilized and decreased gradually from 1983 to 1986.

In 1981 the 1,2-dichloroethane plume extended to 691 South 4th Street and was at its maximum width (Figure 86). From 1982 through 1985, the perimeter of the plume fluctuated. By 1986, 1,2-dichloroethane was only detected in a few wells. The 1,2-dichloroethane plume has generally decreased in area with time, but with rather large fluctuations in concentration (Figure 88). The fact that both of these organic chemicals fluctuate markedly, perhaps reflects rapid anaerobic biotransformation. Both of these alkanes are secondary biotransformation products within the first alkane biotransformation sequence. Other Group 1 organic chemicals were far more stable and persistent.

Concentrations Relative to Depth

When 1,1-dichloroethane was plotted with depth, the highest concentrations generally appeared in shallow wells between 5 and 15 ft below static water level (S.W.L.) (Figure 89). The maximum 1,1-dichloroethane concentration
Figure 87. Graph Illustrating the General Increase in Area of the 1,1-Dichloroethane Plume With Time (1980-1986).
Figure 88. Graph Illustrating the General Decrease in Area of the 1,2-Dichloroethane Plume With Time (1980-1986).
Figure 89. 1,1-Dichloroethane Concentrations Versus Depth (1981). (Percent Concentration Relative to TW4 (3/83) 3,300 ug/L).
(3,300 ug/L), detected at the site, during the 7-year monitoring period (3/83), was in TW4 (16 ft below S.W.L.). However, during 6/80, when 1,1-dichloroethane first appeared in wells at the site, a high concentration of 49% was detected in the well at 691 S. 4th St. (30 ft below S.W.L.), but from 9/80 to 3/86 the highest concentrations were detected in shallow wells closer to the landfill (Figure 89).

1,2-Dichloroethane only reached high concentrations in the shallow wells between 5 and 15 ft below S.W.L. The maximum concentration (426 ug/L) was recorded during 6/80 in TW4 (16 ft below S.W.L.) (Figure 90). High concentrations were also recorded in M3, TW1, and M4.
Figure 90. 1,2-Dichloroethane Concentrations Versus Depth (1980-1981). (Percent Concentration Relative to TW4 (6/80) 426 ug/L).
CHAPTER VIII

GROUP 2 ORGANIC CHEMICALS

Biotransformation Sequences

Temporal and spatial variations in concentrations of organic chemicals in the KL Landfill plume can be explained by biotransformation sequences. Transformation of chlorinated hydrocarbons is enhanced by the presence of non-chlorinated carbon which promotes rapid co-metabolism to dehalogenate the chlorinated compounds. More specifically, the non-chlorinated carbon sources provide the electrons for the active microorganisms to perform the reduction (Wilson, Leach, Henson, & Jones, 1986). Non-chlorinated carbon sources in the KL Landfill leachate plume include the other synthetic organic chemicals present such as benzene, toluene, xylenes and phenols; gaseous hydrocarbons such as methane or propane; decomposing organic refuse; or natural organic matter in the aquifer (Cline & Viste, 1984). The average pH of the KL plume is 7.2 and is favorable for microbial degradation of organic compounds (Parsons & Lage, 1985).

Biotransformation is indicated by the low concentrations and lack of persistence of the primary organic
chemicals 1,1,1-trichloroethane; 1,1,2-trichloroethane; tetrachloroethane; tetrachloroethene; and 1,1,2-trichloroethene, and the relatively high concentrations of biotransformation products such as 1,1-dichloroethane; 1,2-dichloroethane; and cis-1,2-dichloroethene. Biotransformation products that are found in wells at high concentrations and are widely distributed across the site (appearing in several wells) can sometimes be contoured for isoconcentration maps. The primary compounds such as 1,1,1-trichloroethane; trichloroethene; and tetrachloroethene are all manufactured in large quantities in the United States (Wood, Lang, & Payan, 1985) as dry cleaning agents, propellants, solvents, extractors, and degreasers (e.g. Sax, 1979; Sittig, 1981). The biotransformation products such as vinyl chloride; 1,1-dichloroethene; cis-1,2-dichloroethene; trans-1,2-dichloroethene; 1,2-dichloroethane; and chloroethane are chemicals that either are not produced or are not in common use across the entire country as are the primary compounds (Wood et al., 1985). Because they are highly susceptible to reductive dehalogenation, alkanes generally develop transformation products more rapidly and at higher concentrations than the alkenes (Parsons & Lage, 1985) as illustrated by the following sequence indicating relative biodegradability:
1,1,1-trichloroethane > carbon tetrachloride >
trichloroethene > tetrachloroethene

Three anaerobic biotransformation sequences are indicated by the data from the KL Landfill plume:

1. \[1,1,1\text{-trichloroethane} \rightarrow \begin{cases} 1,1\text{-dichloroethane} \\ 1,2\text{-dichloroethane} \end{cases} \rightarrow (\text{long})
(16 \text{ days})^* \rightarrow (\rightarrow) \text{ chloroethane} \rightarrow (10 \text{ days})

2. \[\text{carbon tetrachloride} \rightarrow \text{chloroform} \rightarrow \text{methylene chloride} \rightarrow \text{vinyl chloride} \rightarrow \text{vinyl chloride} \]
(14 \text{ days}) \rightarrow (36 \text{ days}) \rightarrow (11 \text{ days})

3. \[\text{tetrachloroethene} \rightarrow \text{trichloroethene} \rightarrow (34 \text{ days}) \rightarrow (43 \text{ days}) \]
(10) \[\begin{cases} \text{cis-1,2-dichloroethene} \\ \text{trans-1,2-dichloroethene} \end{cases} \rightarrow \text{vinyl chloride} \rightarrow \text{vinyl chloride} \rightarrow (53 \text{ days}) \rightarrow (\text{long})

*Biodegradation half-lives (Wood et al., 1985).

If chemicals were released instantaneously and were not adsorbed, parent chemicals should initially be found close to the landfill, whereas secondary and tertiary biotransformation products should be found along the flow path further from the landfill (Cline & Viste, 1984). This, however, is not generally the case at the KL Landfill.
Alkane Biotransformation Sequence 1

1,1,1-trichloroethane $\rightarrow$ 1,1-dichloroethane $\rightarrow$ 1,2-dichloroethane $\rightarrow$ chloroethane

The organic chemicals involved in the first alkane biotransformation sequence exhibit significant variations in concentration and erratic areal distributions. 1,1,1-trichloroethane is the primary or parent chemical of the sequence, but it was not detected in the KL contaminant plume until September, 1984 (Figure 91). The highest detected concentration (190 ug/L) was found at 710 South 4th Street, approximately 2,250 feet west of the landfill. Generally, lower concentrations of 1,1,1-trichloroethane were detected in wells on or adjacent to the landfill, for example M4 (66 ug/L) and TW4 (55 ug/L). After September, 1984, 1,1,1-trichloroethane concentrations decreased rapidly to non-detectable levels.

The secondary biotransformation products were detected at much higher concentrations than the other biotransformation intermediaries. Additionally, 1,1-dichloroethane, the preferred secondary biotransformation product, occurred at much higher concentrations, ranging from the mid-hundreds to the low thousands of micrograms per liter, whereas 1,2-dichloroethane reached maximum

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Figure 91. Alkane Biotransformation Sequence (1) Compounds Versus Time (1980-1986) Using Quarterly Average Plume Concentrations.
concentrations in the low hundreds of micrograms per liter (Figure 92). The concentrations of these two secondary biotransformation products were highest adjacent to the landfill in TW4, M3, and M4. However, 1,1-dichloroethane was detected at much higher levels and was more persistent at downgradient wells such as 691 South 4th Street and 710 South 4th Street than 1,2-dichloroethane (Figure 93). A concentration of 1,609 ug/L 1,1-dichloroethane was found as early as March, 1980 at 691 South 4th Street. This preceded the appearance of 1,1,1-trichloroethane at 710 South 4th Street. This sudden appearance of such a high concentration of the secondary biotransformation product approximately 1,950 feet downgradient of the landfill, could be due to an excessive precipitation event or an early discharge of the anaerobically degraded biotransformation product. This could also reflect anaerobic conditions existing along the flow path causing degradation of primary compounds downgradient of the filled area. Since several biodegradable organic chemicals are detectable within the plume such as phenols, benzene, toluene, and xylenes, microbiological degradation with time would promote anaerobic conditions. Additionally, as the anaerobic conditions extended further downgradient, anaerobic biotransformations would occur
Figure 92. Alkane Biotransformation Sequence (1) Compounds Relative to Chloride With Time (1980-1986) in TW4.
Figure 93. Alkane Biotransformation Sequence (1) Compounds Relative to Chloride With Distance From the Landfill (June, 1980).
further from the landfill. A rapid decrease in TOC values downgradient of the landfill proper, along the flow path (Figure 94), indicates that active biodegradation of organic chemicals in the leachate plume is occurring (Kehew et al., 1988).

The tertiary or final biotransformation product in the sequence is chloroethane. It was detected in March, 1984, again prior to the appearance of 1,1,1-trichloroethane, at concentrations ranging between 60 and 110 ug/L. The chloroethane plume is limited to wells closer to the landfill and extends west approximately 500 feet to M8 where concentrations reached 60 ug/L (Figure 95). The number of wells containing chloroethane and the concentrations within each well decreased by September, 1984, to between 25 and 35 ug/L.

Previous studies indicate that primary compounds, such as 1,1,1-trichloroethane, tend to decrease with distance from the contamination source as concentrations of 1,1-dichloroethane increase (Wood et al., 1985). The following are possible explanations for the relatively low concentrations of 1,1,1-trichloroethane adjacent to the KL Landfill and the higher levels occurring further downgradient.
Figure 94. Isoconcentration Map of TOC (May, 1987) With TOC Concentrations in Wells Sampled (Adapted from Kehew et al., 1988). (The Plume is Defined by the 100 mg/L Contour).
Figure 95. Isoconcentration Map of Chloroethane (March, 1984) With Concentrations Detected in Various Wells.
1. 1,1,1-trichloroethane has a short biodegradation half-life and could be biotransformed directly beneath the landfill and would, therefore, not appear in the monitoring wells on the edge or adjacent to the landfill. However, a slug of 1,1,1-trichloroethane could have been mobilized, at an earlier date (prior to sampling), that was not completely biotransformed and was carried downgradient to wells further from the landfill resulting in its initial detection at 710 South 4th Street.

2. The microbial populations required for significant biotransformation are concentrated in the anaerobic environment beneath and adjacent to the landfill, biodegrading the 1,1,1-trichloroethane and lowering concentrations in this area. However, in the more oxygenated groundwater downgradient, the 1,1,1-trichloroethane persists without being completely biotransformed.

3. The environmental and chemical conditions that control rates of biotransformation such as water temperature, pH, organic compounds, the concentration of the substrate, the presence of microbial toxicants, the presence of nutrients, and the availability of electron acceptors (Mackay et al., 1985), may have been temporarily unavailable allowing the 1,1,1-trichloroethane to be carried further downgradient.
4. The specific microorganism populations necessary for biotransformation (Wood et al., 1985) were not established before a slug of 1,1,1-trichloroethane moved downgradient from the landfill.

5. A large, sudden discharge of the primary organic chemicals, such as from a tanker truck, overwhelmed the system inhibiting the biotransformation process on the landfill allowing the 1,1,1-trichloroethane to be carried downgradient (Wood et al., 1985).

6. A major precipitation event could have flushed the 1,1,1-trichloroethane slug into the flow system faster than the bacteria were able to biotransform the compound.

7. The monitoring well network does not accurately represent the distribution of some chemicals at the site, due to the lack of several multi-level well nests.

Generally, however, average monthly precipitation does not correlate well with the concentrations of the transitional organic chemicals of Group 1 over the 7-year monitoring period. The correlation coefficient is .12 for 1,1-dichloroethane and .25 for 1,2-dichloroethane. The concentration of 1,2-dichloroethane however, was detected in June, 1980 and the average monthly rainfall for the sampling quarter ending June, 1980 was 6.98 inches, one of the highest recorded precipitation levels of the 7-year sampling period. The data indicate that sampling quarters
having exceptionally high precipitation tend to have a significant effect, increasing the organic chemical concentrations markedly. The apparent negligible effects of low or average precipitation events may be due to the fact that the landfill is covered with the bentonite-natural soil cover, although this final cover does have a wide range of permeabilities (Carey, in preparation).

The chloroethane plume is limited to an area adjacent to the KL Landfill (Figure 95). In previous studies (Wood et al., 1985), chloroethane appeared only when the concentration of the primary compound was high, whereas at the KL Landfill these primary compounds such as 1,1,1-trichloroethane and 1,1,2-trichloroethane are present at low to non-detectable levels and do not always appear at detectable levels until well into the monitoring program. Additionally, when moving downgradient from the source, only 1,1-dichloroethane was present while chloroethane, the final biotransformation product, was not detected in the same downgradient wells. Chloroethane, however, has a short laboratory-derived biodegradation half-life of 10 days and would probably exist only in wells near the landfill. The highly anaerobic conditions close to the landfill favor the growth of anaerobic bacteria responsible for the biodegradation restricting the plume to the area beneath and immediately downgradient from the
landfill.

Alkane Biotransformation Sequence 2

carbon tetrachloride → chloroform → methylene chloride

Carbon tetrachloride was not detected during the 7-year sampling period. Chloroform, however, was detected in several wells in March, 1980, when the plume reached its maximum downgradient extent in the vicinity of 710 South 4th Street (Figure 96). The highest concentrations of chloroform, in March, 1980, were found within 1,000 feet of TW4 and ranged between 110 ug/L to 590 ug/L. Chloroform levels increased to 6,250 ug/L in M4 and 380 ug/L in M8 during September, 1980 but were non-detectable to less than 10 ug/L in all other wells. From December, 1980 through 1986, chloroform concentrations remained at or near non-detectable levels (Figure 97).

Methylene chloride concentrations (Figure 96) were high in March, 1980 when 490 ug/L were detected at 710 South 4th Street (Figure 98). In June, 1980, a concentration of 2,430 ug/L methylene chloride was detected in TW4 and by September, 1980 concentrations had increased to 2,600 ug/L. Generally, from 1980 through 1986 the concentrations of methylene chloride ranged between 2 ug/L and 2,600 ug/L, whereas chloroform
Figure 96. Map of the Chloroform Plume (March, 1980) and the Methylene Chloride Plume (March, 1981). (Concentrations Shown are Maximum Values for 1980 and 1981).
Figure 97. Alkane Biotransformation Sequence (2) Compounds With Time (1980-1986) Using Quarterly Average Plume Concentrations.
Figure 98. Alkane Biotransformation Sequence (2) Compounds Relative to Chloride Versus Distance From the Landfill (March, 1980).
concentrations were non-detectable after September, 1982.

The persistence of methylene chloride compared with the disappearance of chloroform may be due to disposal of methylene chloride in the landfill and/or the biotransformation of chloroform to methylene chloride. Chloroform droplets may have been retained within the pore spaces of the upper aquifer beneath the landfill even after the majority of the slug had passed through the flow system (Mackay et al., 1985). Subsequent release, possibly during periods of increased precipitation, may have resulted in continued biotransformation of chloroform to methylene chloride.

The high concentrations of methylene chloride detected in June, 1980 (2,430 ug/L); September, 1983 (58 ug/L); and September, 1984 (64 ug/L), may possibly be related to the three corresponding average monthly precipitation maxima of 6.98 inches, 7.75 inches, and 6.37 inches. These values are twice the expected average monthly precipitation levels for Kalamazoo County during those months. Once again, it appears that only during months of exceptionally high precipitation will there be sufficient infiltration through the bentonite-natural soil cover to mobilize organic chemicals contained within the landfill materials or previously adsorbed onto mineral surfaces or trapped within pore spaces. During these
periods significant correlations may exist between precipitation and organic contaminant concentrations in the groundwater.

Generally, wells that contain high concentrations of chloroform eventually yield high concentrations of methylene chloride such as at 710 South 4th Street, TW4 (Figure 99), and M3. Additionally, methylene chloride concentrations were detectable consistently through March, 1985, ranging from 50 ug/L to 200 ug/L and remained detectable after chloroform had decreased to non-detectable levels, suggesting that the chloroform may have been biotransformed to methylene chloride.

Alkene Biotransformation Sequence 3

\[
tetrachloroethene \rightarrow \text{trichloroethene} \rightarrow \]
\[
( \rightarrow ) \begin{bmatrix} \text{cis-1,2-dichloroethene} \\ \text{trans-1,2-dichloroethene} \end{bmatrix} \rightarrow \text{vinyl chloride}
\]

Of the biotransformation sequences discussed in this paper, the alkenes exhibit the greatest concentration variations and frequency of appearances and disappearances of the primary, secondary, tertiary and quaternary alkene intermediates (Figure 100).

With few exceptions, tetrachloroethene and trichloroethene were non-detectable or at very low
Figure 99. Alkane Biotransformation Sequence (2) Compounds Relative to Chloride Versus Time (1980-1986) in TW4.
Figure 100. Alkene Biotransformation Sequence Compounds Versus Time (1980-1986) Using Quarterly Average Plume Concentrations.
concentrations in 1980. In March, 1980, tetrachloroethene concentrations were 8 ug/L in M8 and 5 ug/L in TW4 (Figure 101). By June, 1980, the concentration in TW4 had increased to 488 ug/L, but then tetrachloroethene decreased to non-detectable levels, and 1,1,2-trichloroethene began to appear in higher concentrations (5 ug/L to 100 ug/L) in TW4 and M8. In September, 1984, after decreasing in concentration, 1,1,2-trichloroethene reappeared in higher concentrations in several wells reaching a maximum concentration of 160 ug/L in TW4 and 73 ug/L at 710 South 4th Street.

The higher concentration of tetrachloroethene in TW4 (488 ug/L) in June, 1980, relative to only 2 ug/L, 1,1,2-trichloroethene conforms to the sequence of susceptibility to reductive dehalogenation. 1,1,2-Trichloroethene has a higher susceptibility to biotransformation. The lack of persistence and the low- to non-detectable levels of both the primary and secondary compounds appear to be due to short biodegradation half-lives and rapid biotransformation to cis-1,2-dichloroethene and trans-1,2-dichloroethene. According to Wilson, Leach, Henson, & Jones (1986), anaerobic degradation occurs rapidly without a lag time which would account for the low levels of the primary compounds and the higher levels of the biotransformation products. Since 1,1,2-trichloroethene
Figure 101. Alkene Biotransformation Sequence Compounds Relative to Chloride Versus Distance From the Landfill (March, 1980).
has a higher susceptibility to biotransformation, is known to undergo anaerobic biotransformation immediately without a lag time, and is found at low to non-detectable levels early in the monitoring program, there is a possibility that this secondary organic intermediary is the sole source of the cis-1,2-dichloroethene. Generally at the KL Landfill, the primary alkenes tended to disappear or remain at low levels, until 1984.

The sudden reappearance of the primary compounds in September, 1984 (Figure 102), which is characteristic of organic chemicals in biotransformation sequences (Wood et al., 1985), even though their half-life values are short, may be due to intermittent discharges to or releases from the landfill resulting in inhibited growth of the biotransforming bacteria. However, as the slug moves downgradient and dilution takes place, biodegradation would be reinitiated (Wood et al., 1985). Another possibility might be the levels of trace nutrients present in the surface water that infiltrates into the groundwater or the level or quality of organic carbon present. Both may inhibit biotransformation (Parsons, Wood, & DeMarco, 1984).

Generally during the early sampling years, cis-1,2-dichloroethene existed at higher concentrations in several of the wells compared with tetrachloroethene and 1,1,2-
Figure 102. Alkene Biotransformation Sequence Compounds Relative to Chloride Versus Distance From the Landfill (September, 1984).
trichloroethene. The cis-1,2-dichloroethene concentrations were 2,160 ug/L at TW4 (Figure 103) and 470 ug/L at 710 South 4th Street in March, 1980 (Figure 101). The persistence of the tertiary and quaternary biotransformation intermediaries, cis-1,2-dichloroethene; trans-1,2-dichloroethene; and vinyl chloride, is probably a result of their long biodegradation half-lives. The high levels of cis-1,2-dichloroethene in wells on and adjacent to the filled area indicates that biotransformation is occurring directly beneath and immediately adjacent to the landfill. By December, 1981, the cis-1,2-dichloroethene levels in several wells declined, while 1,1,2-trichloroethene was first appearing at detectable levels. The greatest areal extent of the cis-1,2-dichloroethene plume occurred in June, 1980, when 7 monitor wells contained detectable levels of cis-1,2-dichloroethene. Thereafter, cis-1,2-dichloroethene concentration levels tended to decrease and after September, 1983, were non-detectable. Later in September, 1984, 1,1,2-trichloroethene was again detected at its highest recorded concentration level, reaching its maximum areal extent appearing in 8 wells across the site. This once again appears to indicate that 1,1,2-trichloroethene and cis-1,2-dichloroethene are directly related.
Figure 103. Alkene Biotransformation Sequence Compounds Relative to Chloride Versus Time (1980-1986) in TW4.
Trans-1,2-dichloroethene, on the other hand, was non-detectable until March, 1984, when 3 ug/L were detected in TW3. Concentrations of trans-1,2-dichloroethene then gradually increased until September, 1984, appearing in a maximum of 7 wells.

An interesting relationship in the KL plume involves the occurrence of cis-1,2-dichloroethene and trans-1,2-dichloroethene. As stated above, they do not appear to co-exist within the contaminant plume. The cis-1,2-dichloroethene decreased to non-detectable levels by October, 1983, whereas trans-1,2-dichloroethene was first detected in March, 1984. In a previous study conducted by Cline and Viste (1984), it was observed that trans-1,2-dichloroethene only occurred simultaneously with cis-1,2-dichloroethene when concentrations were extremely high. In the KL plume, the appearance of trans-1,2-dichloroethene after cis-1,2-dichloroethene may be due to the presence of increased levels of the synthetic organic chemicals becoming trapped within the pore spaces of the aquifer (Mackay et al., 1985). Through time this may create a non-polar flow environment as a result of higher levels of the organic compounds eventually becoming soluble within the groundwater, decreasing the polarity of the water, favoring the formation of the non-polar transformation product or the trans-1,2-dichloroethene.
The formation of one biotransformation product at the expense of another is governed by the reductive dechlorination mechanism. According to the laboratory study of Parsons and Lage (1985), during reductive dechlorination the chlorinated organic compound captures a free electron and dissociates into a chloride ion and a free radical. When the free radical is formed it will be affected by the surrounding solvent. If the solvent is water, a polar solvent, the more polar form of the transition state radical will be formed leading to the cis-1,2-dichloroethene isomer. If however, the surrounding solvent is less polar, the trans-1,2-dichloroethene isomer would be favored. Of course there is a possibility that the specific microorganisms required to transform the tetrachloroethene or 1,1,2-trichloroethene to trans-1,2-dichloroethene may not have been available within the aquifer until later when conditions were achieved that favored their growth (Mackay et al., 1985).

In January of 1987, during a more recent EPA investigation of the site, vinyl chloride was detected for the first time in MW9 at 120 ug/L. Trans-1,2-dichloroethene was detected at a concentration of 8 ug/L in MW9, 7 ug/L in MW1, and 46 ug/L in MW7, whereas cis-1,2-dichloroethene was non-detectable. Trans-1,2-
dichloroethene may be the only alkene constituent of the biotransformation sequence other than vinyl chloride that is still present in detectable levels in the contaminant plume.

It is also possible that the later appearance of trans-1,2-dichloroethene and vinyl chloride may be due to the fact that both have lower solubilities than cis-1,2-dichloroethene and would require more time for mobilization. The fact that vinyl chloride was detected for the first time in 1987, 1,900 feet away from the landfill, suggests that this is not the case and that biotransformation is occurring at the landfill and downgradient.
CHAPTER IX

SUMMARY AND CONCLUSIONS

Flow and Physical Properties

Organic chemical contaminants at the KL Landfill site tend to be carried horizontally through the aquifer, except adjacent to the landfill where mounding of the groundwater appears to be superimposing a slight vertical hydraulic gradient on the system, possibly carrying the organic chemicals down to greater depths (M8). Therefore, the leachate plume extends at least to a depth of 72.5 ft below static water level; however, the plume most likely extends to the till (Unit 5). There appears to be no distinct relationship between the organic chemical distribution and behavior, and the physical properties of these chemicals. Only a 0.04-0.38 g/cm$^3$ density difference exists between the Group 1 and Group 2 organic chemicals delineated.

The contaminant plume is predominantly coincident with a portion of the interpreted buried channel at the site. This buried channel tends to divert local groundwater flow and the subsequent contaminant migration from the landfill in a southwesterly direction. Due to
the composition of the glacial deposits in the area, consisting primarily of sand, gravel, and silt, with little or no clay or organic carbon, the glacial deposits do not appear to contribute significantly to the attenuation of the organic chemicals. This is illustrated by the high mobility of the organic chemical contaminants (ethylbenzene, toluene, and tetrachloroethene) possessing high octanol/water partition coefficients.

Precipitation

Precipitation events appear to increase the organic chemical concentrations within the flow system only during periods of unusually high precipitation, when it is about twice the normal average monthly value. However, there is no general correlation between the organic chemical concentrations and average quarterly precipitation levels.

Statistical Analysis

A stable moderate correlation exists between the plume average quarterly values for benzene, toluene phenols, 1,1-dichloroethane and 1,2-dichloroethane versus chloride, generally ranging from .45 to .57. This indicates that the occurrence of organic chemicals at the site has been similar to chloride. The plume average quarterly values versus precipitation exhibits only a low
correlation ranging from -.02 for toluene to .31 for 1,1-dichloroethane. The correlation coefficients for plume average quarterly values and COD are extremely variable. Yet these correlation coefficients are all positive and significant, ranging from a low of .24 for 1,2-dichloroethane to a high of .71 for 1,1-dichloroethane.

All of the correlation coefficients determined for the organic chemicals relative to precipitation, COD, and chloride in TW4, were generally variable and extremely low with the majority of the coefficients falling within the low correlation category indicating a definite but small relationship.

Plume Area

The two organic chemicals found at the highest concentration levels in groundwater at the KL Landfill site are the phenols and toluene. The maximum westerly extent of the contaminant plume is M5, about 375 feet east of Dustin Lake. Phenols, iron, lead, and chromium have been detected in M5. The phenols plume periodically expanded and contracted throughout the 7-year monitoring period perhaps due to rapid aerobic biodegradation or dilution, yet, overall, exhibited a gradual increase in plume area from 1980 through 1986. The phenols plume reached a maximum area of 0.22 mi². The benzene plume had
a general tendency to decrease in area, but concentrations in individual wells remained relatively steady during this period. The maximum areal extent of the benzene plume was 0.08 mi$^2$. The toluene plume also gradually increased in areal extent, as the phenols, with only minor plume area fluctuations. The maximum toluene plume area was 0.09 mi$^2$. The concentration fluctuations of the phenols, benzene, and toluene within the core of the plume could be due to anaerobic biodegradation, or perhaps variable release of the organic chemicals from the landfill. The low redox potential within the plume would allow the organic contaminants to degrade anaerobically. In the wells at the margins of the KL Landfill plume, aerobic biodegradation appears to be oxidizing organic compounds such as the phenols, benzene, and toluene.

Organic Chemical Concentrations in Wells With Time and Depth

Phenols concentrations gradually increased downgradient throughout the study period. Phenols were first detected in shallow wells (16-24 ft below static water level) and later appeared in deep wells also. Phenols appear to be undergoing rapid biodegradation in deep and shallow wells. This suggests that wells screened closer to the air-water interface are not necessarily

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displaying any greater degree of aerobic degradation relative to the degree of anaerobic degradation occurring in wells of greater depth. However, only in wells at the periphery of the plume, where there is a greater influx of oxygenated water, does there appear to be any enhanced rates of biodegradation. This is due to the fact that aerobic degradation is faster and more efficient than anaerobic degradation.

Initially, benzene concentrations were high adjacent to the landfill and downgradient. The highest concentrations of benzene were always detected about 1,000 feet downgradient from the landfill proper (TW4) at M8. Through time, concentrations decreased slightly on and adjacent to the landfill, but drastically decreased downgradient. Benzene concentrations are generally far more stable throughout the study period in wells than the phenols, which fluctuated drastically in all wells. Therefore it appears that anaerobic biodegradation does not reduce benzene concentrations as much as other petroleum by-products. Instead benzene may be undergoing aerobic degradation more rapidly at the periphery of the plume than anaerobic degradation within the core of the plume, because the plume area is smaller and concentrations are very low in wells at the perimeter of the plume. Unlike phenols, benzene concentrations are
generally higher consistently at greater depths (72.5 ft below S.W.L.) in M8.

Toluene concentrations are far more variable than benzene concentrations, but much less variable than the phenols concentrations. This may indicate that toluene is undergoing a greater degree of anaerobic degradation than benzene. Toluene concentrations are initially higher downgradient, increase on and adjacent to the landfill, and near the end of the monitoring period, concentrations increased much further downgradient, decreasing adjacent to the landfill. Toluene was detected consistently in the same wells during the 7-year monitoring period, and the stability of the toluene plume area may indicate that lesser degrees of aerobic degradation may be occurring along the fringes of the toluene plume. Initially, toluene concentrations are higher at greater depths; however, through time concentrations began to increase in the shallow wells.

Chloride

The areal distribution of chloride is generally much different from the organic chemical distribution. Chloride concentrations in several wells display a steady increase followed by a steady decrease in concentration with only minor concentration fluctuations superimposed on
those trends. When comparing chloride concentrations versus distance from the landfill (TW4), the only notable similarity occurs between benzene and chloride. Chloride and benzene concentrations are high at M8 consistently from 1980 to 1986. The chloride plume is similar to the phenols plume in that both appear to have reached M5, the well farthest downgradient of the landfill, and both were detected in wells slightly upgradient. Fluctuations in the phenols plume, however, are more extreme and out of phase with the chloride plume fluctuations. The only organic chemical detected as far upgradient as chloride was benzene. When comparing their plume area trends, the only similarity is that benzene exhibits a general decrease with time as does chloride. Relative to depth, the chloride appears in shallow wells or closer to static water level, while the organic chemicals tend to remain at greater depths below static water level, consistently. The organic chemical in this study that behaved most similarly to chloride was the phenols. Both the area of the phenols plume and its distribution with depth resemble chloride.

Arenes, Alcohols, Ketones, and Ethers

The xylenes and ethylbenzene were detected late in the study period; this appears to be due to their low
solubilities in water. Both the xylenes and ethylbenzene plumes are small plumes located on and adjacent to the landfill. According to the literature, losses due to sorption and volatilization would be negligible and the majority of the attenuation resulting in the greatest losses of these chemicals would be attributed to biodegradation. The alcohols, ketones, and ethers were detected too late in the monitoring program to assess their distribution and behavior.

1,1-Dichloroethane and 1,2-Dichloroethane

1,1-Dichloroethane and 1,2-dichloroethane, both exhibited a general decrease in plume area during the study period. Extreme plume fluctuations, and abrupt decreases in chemical concentration levels, are interpreted to be due to the fact that both of these chemicals are secondary biotransformation intermediaries within the first alkane biotransformation sequence.

Biotransformation Sequences

Biotransformation appears to be a plausible model for the temporal and spatial distributions of chlorinated alkanes and alkenes within the contaminant plume emanating from the KL Avenue Landfill. Several of these organic contaminants were found in only a few wells, and occurred
at lower concentrations, appeared or disappeared in wells within the center of the plume, or appeared in wells located further downgradient from the landfill. In the anaerobic portions of the plume, the primary organic chemicals of the aforementioned biotransformation sequences, were detectable at low concentrations and generally were not detected until well into the monitoring program: 1,1,1-trichloroethane (9/84); 1,1,2-trichloroethane (6/80); tetrachloroethene (6/80 & 9/84); and 1,1,2-trichloroethene (12/81 & 9/84), in monitor wells located downgradient of the source. These primary organic chemicals tended to disappear abruptly, possibly being biotransformed to secondary or tertiary products such as 1,1-dichloroethane, 1,2-dichloroethane, and cis-1,2-dichloroethene that were detectable across the site at higher concentrations. 1,1-Dichloroethane is the preferred secondary biotransformation product of the first alkane biotransformation sequence, occurring more consistently and at higher concentration levels in several of the monitor wells relative to 1,2-dichloroethane.

In the alkene biotransformation sequence, since 1,1,2-trichloroethene has a higher susceptibility to biotransformation, is known to undergo anaerobic biotransformation immediately without a lag time, and is found at low to non-detectable levels early in the
monitoring program, there is a possibility that this secondary organic intermediary may be the sole source of the cis-1,2-dichloroethene. When cis-1,2-dichloroethene levels decrease, 1,1,2-trichloroethene levels begin to increase, because 1,1,2-trichloroethene is not being biotransformed. Therefore when biotransformation is inhibited, cis-1,2-dichloroethene would decrease to non-detectable levels.

Concentrations of the primary organic chemicals, at some distance from the landfill, suggest that biotransformation near the landfill was not always complete perhaps due to decreases in microbial populations, sudden discharges of chemicals from the landfill into the flow system, increased precipitation levels, environmental and chemical conditions within the flow system, or biodegradation half-lives. The restricted distribution of the tertiary biotransformation product of biotransformation sequence one, chloroethane, may be due to extensive biodegradation beneath the landfill, since, technically, it should be detected further downgradient. In the second alkane biotransformation sequence, when chloroform reaches non-detectable levels in several monitor wells, methylene chloride levels increase in concentration in the same wells suggesting that chloroform was largely biotransformed to methylene chloride. In the
alkene biotransformation sequence, the later appearance of vinyl chloride, in MW9 approximately 1,000 feet west of TW4, seems to suggest that anaerobic conditions may be advancing further downgradient causing biotransformation at greater distances from the landfill. The later formation of trans-1,2-dichloroethene, at the expense of cis-1,2-dichloroethene within the plume, may be due to a gradual decrease in polarity of the groundwater flowing within the aquifer, favoring the formation of the less polar trans-1,2-dichloroethene intermediate. However, it may also be due to the solubility differences of the chemicals or the rate of bacterial development. The biotransformation model, therefore, can be used to explain several aspects of the organic chemical behavior at the KL Landfill site.
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