

# LEACHATE CHARACTERISTICS FOR MSW LANDFILLS

R.K. Rowe

Geotechnical Research Centre  
Department of Civil Engineering  
The University of Western Ontario  
London, Canada, N6A 5B9

# LEACHATE CHARACTERISTICS FOR MSW LANDFILLS

R. Kerry Rowe

Geotechnical Research Centre, Dept. of Civil Engineering  
University of Western Ontario  
London, Ontario, Canada N6A 5B9

**SUMMARY:** Leachate characteristics from five Ontario landfills are compared with typical values for both European and U.S. landfills. The time history of key constituents are examined and the half-life for first order decay is estimated based on the available data. An examination of the mass of chloride in North America's MSW indicates that it likely represents about 0.18% of the total in place mass of MSW.

## INTRODUCTION

The potential long term environmental impact of a landfill on groundwater quality will depend on the leachate characteristics, the mass of contaminant in the facility, the percolation of fluid through the waste, the nature of the leachate containment system and the site hydrogeology. The objective of this paper is to discuss the characteristics of modern MSW landfill leachate as identified in a number of Ontario landfills in terms of concentration and potential for degradation. In a companion paper (Rowe, 1995), the potential impact of this landfill leachate on groundwater quality will be discussed with particular emphasis being placed on the implications for long term maintenance after closure of the facility.

## LEACHATE CHARACTERISTICS

Any assessment of the potential impact of a landfill on groundwater quality requires consideration of the components of the leachate most likely to cause an environmental impact as well as the source of concentration of those components. Leachate characteristics may be expected to evolve over time, increasing from initial values to a peak (ie. maximum value) and then subsequently decreasing as the potential contaminants are either flushed out of the system (ie. are collected as leachate), biodegraded or precipitated. To illustrate the dynamics of leachate characteristics, consideration will be given to the leachate characteristics of a number of Ontario (Canada) landfills.

### Keele Valley Landfill

The Keele Valley Landfill (KVL) near Toronto, Canada covers an area of approximately 99 ha and has a current planned capacity of about 20 Mt (million tonnes). Based on 1991 data, the waste stream consists of approximately 69% residential/municipal waste, 14% industrial waste, 10% commercial waste, 4% construction/demolition waste and 3% contaminated soil with a total of 1.6 Mt being landfilled in 1991.

The KVL has a compacted clayey liner and a leachate underdrain system as described by King et al. (1993). It has been developed in four stages, commencing with Stage 1 in 1983. The landfill is still operational and the final cover has not yet been constructed. The leachate which is a mix of leachate generated from waste of different ages (up to 10 years old), has been monitored on a regular basis each year since landfilling began. As is usually the case for leachate, the data can vary quite considerably from one sampling event to the next, even over short periods of elapsed time. For example, in 1993 20 sampling events gave a variation in chloride concentration between 1230 mg/L and 3480 mg/L, with an arithmetic mean of 2332 mg/L (standard deviation, s.d. = 622 mg/L) and a geometric mean of 2247 mg/L (s.d. log c = 0.12). The geometric mean of the data collected in a given year will be taken as representative of the leachate characteristics in a given year. Thus for 1993, the "annual mean" leachate concentration for chloride was 2247 mg/L.

It may be expected that the leachate characteristics will change with time. That this is the case is evident from Table 1 which summarizes the annual (geometric) mean values for a number of leachate constituents over a 10 year period (1984-1993). In general, the concentrations of chloride, DOC, BOD, COD and BOD/COD are still increasing with time although the trend is not monotonic from year to year. This is illustrated for chloride in Figure 1. There is an evident trend of increasing concentrations with time with a peak concentration of between 1500 mg/L and 2500 mg/L being projected based on the available data. The average of the annual (geometric) mean values from 1989 to 1993 (inclusive) is 1646 mg/L. Based on available data, the representative peak chloride concentration,  $c_p$ , is taken to be 2247 mg/L. Values of 2500 mg/L and 1600 mg/L would appear to be reasonable upper and lower limits for use in calculating potential impact. The range of data values and the representative peak annual average concentrations are summarized in Table 2.

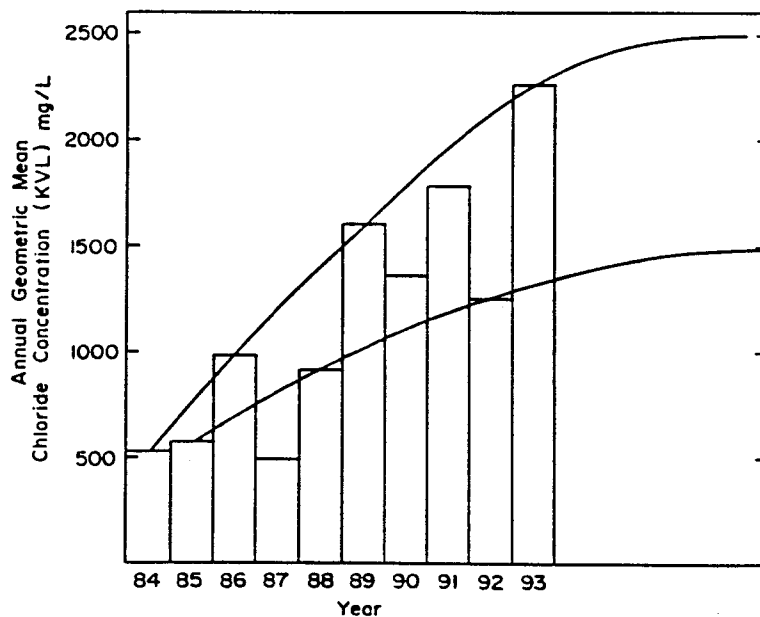


Figure 1. Variation in annual geometric mean chloride concentration with time - Keele Valley Landfill

Table 1. Keele Valley Landfill - Annual Average Concentrations for Selected Parameters

Years Elapsed	Annual Mean Concentration (mg/L except pH and BOD/COD)									
	Chloride	pH	Phenols	DOC	BOD	COD	BOD/COD	Iron	Calcium	
1	521	6.3	0.784	2545		9536	-	144	989	
2	568	6.0	2.04	2313	7462	9785	0.76	192	1049	
3	982	5.8	3.17	4125	7151	15130	0.47	487	1520	
4	489	6.1	3.11	2862	7865	8960	0.88	145	985	
5	923	6.5	2.84	2761	3641	7065	0.51	148	759	
6	1598	6.1	5.12	4580	8586	13857	0.62	240	1379	
7	1353	6.3	3.05	2734	4752	8698	0.55	30	801	
8	1779	6.3	3.88	3448	8429	15366	0.54	106	1557	
9	1251	6.2	3.25	4014	9273	11948	0.78	177	1239	
10	2247	6.5	3.06	5315	12367	17116	0.72	176	1193	
c <sub>p</sub>	2247	-	5.12	5315	12367	17116	-	487	1557	

Table 2. Summary of Data for Selected Leachate Parameters

	L1		L2		L3		Keele Valley (KVL)	
	Range	c <sub>p</sub>	Range	c <sub>p</sub>	Range	c <sub>p</sub>	Range	c <sub>p</sub>
Chloride (mg/L)	81-4640	1034	35-4470	3572	18-1457	851	173-3810	2247
Calcium (mg/L)	74-1700	640	25-1100	322	190-432	360	62-2860	1557
Cadmium (mg/L)	.001-<1	0.036	nd-0.05	0.05	0.001-0.1	0.015	.0002-0.34	0.024
Chromium	0.006-0.7	0.11	0.001-0.6	0.15	0.004-0.76	0.30	0.011-2.5(?)	0.22
Iron (mg/L)	.38-561	106	0.9-305	119	0.3-410	86	0.5-1910	487
Lead (mg/L)	.009-2.1	0.57	nd-0.4	0.4	0.004-0.8	<0.14	.001-33(?)	0.1
Mercury (mg/L)	.00004-.0011	.00026	nd-0.05	0.005			.00003-.0025	0.0007
Zinc (mg/L)	.0078-16	2.1	.02-16.8	1.32	0.003-22	3.9	.072-5.6	2.6
DOC (mg/L)	10-7300		330-4500	1959	25-2500	1640	929-7753	5315
BOD (mg/L)	450-12500	3891	128-9600	6540	16-9860	3361	2330-16000	12367
COD (mg/L)	1800-21800	6075	19-14700	6981	114-16330	5238	1410-27600	17116
pH (-)	5.4-8.2	6.8	6.2-8.1	7.7	6.3-7.8	7.3	5.7-6.8	6.3
Benzene (µg/L)	nd-57	<26	nd-3.1	<3	7-238	<26	<0.1-25	<20
Ethylbenzene (µg/L)	42-310	170	27.1-134	70.6	36-790	82	30-1400	<160
Dichloromethane (µg/L)	<0.4-3700	2436	nd	nd	0.3-2300	941	215-7100	3272
Toluene (µg/L)	3.15-1600	956	120-600	156	2-7000	1226*	485-1821	950
m&p Xylene (µg/L)	2.1-860	565	186-1230	238	101-2350	192	70-3900	<433
o Xylene (µg/L)	19.5-400	228	93.7-1110	118	57-1290	90	30-1450	<169
Vinyl chloride (µg/L)	nd	<122	nd-23.1	<23	2-2010	65*	nd-70	55
1,1 Dichloroethylene (µg/L)	nd	<16	-	-	<1-<100	<16	nd-60	nd
1,2 Dichloroethylene (µg/L)	nd-230	<146	-	-	11-2080	97	nd-900	<480
Trichloroethylene (µg/L)	<1.9-79	<39	nd	nd	1-80	48*	nd-<230	55
Tetrachloroethylene (µg/L)	6.7-23	<10.6	nd	nd	6-582	16*	nd-<86	10
1,4 Dichlorobenzene (µg/L)	1-22	<10	nd-390	40	<1-18	6	nd-<86	10
1,2 Dichloroethane (µg/L)	nd-<40	<16	nd	nd	0.9-<16	<3	nd-<86	10
Approx. No. of Data Sets	17-85		7-95		2-31		16-99	
Site Area (ha)	80		65		35		99	
Year Opened	1980		1975		1972		1983	
Year Closed	Active		Active		1988		Active	
Waste Thickness (m)	18		29		12		26	
Data Period Examined	1982-1993		1979-1993		1985-1993		1984-1993	

TABLE 2. (cont'd)

	L4		ODWO	U.S. Data <sup>1</sup>	Robinson & Gronow (1993)		Ehrig & Scheelhaase (1993)	
	Range	C <sub>p</sub>			Acet.	Meth.	Acet.	Meth.
Chloride (mg/L)	380-4670	1874	250[AO]	-	1803	2074	2100	2100
Calcium (mg/L)	190-3705	1643	-	-	2241	151	1200	60
Cadmium (mg/L)	0.01-0.14	0.036	0.005	0.024	0.02	0.02	0.006	0.006
Chromium (mg/L)	0.01-3.1	0.39	0.05	0.02	0.13	0.09	0.3	0.3
Iron (mg/L)	11.5-3360	966	0.3[AO]	-	654	27.4	780	15
Lead (mg/L)	0.09-1.02	0.37	0.01	0.16	0.28	0.2	0.09	0.09
Mercury (mg/L)			0.001	0.002	.0004	.0002	.01	0.01
Zinc (mg/L)	.17-85.5	11	5.0[AO]	8.3	17.4	1.1	5	0.6
DOC (mg/L)	2-178000	25,598	5.0[AO]	-	-	-	-	-
BOD (mg/L)	19-99000	7528	-	-	18632	374	13000	180
COD (mg/L)	250-73200	16,412 <sup>4</sup>	-	-	36817	2307	22000	3000
pH (-)			6.5-8.5	-	6.7	7.5	6.1	8
Benzene (µg/L)	1.8-590	22.3	5	7	-	-	-	-
Ethylbenzene (µg/L)	52-1300	93	2.4[AO]	60	-	-	-	-
Dichloromethane (µg/L)	nd-8300	1733	50	1390	-	-	-	-
Toluene (µg/L)	350-5900	1103	24[AO]	406	-	-	-	-
m&p Xylene (µg/L)	nd-1400	244	300[AO]	-	-	-	-	-
o Xylene (µg/L)	nd-670	99	-	-	-	-	-	-
Vinyl Chloride (µg/L)	nd-13.6	<13	2	51	-	-	-	-
1,1 Dichloroethylene (µg/L)			-	nd	-	-	-	-
1,2 Dichloroethylene (µg/L)			-	104	-	-	-	-
Trichloroethylene (µg/L)	nd-110	37.3	50	71	-	-	-	-
Tetrachloroethylene (µg/L)	nd-2000	25.2	-	nd	-	-	-	-
1,4 Dichlorobenzene (µg/L)	nd-4	<4	1[AO]	nd	-	-	-	-
1,2 Dichloroethane (µg/L)	nd	nd	5	nd	-	-	-	-
Approx. No. of Data Sets		33-59						
Site Area (ha)		71						
Year Opened		1972						
Year Closed		Active						
Waste Thickness (m)								
Data Period Examined		1985-1990						

<sup>1</sup>Gibbons et al. (1992)

The ratio of BOD/COD and the pH (Tables 1 and 2) of the KVL leachate are indicative of acetogenic leachate (eg. Robinson & Gronow, 1993; Ehrig & Scheelhaase, 1993). The concentrations of iron and zinc in the KVL leachate are less than typically found in European leachate (Table 2). For 1986, 1989, 1991 and 1992 the annual mean concentration of calcium in the KVL leachate was between the values reported by Ehrig and Scheelhaase (1993) and Robinson and Gronow (1993). The averages over the last 5 and 10 year periods (1234 mg/L and 1147 mg/L respectively) are close to, or less than, the value of 1200 mg/L reported by Ehrig and Scheelhaase (1993) and well below the value of 2241 mg/L reported by Robinson and Gronow (1993). Calcium and iron are of particular significance due to the contribution that they make to clogging of leachate collection systems (Brune et al., 1991).

The concentration of volatile organic compounds (VOCs) has been monitored with increasing frequency with elapsed time. The range of values and maximum geometrical mean values for some of the most commonly detected organic compounds of concern to the public are summarized in Table 2. PCBs were below the detection limit of 20 ng/L and are not listed. Of the compounds that were most commonly detected, dichloromethane (DCM, methylene chloride) was the most prevalent having a representative peak concentration of about 3272  $\mu\text{g/L}$  (obtained over the period 5/85-4/88; 5 data points) however the concentration had decreased to 1266  $\mu\text{g/L}$  in 1993 (6 data points; Figure 2) despite the fact that the chloride concentration was still increasing over this period (Figure 1). This is

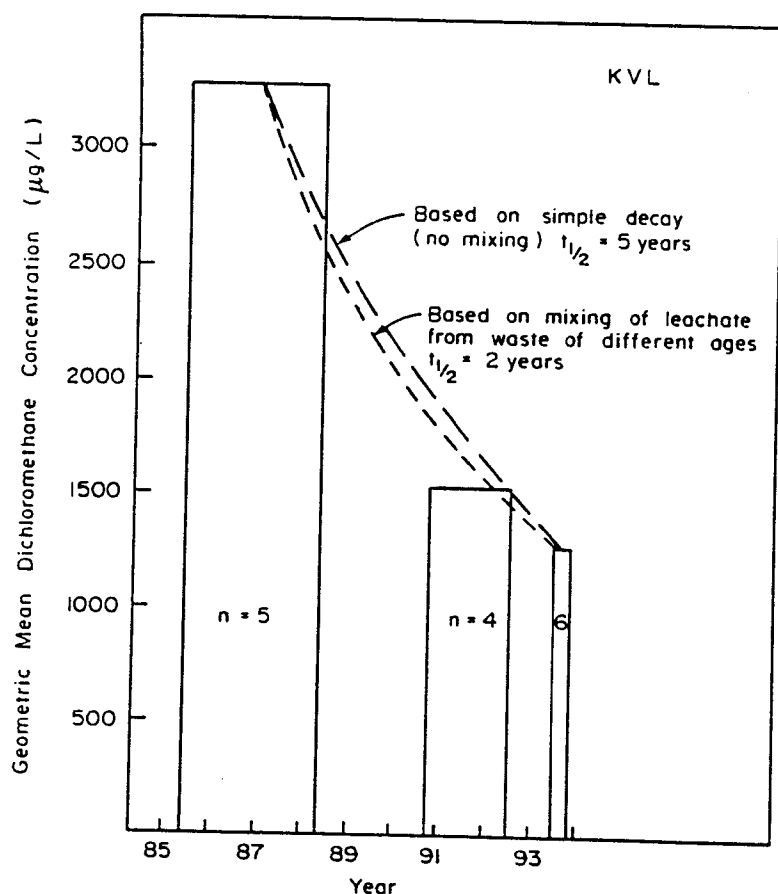


Figure 2. Variation in geometric mean dichloromethane concentration with time - Keel Valley Landfill (n=number of data points)

considered to imply that there has been degradation of DCM in the waste as will be discussed subsequently. Similarly, there was an apparent decrease in the concentration of toluene, xylene (m&p, o), trichloroethylene, tetrachloroethylene and ethylbenzene over the period monitored. The representative peak concentration,  $c_p$ , of these organic compounds and a number of others are given in Table 2 together with the range of values observed.

### Data from Landfill L1

Landfill L1 is also located near Toronto. It was opened in 1980 and is still operating. The landfill covers an area of approximately 80 ha and has an underdrain leachate collection system underlain by up to 18 m of clay. The waste stream is reported to be approximately 40% residential, 37% industrial, 6% commercial, 6% construction/ demolition, 7% contaminated soil and 4% other. Although some leachate data has been collected since 1982, the data are quite limited until 1988/89. Table 2 summarizes the range of data values and the representative peak concentration. There are insufficient data to identify a trend and the peak annual concentration may have been, or may still be, greater than that reported. Notwithstanding this, it is notable that the annual (geometric) mean,  $c_p$ , concentration for DCM is 2436  $\mu\text{g/L}$  and hence quite high. For some of the organic compounds the annual mean value was controlled by the detection limit used in the chemical analysis (usually due to the dilutions used) and these are expressed as "<" (ie. less than) values.

### Landfill L2

Landfill L2 was opened in 1975 and is still operating. It is understood to have a limited underdrain leachate collection system over a 0.15 m - 0.3 m thick compacted bentonite-sand liner. There is evidence to suggest that the underdrain system has been affected by clogging. In 1986, the leachate mound began to build and stabilized at an average level of 23 m above the liner in 1988. Unlike the other landfills discussed, landfill L2 is known to have accepted significant quantities of sewage sludge which contributed to the fluid input of the landfill (Dames & Moore, 1992).

Table 3 summarizes leachate data for Landfill L2 for the same parameters considered for the KVL in Table 1.

Inspection of these two tables shows a distinct difference in several respects. Firstly, the chloride concentration increased significantly from an average value of 686 mg/L in the five years of monitoring from years 4 to 8, to an average of 3218 mg/L over the last five years (13-18). Similarly, there was a change in pH and the ratio of BOD/COD between years 5-8 and years 13-16 with the landfill leachate changing its characteristics (ie. increased pH; substantial drop in BOD/COD) during this period. This change appears to correspond to the mounding of leachate in the landfill which can be expected to have increased the level of anaerobic biological activity which increases pH and reduces BOD, DOC and the concentration of metals. These changes are all beneficial (reducing the undesirable characteristics of the leachate) except for the increased chloride concentration which is attributed to the longer contact time between fluid and waste in the extensively saturated portion of the landfill. Thus it would appear that impaired performance of the primary leachate collection system and consequent leachate mounding may increase chloride concentration.

There is limited organic data available for Landfill L2 except phenolics. Although limited, the data for phenols suggests that the peak concentration was reached in the 1986-





1988 period (ie. as the leachate mound developed). Subsequent to 1988, the phenolic concentration has dropped significantly as time has progressed implying a half-life for phenolics of about 1 year over the period 1988-1991. There are insufficient data to detect trends for the VOCs, however the representative concentrations (as recorded in Table 2) of VOCs are well below those observed in the KVL suggesting that there is a significant decrease in the concentration of organics in the leachate when the landfill is in the methanogenic phase of decomposition.

### Landfill L3

Landfill L3 is interesting because it is a closed landfill and the monitoring of organic compounds has been more systematic than at most other closed landfills. Thus it has the potential of providing some insight concerning post-closure concentration trends. In addition, there is a leachate underdrain beneath a significant portion of the site. The analyses of leachate from the collection system provide an "average" of the overall characteristics of the waste rather than a value at a specific point. This underdrain also provides a means of flushing contaminants out of the system and hence if there is going to be a concentration reduction due to leaching it would be expected to be more evident at Landfill L3 than at other landfills where there is no underdrain system.

The concentrations of a number of leachate constituents are summarized in Table 2. Landfill L3 arguably shows some decrease in chloride concentration with time (Figure 3), however because of the scatter of data and the relatively short monitoring period (1985-92), it is not possible to clearly establish the rate of decrease in concentration (note that insufficient chloride data was gathered in 1988 and 1989 to allow calculation of a meaningful geometric mean).

Of the VOCs, dichloromethane (DCM) had the highest annual average value (for the years where there are data) in 1985 and exhibited a significant decrease in concentration in subsequent years. Based on the decrease from 1985 to the 1993 values, the half-life is approximately 2 years assuming some dilution ( $q_0/H_r = 0.1$ , see Figure 4) and about 1.5 years if one assumes no dilution.

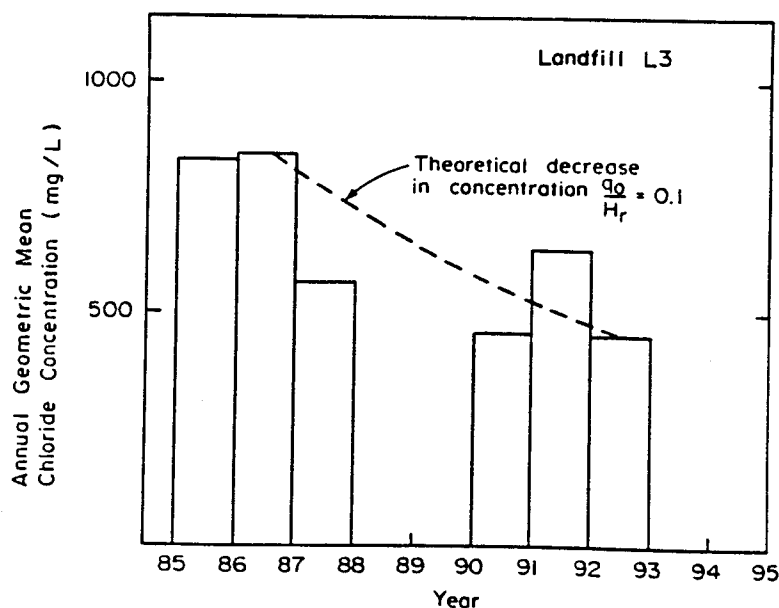


Figure 3. Variation in annual geometric mean chloride concentration with time - Landfill L3

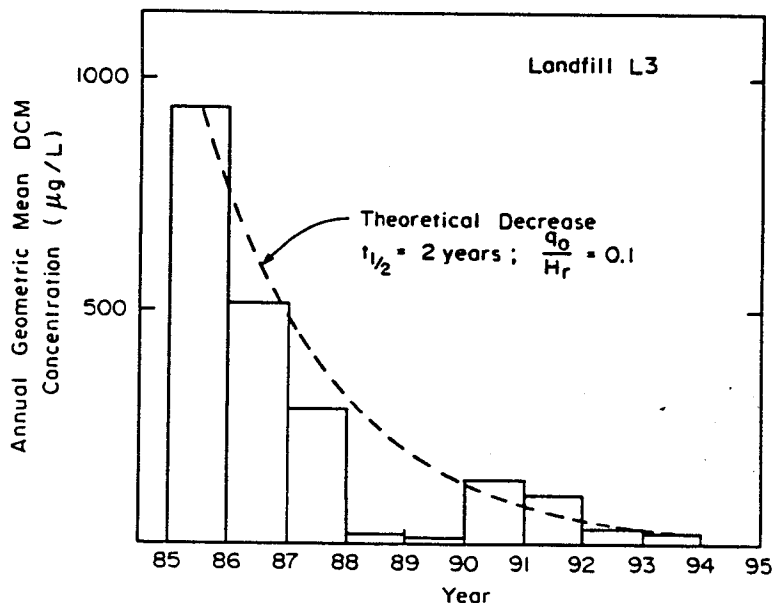


Figure 4. Variation in annual geometric mean dichloromethane concentration with time - Landfill L3

The toluene concentration increased to a maximum value in 1986, then decreased with an estimated half-life of between 1.8 to 5.7 years. Xylene concentrations also peaked in 1986 and have decreased erratically since then.

#### Landfill L4

Opened in 1972, and still operating, the Landfill L4 covers an area reported to be 71 ha and represents an evolution in landfill technology with older portions of the landfill not having any leachate collectors while newer portions do. Some of the leachate chemistry has been obtained from wells in the old waste, while other chemistry is also available based on analyses of the data from the more recent leachate collection system. There is a wide disparity in the data. Two wells consistently appear to be "hot spots" with very high annual geometric mean concentrations of chloride (3064 mg/L), phenol (37.7 mg/L) and zinc (50 mg/L). The representative concentrations given in Table 2 are for the entire landfill and incorporate data from both the "hot spot" wells and the other wells. Based on all the data, the representative peak concentration for chloride is less than at Keele Valley. Calcium is similar to that for the KVL.

The representative concentrations of some organic compounds are also summarized in Table 2. The concentrations are generally of the same order of magnitude to those obtained from Keele Valley, with dichloromethane, toluene and xylenes (m&p, o) again being the most abundant.

#### Comparison of Ontario Data With Literature Values

Table 2 summarizes both the peak annual values for the five Ontario landfills examined together with published U.S. and European data. Inspection of this data indicates that

- chloride concentrations at the KVL and Landfill L4 are generally consistent with European data. The concentrations at Landfills L1 and L3 are considerably lower and this may be due to the fact that the peak concentration was missed due to

limited early time data. Landfill L2 is notable for the high chloride concentration since the development of the leachate mound. This is attributed to longer leachate retention times in the waste due to the degraded leachate collection system.

- calcium concentrations in both Landfill L4 and KVL fall between the values reported by Robinson and Gronow (1993) and Ehrig and Scheelhaase (1993) in the acetogenic phase. At Landfill L2, the peak observed annual mean concentration (322 mg/L in 1988 when the leachate mound stabilized) is greater than reported for European data in the methanogenic phase, however the concentration has subsequently dropped to values only marginally above that reported by Robinson and Gronow (1993).
- BOD and COD concentrations for KVL are marginally below those reported by Ehrig and Scheelhaase in the acetogenic phase and well below the values reported by Robinson and Gronow (1993). However, since the concentration still appears to be rising at KVL, the results are regarded as being generally consistent with European leachate. The peak assumed mean value at all other landfills is well below that reported for European leachate. In the methanogenic phase, the BOD and COD concentrations in Landfill L2 (1992) are reasonably consistent with the range of values from European data.
- the concentration of dichloromethane is considerably higher than the values reported for modern U.S. landfills (Gibbons et al., 1992) at Landfills L1, L4 and the KVL. The peak value may have been missed at Landfill L3.
- the concentrations of toluene and ethyl benzene are all also generally elevated compared to the U.S. data. The concentrations of vinyl chloride (VC) and trichloroethylene (TCE) are comparable to, or less than, the U.S. data.

In summary, although there are some differences (eg. as noted above), the Ontario MSW leachate appears to be reasonably consistent with what would be expected based on existing European and U.S. data for recent (post 1984) landfills.

## DECREASE IN LEACHATE STRENGTH WITH TIME

There is considerable evidence to suggest that the strength of leachate decreases with time (e.g. see Figure 2; also Lu et al., 1981; Ehrig & Scheelhaase, 1993). This decrease may be the result of biological breakdown of organic compounds to simpler compounds/elements or precipitation of soluble elements (e.g. heavy metals). It can also occur due to dilution effects. It has long been recognized that the decline in concentration,  $c$ , with time,  $t$ , can often be empirically approximated by a first-order rate equation (e.g. Lu et al., 1981) of the form

$$c = c_0 \exp [-kt] \quad [1]$$

where  $c_0$  is the representative peak source concentration  
 $k$  is the first order constant =  $\ln 2 / (\text{half-life})$

Based on empirical observations relating to a collection of (essentially U.S.) landfill leachate data Lu et al. (1981) established a number of values of  $c_0$  and  $k$  as summarized in Table

Table 4. Decline of Constants Based on Lu et al. (1981) with Inferred Biological/Chemical Half-Life Added

Parameter	$c_o$ (mg/L)	$k$ ( $a^{-1}$ )	Inferred Biological/ Chemical Half-Life (years - a)*
BOD <sub>5</sub>	35,000	0.225	4.3
COD	89,000	0.192	5.5
TOC	14,000	0.260	3.6
NH <sub>3</sub> -N	12,000	0.100	19.8
Cl	2,470	0.065	$\infty$
SO <sub>4</sub>	15,000	0.079	49.5
Cd	0.160	0.125	11.6
Cu	10	0.200	5.1
Cr	0.330	0.900	0.8

$$* t_{1/2} = \ln 2 / [k[\text{parameter of interest}] - k[\text{Cl}^-]]$$

Chloride considered non degradable; decrease in concentration attributed to dilution.

4. This approach which lumps together data from many landfills without consideration of the size of landfill (ie. mass of contaminant) or the infiltration represents "average" conditions for the range of cases considered in the study used to derive the values of  $c_o$  and  $k$ .

Rowe (1991) examined the issue of leachate strength decrease for conservative contaminant species (e.g. chloride) where the decrease in strength is essentially due to dilution (i.e. no biological breakdown or precipitation) as water infiltrated through the waste with time. Assuming that the decrease is due to dilution and first order degradation, the variation in concentration at any time  $t$  is given by

$$c = c_o \exp \left[ -\left( \frac{q_o}{H_r} + \lambda \right) t \right] \quad [2]$$

where  $q_o$  is the volume of leachate generated per unit area of landfill  
 $H_r$  is referred to as the reference height of leachate, given by

$$H_r = \frac{p m_o}{A_o c_o} \quad [3]$$

- $m_o$  is the total mass of waste (i.e. excluding daily, intermediate and final cover)  
 $p$  is the proportion of total mass of waste that is contributed by the chemical of interest  
 $A_o$  is the area of the landfill, and  
 $\lambda$  is the first order decay constant  
 $= \ln 2 / (\text{half-life of the contaminant})$ .

Comparing Eqs. [1] and [2], it is evident that the theoretically derived Eq. [2] is of identical form to the empirically derived Eq. [1] where, on expanding  $H_r$ ,

$$k = \frac{q_o A_o c_o}{p m_o} + \lambda \quad [4]$$

and the theoretically derived equation indicates that the empirical decay constant  $k$  should depend on the volume of leachate generated per unit time ( $q_o A_o$ ), the mass of waste ( $m_o$ ) or, more specifically, mass of contaminant ( $p m_o$ ), and the representative peak concentration,  $c_o$ .

## MASS OF CHLORIDE

As discussed in the preceding section, the mass of contaminant in the waste is an important consideration in assessing the decline in leachate strength with time and hence the contaminating lifespan of a landfill. The mass of contaminant can be characterized in terms of the mass of waste and the proportion of that mass which is the chemical of interest.

Data on the mass of contaminants in waste are relatively sparse. Published data by Hughes et al. (1971) indicate that chloride represents 0.097% of the dry mass of refuse. (This would be about 0.07% of the in-situ or wet mass of waste.) Based on Fungaroli and Steiner (1979), leachable chloride represents 0.15-0.2% of the in-situ (wet) mass of refuse while a range of 0.07%-0.21% of the initial refuse mass can be inferred from the data of Wigh and Brunner (1979). A value of about 0.18% can be inferred for the largest test cells examined by Wigh and Brunner (1979). The leaching data collated by Reitzel (1990) can also be used to estimate the mass of chloride in waste and yield a value of 0.18% of the dry mass of refuse (ie. about 0.13% of wet mass for 28% moisture content).

Based on these sources, it would appear that chloride represents between about 0.07% and 0.21% of the in situ mass of refuse; with a value of 0.18% being the anticipated leachable chloride mass and 0.2% (ie.  $p = 0.002 = 2 \times 10^{-3}$ ) being a reasonable value for leachable chloride mass in North America that may be used for sensitivity analyses (ie. it errs on the side of overestimating the values deduced from all sources examined except for one small cell (2.6 m<sup>2</sup>) which gave a value of about 0.21%.

There are limited data concerning the mass of contaminants other than chloride in waste. For non-conservative contaminants which experience first-order decay due to biological/chemical processes, the rate of decrease in concentration is given by Eq. 2 and the empirical constant  $k$  (see Eq. 4) will have two components: namely, the decrease due to dilution ( $q_o A_o c_o / p m_o$ ) which depends on the mass of contaminant ( $p m_o$ ) and the chemical/biological decay,  $\lambda$ . If one assumes that the mass of contaminant is proportional to the representative peak concentration, then the decrease due to dilution will be the same for all contaminant species. Based on this assumption, it is possible to estimate the

chemical/biological half-life ( $\ln 2/\lambda$ ) implied by the Lu et al. (1981) decay constants as given in Table 4.

## HALF-LIFE OF ORGANIC CONTAMINANTS

As discussed in the previous sections, many components of landfill leachate experience a decrease in concentration due to biological/chemical processes. The inferred half-life of the components examined by Lu et al (1981) have been given in Table 4. This section will examine the half-life of a number of organic contaminants identified as being potentially significant.

### Dichloromethane

Dichloromethane (DCM) appears to be the most prevalent volatile organic compound found in the landfills examined, having an anticipated peak concentration of about 3300  $\mu\text{g/L}$  (Table 2). This is 66 times the drinking water objective. Dichloromethane is a soluble compound ( $\approx 20000 \text{ mg/L}$  at  $25^\circ\text{C}$ ) which has been reported to biodegrade completely under aerobic conditions, with sludge seed, in 6-7 hours. Until recently, there appears to have been little known concerning the biodegradation of dichloromethane under anaerobic conditions. It used to be accepted that biodegradation was unlikely and that DCM and related chlorinated solvents were only likely to be susceptible to abiotic degradation (ie. transformations that are not biologically mediated). This opinion was based on negligible oxygen consumption over 20 days during standard biochemical oxygen demand (BOD) tests performed for dichloromethane. Potential mechanisms for removal of dichloromethane from solution in landfill applications include evaporation, sorption onto soil, chemical reaction (most likely hydrolysis) and biodegradation. The reported half-life for DCM due to hydrolysis varies widely with estimates ranging from as little as 1.5 years to 704 years. However, there is growing evidence to suggest that, in fact, DCM can be readily biodegraded at concentrations comparable to that in leachate.

Freedman and Gossett (1991) have demonstrated that DCM can be anaerobically degraded to predominantly non-toxic products by a mixed bacterial culture isolated from anaerobic digester. Only trace levels of chloromethane were detected as a breakdown product. In these tests, performed at  $35^\circ\text{C}$ , the degradation process typically involved two stages; a lag phase of about 10 days or less when there was relatively slow degradation followed by a second stage where there was relatively rapid degradation over a period of 5 days (or less). Including both stages, essentially complete degradation typically occurred in less than 16 days. These general findings have been confirmed by the work of Braus-Stromeyer et al. (1993) who also demonstrated relatively rapid biodegradation of DCM under a range of anaerobic conditions.

Rowe et al. (1994) undertook an applied research project to examine the potential for anaerobic degradation of dichloromethane. The tests conducted as part of this study demonstrated that degradation of dichloromethane can occur under anaerobic conditions both in leachate (and hence in the landfill) and as it diffuses through clayey soil into a receptor solution similar to groundwater. Typically the degradation occurs in two stages. The first stage or lag period involves relatively slow degradation. After the bacterial population has acclimated to the DCM the second stage of degradation is quite fast. At  $24^\circ\text{C}$  the degradation in leachate typically corresponds to a half-life of 2-5 days with a maximum of less than 19 days being observed. In the second stage the half-life is typically

less than 1 day. The presence of soil appears to slow the rate of degradation. In the diffusion tests, the lag period was typically 40-60 days after which the second stage half-life was about 20 days or less. Based on these results and including the lag time the half-life for DCM degradation at 24°C is between 2 and 3 months.

Batch tests conducted at 10°C indicate that a reduction in temperature increases the lag time by up to an order of magnitude and increases the second stage half-life by a factor of six. Diffusion-degradation tests were not performed at 10°C, however based on the results of the diffusion-degradation tests at 24°C and extrapolating based on the batch test results it is anticipated that the lag time would be less than 400-600 days and the subsequent half-life would be less than 120 days. Including the lag time, the estimated half-life for DCM at 10°C is less than 2 years.

The degradation process did not produce detectable levels of chloromethane. Based on the test observations and the work of Freedman and Gossett (1991) and Braus-Stromeyer et al. (1993), it is likely that DCM is biologically converted to acetate and ultimately to CH<sub>4</sub> and CO<sub>2</sub>.

Although there are limited data that can be used to examine the degradation of DCM in landfills, the concentration history observed at both the Keele Valley Landfill and Landfill L3 can be used to obtain an independent estimate of the order of magnitude of half-life that would be consistent with the observed decline in concentration with time.

As previously discussed, the concentration of chloride at the Keele Valley Landfill is still rising (see Figure 1), however as shown in Figure 2, the available evidence would suggest that the concentration of DCM is decreasing. The rate of decline in DCM concentration can be explained in terms of a first order decay with a half-life of about 5 years based on a simple model of first order degradation. However, this represents an upper bound value since it assumes that all the DCM was in the landfill in the May 85-April 88 period and that since then there has been a decline in this concentration with time without any addition of DCM. In fact, the landfill is still operating and the leachate that is analyzed represents a mixture of leachate that has been generated by passage of fluid through waste ranging in age from recently placed to up to 10 years. Thus DCM is being added to the landfill as new waste arrives. Thus some of the leachate collected in 1993 represents fluid that has passed through waste where there has been up to 6.9 years of degradation since the median time when the representative concentration was reached in the May 85-April 88 period. One would expect this leachate to have a lower strength than in 1985/88. Another portion of this leachate collected in 1993 passes through waste which is relatively new and there has been little time for degradation of DCM thus one would expect the leachate to be similar to the leachate generated in the older part of the landfill back in the 1985/88 period. Adopting this hypothesis and calculating the time weighted average leachate strength with time T, a good fit can be obtained to the KVL data shown in Figure 2 for a half-life of 2 years. Based on the Keele Valley Landfill data, the half-life for DCM appears to be about 2 years with a worst case interpretation being 5 years.

Figures 3 and 4 show the available time history for chloride and DCM respectively at Landfill L3. As previously noted, it could be argued that there has been some decrease in chloride concentration since the landfill was closed (Figure 3), however there has been a much more significant and clearer decrease in DCM concentration (Figure 4). Based on a simple fit to the data given in Figure 4, one would estimate a half-life of about 1.5 years. If one assumes that part of the decrease is due to dilution, as might be implied by the



chloride data in Figure 3, and adjust for this then the half-life implied by the data in Figure 4 is about 2 years. This value of 2 years is based on the assumption that the ratio of the mass of DCM to the representative concentration is the same as that for chloride. If the ratio for DCM was higher than for chloride then the half-life would be less than 2 years.

Based on all the available data, including the laboratory study reported by Rowe et al. (1994) and the KVL and Landfill L3 data discussed above, it would appear that the likely half-life for DCM is about 2 years with 5 years being an upper bound estimate for Southern Ontario conditions.

### **Benzene**

Benzene appears in relatively low concentrations in typical landfill leachate (see Table 2); nevertheless, it appears to be a chemical of interest to the public and to hydrogeologists. Grbić-Galić (1990) has described a mechanism for the anaerobic transformation of benzene (and other aromatic compounds) based on laboratory studies. The suggested pathway involved transformation of benzene initially to phenol which subsequently degrades to carbon dioxide and methane. In a study by Barker et al. (1988), it was found that leachate from the North Bay landfill (which contained a mixture of benzene, toluene, xylenes etc.) experienced significant biodegradation under anaerobic conditions. Based on their data and correcting for dilution, the author calculated the half-life for benzene to be between 1.8 and 4.9 years.

### **Ethylbenzene**

Ethylbenzene is more prevalent in leachate than benzene (see Table 2) and may be present with average concentrations 70 times the drinking water objective. Based on the Barker et al. (1988) study, a half-life (under anaerobic conditions) of 0.9-6.4 years was inferred.

### **Toluene**

Toluene is found in landfill leachate with an anticipated source concentration (Table 2) 40 times the drinking water objective. In the Barker et al. (1988) study, the biodegradation was relatively rapid and the inferred half-life is of 0.3-2.1 years under anaerobic conditions in a leachate plume. The leachate data from the Keele Valley Landfill showed a significant decline in concentration since the representative peak concentration was reached in the 1985/88 period. A simple application of first order decay to the data yields an upper bound half-life of 12.3 years. Consideration of mixing of leachate gives a best estimate half-life of 5.7 years.

The data for Landfill L3 provides scope for a number of different interpretations of the data however the corresponding half-lives fall into a relatively narrow range between 1.8 and 5.7 years.

### **Vinyl Chloride and Trichloroethylene**

It has been reported (HSDB) that vinyl chloride will degrade under anaerobic conditions. In one study quoted by HSDB, vinyl chloride was approximately 50% and 100% degraded in 4 and 11 weeks respectively in the presence of sand, by methanogenic microorganisms, under anaerobic conditions in laboratory scale experiments. In the absence of sand 20% and 55% degradation occurred in 4 and 11 weeks respectively (HSDB).

Freedman and Gossett (1989) have examined biologically reductive dechlorination of tetrachloroethylene (PCE) and trichloroethylene (TCE). They demonstrated that under methanogenic conditions microorganisms were able to completely dechlorinate PCE and TCE. The breakdown of PCE and TCE involved the generation of vinyl chloride as an intermediate product. The rate limiting step in this pathway was reported to be the conversion of vinyl chloride to ethylene. It was indicated that methanogenes play a key role in the biotransformation process. Results presented by Freedman and Gossett indicate that under their laboratory conditions (35°C) trichloroethylene had a very short half-life (a few days) and the half-life of vinyl chloride was about 30 days initially but decreased to about 165 days later in the test. Unfortunately, the tests were not carried out long enough to examine the total breakdown of vinyl chloride, however these tests do clearly demonstrate that vinyl chloride can be biologically degraded under methanogenic conditions. TCE has also been seen to degrade relatively rapidly in contaminant plumes (eg. Milde et al., 1988).

The hydrolytic half-life of vinyl chloride has been estimated to be less than 10 years at 25°C (Hill et al., 1976). While this may be dismissed as not being significant for the aquatic fate of vinyl chloride, it is quite significant with respect to potential degradation of vinyl chloride in groundwater applications. It is also noted that the Barker et al. (1988) study did not report the presence of vinyl chloride in the North Bay plume.

## CONCLUSIONS

An examination of leachate from several MSW Ontario landfills indicates that although there are some differences, Ontario leachate characteristics are generally consistent with published data relating to both European and U.S. landfills. Careful examination of leachate concentration history shows an increase in concentration to a peak value followed by a decrease in concentration with time. This decrease is relatively slow for chloride since the primary mechanism for a decrease is dilution. However, for organics such as dichloromethane, toluene, phenols etc. the rate of decrease in concentration is relatively fast. Examinations of laboratory biological degradation mechanisms and observed field behaviour both suggest potential for anaerobic degradation of organic compounds such as dichloromethane, benzene, ethylbenzene, toluene, vinyl chloride and trichloroethylene. An indication is given of potential half-lives for these compounds based on available data. Given the limitations of the half-life data, it would be prudent to use higher values than those reported herein for any sensitivity study associated with assessing potential impact of a proposed facility.

An examination of available data indicates that chloride represents about 0.18% of the total, in place, mass of MSW in North America. This mass combined with the source concentration and volume of leachate collected can be used to estimate the contamination lifespan of a landfill (as described by Rowe, 1991; Rowe et al., 1995) and hence the potential long term maintenance period for a landfill facility.

## ACKNOWLEDGEMENTS

The leachate data collection reported in this paper was conducted with the assistance of Dr. Frank Barone, Ms. Bridget Mills, Mr. Stan Feenstra and Mr. Ian Fleming. The value of discussions with these individuals is gratefully acknowledged.

## REFERENCES

- Barker J.F. Cherry J.A. Reinhard M. Pankow J.F. Zapico M. (1988) The Occurrence and Mobility of Hazardous Organic Chemicals in Groundwater at Several Ontario Landfills. Submitted to Research Committee, Ontario Ministry of Environment.
- Braus-Stromeier S.A. Hermann R. Cook A.M. and Leisinger T. (1993) Dichloromethane as the Sole Carbon Source for an Acetogenic Mixed Culture and Isolation of a Fermentative, Dichloromethane-Degrading Bacterium. *Applied & Environmental Microbiology*, Vol. 59, No. 11, pp. 3790-3797.
- Brune M. Ramke H.G. Collins H.J. and Hanert H.H. (1991) Incrustation Processes in Drainage Systems of Sanitary Landfills. In *Proceedings Third International Landfill Symposium*, Cagliari, Italy, pp. 999-1035.
- Dames & Moore Canada. (1992) Annual Monitoring Report Brock West Sanitary Landfill Site 1991. Report submitted to Municipality of Metropolitan Toronto, Dept. of Works.
- Ehrig H.-J. and Scheelhaase T. (1993) Pollution Potential and Long Term Behaviour of Sanitary Landfills. *Proc., Fourth International Landfill Conference*, Sardinia, pp. 1203-1225.
- Freedman D.L. and Gossett J.M. (1989) Biological Reductive Dechlorination of Tetrachloroethylene and Trichloroethylene to Ethylene Under Methanogenic Conditions. *Applied and Environmental Microbiology*, Vol. 55, No. 9, pp. 2144-2151.
- Freedman D.L. and Gossett J.M. (1991) Biodegradation of Dichloromethane and Its Utilization as a Growth Substrate Under Methanogenic Conditions. *Applied and Environmental Microbiology*, Vol. 57, pp. 2847-2857.
- Fungaroli A.A. and Steiner R.L. (1979) Investigation of Sanitary Landfill Behaviour - Final Report. US EPA-600/2-79-053a.
- Gibbons R.D. Dolan D. Keough H. O'Leary K. and O'Hara R. (1992) A Comparison of Chemical Constituents in Leachate From Industrial Hazardous Waste and Municipal Solid Waste Landfills. *Proc. Fifteenth Annual Madison Waste Conference*, pp. 251-276.
- Grbić-Galić D. (1990) Anaerobic Microbial Transformation of Nonoxygenated Aromatic and Alicyclic Compounds in Soil, Subsurface and Freshwater Sediments. Chapter 3 in *Soil Biochemistry*, Vol. 6, Eds. J.M. Ballog and G. Stoteky, pp. 117-189, M. Dekker Inc., New York.
- Hill J. Hollig H.P. Paris D.F. Wolfe N.L. and Zepp R.G. (1976) Dynamic Behaviour of Vinyl Chloride in Aquatic Ecosystems. EPA, 600/3-76-001.
- HSDB (Hazardous Substances DataBase). 1993. TOXNET. Computerized database of up-to-date information on hazardous chemicals abstracted from primary or other secondary sources.
- Hughes G.M. Landon R.A. and Farvolden R.N. (1971) Hydrogeology of Solid Waste disposal sites in northeastern Illinois. Report SW-12a, US EPA.

- King K.S. Quigley R.M. Fernandez F. et al. (1993) Hydraulic Conductivity and Diffusion Monitoring of the Keele Valley Landfill Liner, Maple, Ontario. *Canadian Geotechnical Journal*, 30.
- Lu C.S.J. Morrison R.D. and Stearns R.J. (1981) Leachate Production and Management From Municipal Landfills: Summary and Assessment. Land Disposal: Municipal Solid Waste - *Proceedings of the Seventh Annual Research Symposium* - EPA - 600/9-81, pp. 1-17.
- McCarty P.L. Reinhard M. and Rittman B.E. (1981) Trace Organics in Groundwater. *Environmental Science and Technology*, 15(1), pp. 40-51.
- Milde G. Nerger M. and Mergler R. (1988) Biological Degradation of Volatile Chlorinated Hydrocarbons in Groundwater. *Wat. Sci. Tech.*, Vol. 20, No. 3, pp. 67-73.
- Reitzel S.F. (1990) The Temporal Characterization of Municipal Solid Waste. M.A.Sc. thesis, University of Waterloo, Waterloo, Ontario, Canada.
- Robinson H.D. and Gronow J.R. (1993) A Review of Landfill Leachate Composition in the U.K. pp. 821-832.
- Rowe R.K. (1991) Contaminant Impact Assessment and the Contaminating Lifespan of Landfills. *Canadian Journal of Civil Engineering*, 18(2), pp. 244-253.
- Rowe R.K. (1995) Considerations in the Design of Hydraulic Control Layers. *Proc. Fifth International Landfill Symposium*, Sardinia '95, S. Margherita di Parla, October.
- Rowe R.K. Booker J.R. and Quigley R.M. (1995). *Clayey Barrier Systems for Waste Disposal Facilities*. E & FN Spon (Chapman & Hall), London.
- Rowe R.K. Hrapovic L. Kosaric N. Cullimore D. and Quigley R.M. (1994) A Laboratory Investigation Into the Degradation of Dichloromethane. Final Report to Interim Waste Authority, Geotechnical Research Centre, University of Western Ontario.
- Wigh R.J. and Brunner D.R. (1979) Leachate Production From Landfilled Municipal Waste: Boone County Field Site. *Proc. Fifth Symp. Municipal Solid Waste Disposal*, EPA-600/9-79-023a.