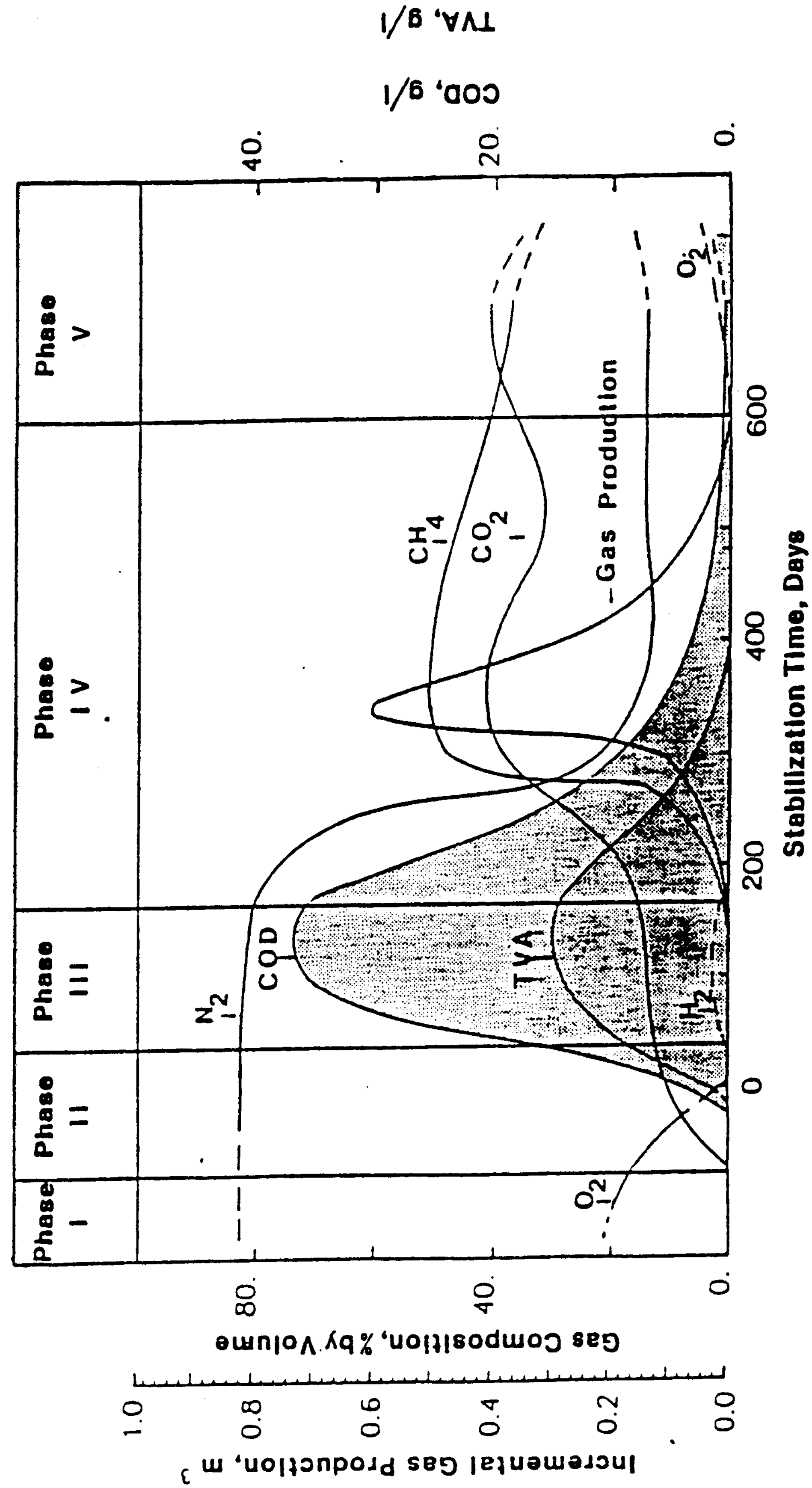

Figure 6-1. Stabilization phases of waste degradation in a landfill (reprinted by permission from F. G. Pohland).

Phase III - Acid Formation Phase
The continuous hydrolysis (solubilization) of solid waste, followed by (or concomitant with) the microbial conversion of biodegradable organic content results in the production of intermediate VOAs at high concentrations throughout this phase. A decrease in pH values is often observed, accompanied by metal species mobilization. Viable biomass growth associated with the acid formers (acidogenic bacteria), and rapid consumption of substrate and nutrients are the predominant features of this phase.

Phase IV - Methane Fermentation Phase
During Phase IV, intermediate acids are consumed by methane-forming consortia (methanogenic bacteria) and converted into methane and carbon dioxide. Sulfate and nitrate are reduced to sulfides and ammonia, respectively. The pH value is elevated, being controlled by the bicarbonate buffering system, and consequently supports the growth of methanogenic bacteria. Heavy metals are removed from the leachate by complexation and precipitation and transported to the solid phase.

Phase V - Maturation Phase
During the final state of landfill stabilization nutrients and available substrate become limiting, and the biological activity shifts to relative dormancy. Gas production dramatically drops and leachate strength stays steady at much lower concentrations. Because gas productions has all but ceased, atmospheric gases may permeate back into the landfill, and oxidized species may slowly appear. The slow degradation of resistant organic fractions may continue with the production of humic-like substances.

Thus, the progress toward final stabilization of landfill solid waste is subject to the physical, chemical, and biological factors within the landfill environment, the age and characteristics of landfilled waste, the operational and management controls applied, as well as the site-specific external conditions.

Leachate Characteristics
The characterization of leachate provides important information necessary for the control of landfill functions and for the design and operation of leachate treatment facilities, facilitates risk analysis of leachate impact on the environment should liners leak, permits comparison of the impact of alternative landfill design or operating protocol on the environment, and reveals the interaction of leachate parameters. Critical parameters for monitoring and control are described in more detail in Chapter 8.

Material is removed from the waste mass via mechanisms which include leaching of inherently soluble material, leaching of soluble products of biological and chemical transformation, and washout of fines and colloids. The characteristics of the leachate are highly variable depending on the composition of the waste, rate of water infiltration, refuse moisture content, and landfill design, operation, and age. These variations are demonstrated in Table 6-1, where ranges in

Table 6-1. Landfill Constituent Concentration Ranges as a Function of the Degree of Landfill Stabilization

Parameter	Phase II Transition		Phase III Acid Formation		Phase IV Methane Formation		Phase V Final Maturation	
	Conventional*	Recirculating#	Conventional*	Recirculating#	Conventional*	Recirculating#	Conventional*	Recirculating#
BOD, mg/l	100-10,000	0-6893	1000-57,000	0-28,000	600-3400	100-10,000	4-120	100
COD, mg/l	480-18,000	20-20,000	1500-71,000	11,600-34,550	580-9760	1800-17,000	31-900	770-1000
TVA, mg/l as Acetic Acid	100-3000	200-2700	3000-18,800	1-30,730	250-4000	0-3900	0	--
BOD/COD	0.23-0.87	0.1-0.98	0.4-0.8	0.45-0.95	0.17-0.64	0.05-0.8	0.02-0.13	1.05-0.08
Ammonia, mg/l-N	120-125	76-125	2-1030	0-1800	6-430	32-1850	6-430	420-580
pH	6.7	5.4-8.1	4.7-7.7	5.7-7.4	6.3-8.8	5.9-8.6	7.1-8.8	7.4-8.3
Conductivity, µmhos/cm	2450-3310	2200-8000	1600-17,100	10,000-18,000	2900-7700	4200-16,000	1400-4500	--

*Pohland and Harper, 1986

#Natale and Anderson, 1985; Watson, 1993; Miller, et al, 1994; Lechner, et al, 1993 concentrations of significant leachate components are presented as a function of stabilization phase.

Organic contaminants of leachate are primarily soluble refuse components or decomposition products of biodegradable fractions of waste. Organic compounds detected in 19 MSW landfill leachates or contaminated groundwater plumes emanating from landfills included organic acids, ketones, aromatic compounds, chlorinated aromatic compounds, ethers, phthalates, halogenated aliphatic compounds, alcohols, amino-aromatic compounds, nitro-aromatic compounds, phenols, heterocyclic compounds, pesticides, sulfur substituted aromatic compounds, polyaromatic hydrocarbons, polychlorinated biphenyls, and organophosphates (Brown and Donnelly, 1988).

The class of organic compounds found at highest concentration in leachates is generally VOAs produced during the decomposition of lipids, proteins, and carbohydrates (Albaiges, et al, 1986; Schultz and Kjeldsen, 1988). Aromatic hydrocarbons, including benzene, various xylenes, and toluene, are also frequently found at lower concentrations (Schultz and Kjeldsen, 1988; Harmsen, 1983). These compounds were considered to be constituents of gasoline and fuel oils. Sawney and Kozloski (1984) reported that the presence of the more soluble, less volatile aromatic components of gasoline in the leachate suggested that the more volatile components were being gas stripped from the landfill. Nonvolatile classes of compounds such as phenolic compounds may be degradative byproducts of lignin. A small complex fraction found in several leachates contained nicotine, caffeine, and phthalate plasticizers (Albaiges, et al, 1986). Oman and Hynning (1993) observed that a total of 150 different organic compounds have been identified in multiple studies, however only 29 were identified in more than one, concluding that leachate composition was quite site specific.

The dominant organic class in leachate shifts as the age of the landfill increases due to the ongoing microbial and physical/chemical processes within the landfill. An investigation of leachates obtained from landfills operated from one to twenty years found that the relative abundance of high molecular weight humic-like substances decreases with age, while intermediate-sized fulvic materials showed significantly smaller decreases (Chian, 1977). The relative abundance of organic compounds present in these leachates was observed to decrease with time in the following order: free VOAs, low molecular weight aldehydes and amino acids, carbohydrates, peptides, humic acids, phenolic compounds, and fulvic acids.

A variety of heavy metals are frequently found in landfill leachates including zinc, copper, cadmium, lead, nickel, chromium, and mercury (Lu, et al, 1985). Again, these metals are either soluble components of the refuse or are products of physical processes such as corrosion and complexation. In several instances heavy metal concentrations in leachate exceed US Toxicity Characteristic Leaching Procedures standards.

Heavy metal concentrations in leachate do not appear to follow patterns of organic indicators such as COD, BOD, nutrients, or major ions (Lu, et al, 1985). Heavy metal release is a function of characteristics of the leachate such as pH, flow rate, and the concentration of complexing agents.

Gas Characteristics
When solid waste decomposes, significant portions of organic wastes are ultimately converted to gaseous end-products. The rate of gas production is a function of refuse composition, climate, moisture content, particle size and compaction, nutrient availability, and buffering capacity. Reported production rates vary from 0.12 to 0.41 m^3/kg (3800 to 13,000 ft^3/ton) dry waste (Pohland and Harper, 1986). Production rates and gas composition also follow typical stabilization phases (see Figure 6-1), with peak flow rates and methane content occurring during the methanogenic phase. Landfill gas is typically 40 to 60 percent methane, with carbon dioxide and trace gases such as hydrogen sulfide, water vapor, hydrogen, and various volatile organic compounds comprising the balance.

Because of their high vapor pressures and low solubilities, many toxic volatile organic compounds (VOCs) are observed in landfill gas. In a report by the State of California Air Resources Board (Bennett, 1987), the average surface emission rate of hazardous chemicals from landfills was estimated to be 35 kg/million kg of refuse. Landfill gas trace constituents include halogenated aliphatics, aromatics, heterocyclic compounds, ketones, aliphatics, terpenes, and alcohols and have been characterized by several researchers (Siu, et al, 1989; Young and Parker, 1983; Wood and Porter, 1987; LaRegina and Bozzeli, 1986).

Leachate Characteristics of Recirculating Landfills
Leachate quality data were collected from five full-scale recirculating landfills located in Lycoming County, PA; the Central Solid Waste Management Center (CSWMA), Sandtown, Delaware; the Southwest Landfill, Alachua County, FL; the Central Facility Landfill, Worcester County, MD, and the Breitnau Research Landfill, Austria, previously described in Chapters 4 and 5. Results of preliminary analysis of the data are summarized in Tables 6-1 and 6-2. Table 6-1 provides leachate characteristics as a function of landfill stabilization phase for both conventional and recirculating landfills, while Table 6-2 compares all data. Due to differences in waste age and heterogeneity of conditions found within each landfill, explicit transitions between stabilization phases cannot be determined exactly. Nevertheless, boundaries between such phases were delineated based on the approximate magnitudes of leachate and gas strength (*i.e.* COD and BOD concentrations, and methane production) obtained from the records at these sites. Furthermore, a comprehensive understanding of stabilization sequence and features as illustrated in the literature, provided the necessary guidance in dividing the stabilization histograms into their consecutive stages, and projecting the overall values of leachate and gas parameters.

From these data it appears that leachate characteristics of recirculating landfills follow a pattern similar to that of conventional landfills, *i.e.*, moving through phases of acidogenesis, methanogensis, and maturation (although few recirculating landfills have reached maturation). These data (as summarized in Table 6-2) do not suggest that contaminants extensively concentrate in the leachate as has been promoted by critics of leachate recirculation (King and Mureebe, 1992). Actually, the overall magnitude of various leachate components, during the consecutive phases of landfill stabilization, are quite comparable in both types of landfills. However, the acidogenic phase tends to be more pronounced in recirculating landfills as opposed to conventional landfills, forming a plateau with consistently high concentration of leachate constituents (Al-Yousfi, 1992). Such a phenomenon can be explained by the fact that uniform, high moisture contact opportunities exist in the leachate recycling landfills. On the other hand, dryness in areas of conventional landfills, accompanied by fewer chances of moisture contact and availability, minimizes the leaching opportunity in such landfills, and result in rapidly peaking leachate histograms.

Table 6-2. Leachate Constituents of Conventional and Recirculating Landfills - Summarizing all Phases

Parameter	Conventional*	Recirculating#
Iron, mg/l	20 - 2100	4 - 1095
BOD, mg/l	20 - 40,000	12 - 28,000
COD, mg/l	500 - 60,000	20 - 34,560
Ammonia, mg/l	30 - 3000	6 - 1850
Chloride, mg/l	100 - 5000	9 - 1884
Zinc, mg/l	6 - 370	0.1 - 66

*Pohland and Harper, 1986

#Natale and Anderson, 1985; Watson, 1993; Miller, et al, 1994; Lechner, et al, 1993

Even in the case where recycled leachates are somewhat stronger than single-pass leachates, they are primarily treated inside the landfill, utilizing its storage and degradation capacity as an effective bioreactor. No extra liability and/or handling requirements will result from such cases, because leachate is repeatedly recirculated back into the landfill until its strength diminishes and stabilizes. In this respect, frequency of recirculation can be employed as a control measure to optimize landfill operations and alter leachate characteristics as desired.

Fate and Transport of Priority Pollutants

The fate of inorganic and organic compounds placed in a landfill is determined by the operative processes inherent to the natural stabilization phases occurring within the landfill. Contaminants tend to partition among aqueous, solid, and gaseous phases of the landfill. Contaminant mobility and fate is largely determined by the magnitude of the preference for one phase relative to another which is a function of the physical/chemical characteristics of both the contaminant and the phases present.

Figure 6-2 depicts the transport/transformation phenomena which may affect the environmental fate of a landfilled contaminant. Mechanisms of mobility and transformation include biotransformation, volatilization, dissolution and advection, sorption, and chemical reactions such as precipitation, reduction, oxidation, and hydrolysis. Biotransformation and chemical reaction can reduce contaminant mass, however, a more toxic and/or mobile compound may be produced. Dissolution and advection results in the movement of the compound with the bulk flow through the refuse pore spaces. Similarly, volatilization and transport by the product gas can remove the

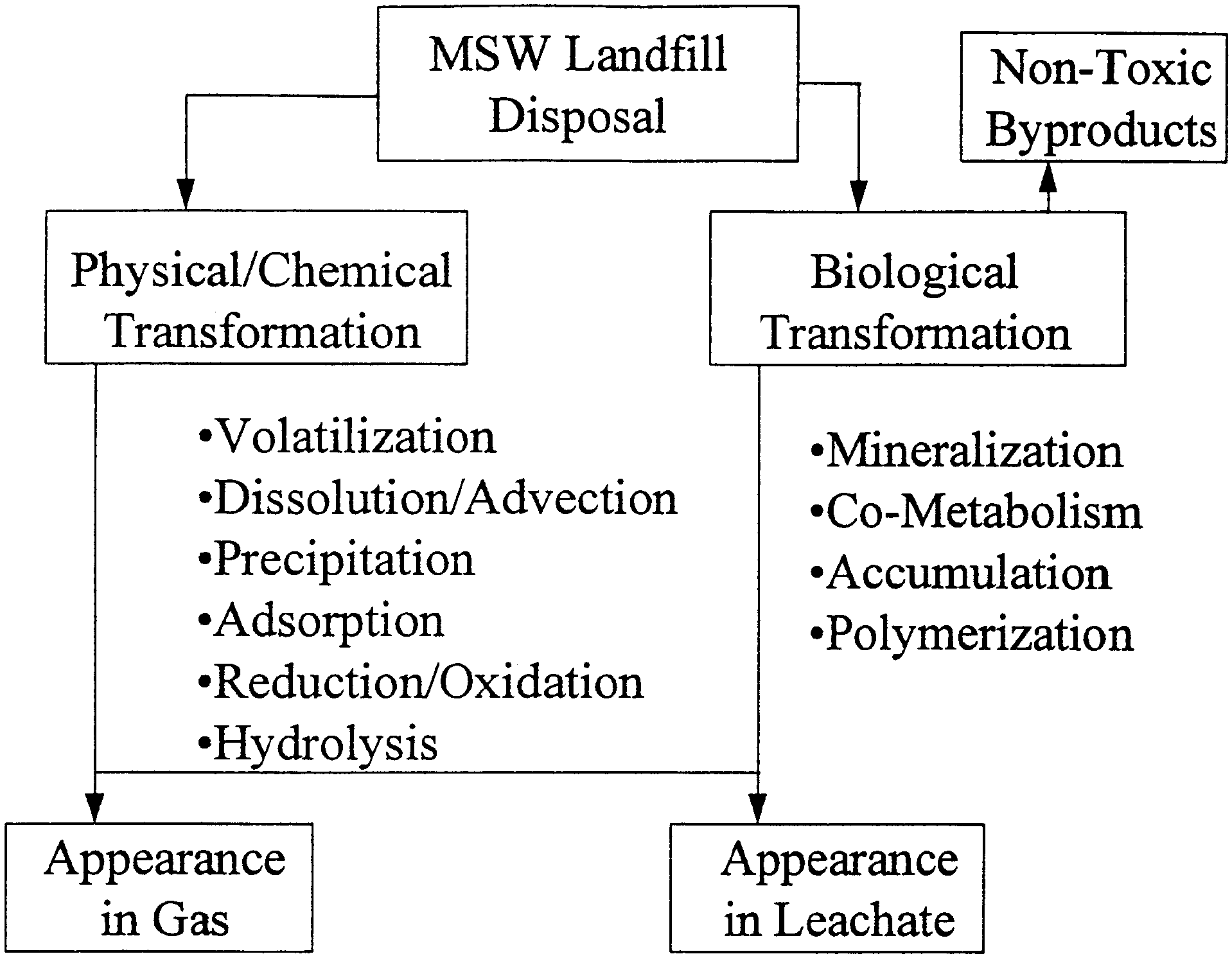

Figure 6-2. Fate and transport mechanisms for contaminants in MSW landfills.

more volatile contaminants from the landfill. Sorption and precipitation can retard contaminant movement as the compound interacts with the solid phase. Transport can be influenced by compound complexation or chelation which can either retard movement if the complex becomes associated with the solid phase or enhance mobility if the compound "piggybacks" on a more soluble complexing agent.

The fate of twelve organic priority pollutants codisposed with municipal solid waste in lysimeters was investigated by researchers at the Georgia Institute of Technology (Pohland, et al, 1992). The lysimeters were constructed in pairs of recirculating and single-pass operation and are described in more detail in Chapter 4. The organic priority pollutants were attenuated by abiotic and biotic transformation as well as partitioning to the waste mass. Reductive dehalogenation was the principal mechanism for halogenated compounds. Evidence suggested the possible reduction and mineralization of some aromatic compounds. The conversion of organic pollutants was enhanced in the recirculating columns due to reduced oxidation-reduction potential and stimulated methanogenesis.

Relatively few metal contaminants were routinely measured in laboratory-scale landfill bioreactor studies other than iron and magnesium, however antimony, arsenic, beryllium, cadmium, chromium, copper, iron, lead, magnesium, and zinc are monitored at pilot and full-scale sites, presumably to meet regulatory requirements. With the exception of iron, magnesium, and arsenic (at the Delaware test cells), metal concentrations were reportedly below detection limits.

In the presence of leachate recirculation, iron concentrations tended to decline with time, while remaining constant in conventionally operated landfills. Where leachate-recirculating sites were continuing to receive waste, however, iron concentrations remained elevated.

The primary removal mechanism for metals in conventionally operated landfills appears to be washout, although limited chemical precipitation may occur. In leachate-recirculating landfills, the primary removal mechanism appears to be metal sulfide and hydroxide precipitation and subsequent capture within the waste matrix by encapsulation, sorption, ion-exchange, and filtration (Pohland, et al, 1992). Gould, et al, (1989) found that leachate recirculation stimulated reducing conditions in lysimeters, providing for the reduction of sulfate to sulfide, which moderated leachate metals to very low concentrations. Chian and DeWalle (1976) reported that the formation of metal sulfides under anaerobic conditions effectively eliminated the majority of heavy metals in leachate. In addition, under neutral or above neutral leachate conditions, promoted by leachate recirculation, metal hydroxide precipitation is enhanced. With time, moderate to high molecular weight humic-like substances are formed from waste organic matter in a process similar to soil humification. These substances tend to form strong complexes with heavy metals. In some instances, a remobilization of precipitated metals can result from such complexation once the organic content has been stabilized and oxic conditions begin to reestablish (Pohland, et al, 1992). The potential for remobilization supports the idea of inactivating the landfill (removing all moisture) once the waste is stabilized.

Comparison of Waste Stabilization Rates

The rate of waste placement can significantly impact leachate characteristics. Waste placed in a laboratory column will behave more or less as described above, following distinct phases of transition, acidogenesis, methanogenesis, and maturation. Once methanogenesis is established, the leachate organic strength generally declines. In order to quantify the impact of leachate recirculation of leachate stabilization, a comparison of the rate of decline in the COD for recirculating and single-pass operations was made. Because of the limited available operational information for these studies, a rigorous kinetic analysis of the sequential reactions was not possible. However, a non-linear regression of chronological, declining COD data was performed for a series of laboratory studies of leachate recirculation and conventional, single-pass operations described in Chapter 4 (Pohland, 1975; Pohland, et al, 1992; Tittlebaum, 1982, Pohland, 1985). From the rate of decline, COD half-lives can be calculated and compared. Half-lives are presented in Table 6-3, where it can be seen that, in most cases, recirculation accelerated leachate stabilization, as attested by the shorter half-life of COD within the recirculating lysimeters.

A similar analysis of leachate COD for full-scale leachate recirculating landfills having moved to maturation phases was made with results also provided in Table 6-3. Here, half-lives were nearly

Table 6-3. COD and Chloride Half-Lives in Laboratory, Pilot and Full-Scale Leachate Recirculation Studies, Years

Study	COD		Chloride	
	Recirculating	Single-Pass	Recirculating	Single-Pass
GIT (Pohland, 1975) (L)	0.21	0.69	0.73	0.29
GIT (Pohland, et al, 1985)(L)	0.19	--	1.2	--
Tittlebaum, 1982 (L)	0.07	3.75	0.43	0.47
GIT (Pohland, et al 1992) (L)	0.43	0.41	1.77	0.51
Austria (Lechner, et al 1993) (P)	0.64	--	--	--
DSWA (Watson, 1993) (P)	0.32	0.27	1.8†	4.21
DSWA (Watson, 1993) (F)	1.05	--	2.89	--
Lycoming, PA (Natale and Anderson 1985) (F)	0.78	--	2.58	--

L = laboratory-scale, P = pilot-scale, F = full-scale
†This value is a doubling time since chloride concentration is increasing

five times greater than those of laboratory recirculating lysimeters. As discussed previously, a full-scale landfill does not usually depict a single degradation phase, but rather overlapping phases representing various sections, ages, and activities within the landfill. In addition, full-scale leachate recirculating devices are generally less efficient than those used in the laboratory, therefore portions of the full-scale landfill may be relatively dry. Also, greater compaction in the field vs. the laboratory will negatively impact leachate routing. Thus full-scale landfills may experience slower decay rates than laboratory fills.

Unfortunately, the relative efficacy of leachate recirculation in enhancing waste degradation relative to conventionally operated landfills at full-scale is difficult to quantify, because of the lack of conventional/recirculation parallel operations. Recognizing this limitation, leachate COD data were gathered from the literature for conventional landfills. These data and their sources are provided in Appendix B and are plotted in Figure 6-3. The data were analyzed to determine a COD half-life as described above. A COD half-life of approximately 10 years was calculated for conventional landfills as compared with values of 230 to 380 days for recirculating landfills.

Clearly, recirculation significantly increases the rate of the transformation of organic matter in leachate and by inference, the rate of waste stabilization. Results for conventional landfills compare favorably with values reported in the literature. Chian and Dewalle (1976) reported effective landfill lives of ten to fifteen years based on gas production data and cited half-lives of 36 to 100 years from the literature. Suflita, et al (1992) calculated a half-life of just over a decade for the Freshkills Landfill in New York City based on cellulose to lignin ratios.

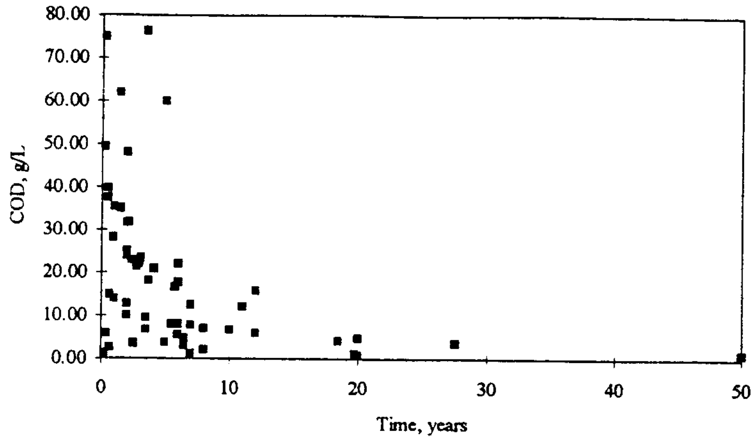

Figure 6-3. Leachate COD from conventional landfills.

COD is removed from single-pass landfills via washout and biological conversion and from recirculating landfills primarily by accelerated biological conversion. A conservative parameter such as chloride would be removed from single-pass landfills via washout, however in a recirculating landfill, chloride would only be removed when leachate was discharged to off-site treatment and disposal. Therefore, chloride would be expected to decline in concentration over time in a single-pass landfill, while staying relatively constant or more slowly declining in a recirculating fill (see Figure 6-4). This behavior has been observed at all scales. Chloride half-lives were calculated as described above for COD and are reported in Table 6-3 where this behavior is confirmed quantitatively (*i.e.* considerably higher chloride half-lives in recirculating fills than in conventional landfills). A comparison of COD and chloride half-lives should provide an independent means of confirming the impact of leachate recirculation on leachate components, assuming the leachate is evenly distributed and methanogenesis is occurring. The opposite effects of leachate recirculation on the conservative parameter chloride and the nonconservative parameter COD should provide a COD/chloride half-life ratio of well below one. For single-pass operations, the value should be greater than or equal to one. Limited data are available to test this hypothesis, however this trend is seen in Table 6-4.

Table 6-4. Ratios of COD/Chloride Half-Lives

Reference	Recirculating	Single-Pass
Pohland, 1975 (L)	0.29	2.38
Pohland, et al 1985 (L)	0.16	--
Tittlebaum, 1982 (L)	0.019	1.08
Pohland, et al, 1992 (L)	0.24	0.8
DSWA, 1993 (P)	0	--
Watson, 1993 (F)	0.36	--
Natale and Anderson, 1985 (F)	0.30	--

Leachate Treatment Implications

Ideally, the bioreactor landfill should be operated to minimize off-site management of leachate, however, eventually treatment of leachate will be necessary. Following extended recirculation, the leachate will be largely devoid of biodegradable organic matter, and will contain recalcitrant organics and inorganic compounds such as ammonia, chloride, iron, and manganese. Table 6-1 and 6-2 provide some indication of the quality of mature leachate from recirculating landfills. Treatment needs depend upon the final disposition of the leachate. Final disposal of leachate may be accomplished through codisposal at a publicly owned treatment works (POTW) or onsite treatment and direct discharge to a receiving body of water, deep well injection, land application, or via natural or mechanical evaporation.

Leachate treatment can be challenging because of low biodegradable organic strength, irregular production rates and composition, and low phosphorous content (if biological treatment is considered). Because of the nature of leachate, physical/chemical treatment processes such as ion exchange, reverse osmosis, chemical precipitation/filtration, and carbon adsorption are the most likely options. Available leachate treatment processes are discussed by several authors (Pohland and Harper, 1986; Lema, et al, 1988; Chian and DeWalle, 1976; Cossu and Urbini, 1989; Venkataramani, et al, 1986). Generally, where on-site treatment and discharge is selected, several unit processes are required to address the range of contaminants present. For example, a recently constructed leachate treatment facility at the Al Turi Landfill in Orange County, New York utilizes polymer coagulation, flocculation, and sedimentation followed by anaerobic biological treatment, two-stage aerobic biological treatment, and filtration prior to discharge to the Wallkill River (King and Mureebe, 1992). Pretreatment requirements may address only specific contaminants which may create problems at the POTW. For example, high lime treatment has been practiced at the Alachua County Southwest Landfill to ensure low heavy metal loading on the POTW.

Leachate Quantities

Leachate volumetric data from full-scale recirculating landfill sites described in Table 5-1 and plotted in Figure 6-5 show that greater volumes of leachate are produced as recirculation rates increase. Also, recirculated leachate represents an increasing percentage of generated flows (asymptotically approaching 100 percent) as recirculation rates increase. With the current landfill capping practices, recirculated leachate volumes will become especially dominant after landfill closure. Of the six operating sites analyzed, leachate generation rates ranged from 1.1 to 13.5 m^3/ha/day (300 to 2100 gal/acre/day), with recirculated leachate representing 40 to 70 percent of leachate generated. As with conventional landfills, leachate generation is a function of climate and site characteristics, as well as leachate recirculation rates.

Off-site disposal of leachate ranged from 0 to 59 percent of leachate generated. Data suggested that, unlike conventional landfills, the volume of leachate requiring off-site management at recirculating landfills was a function of both the volume of leachate generated and the available on-site storage. At sites where large storage volumes were provided relative to the size of the landfill cell, off-site management of leachate was minimized (frequently no off-site management

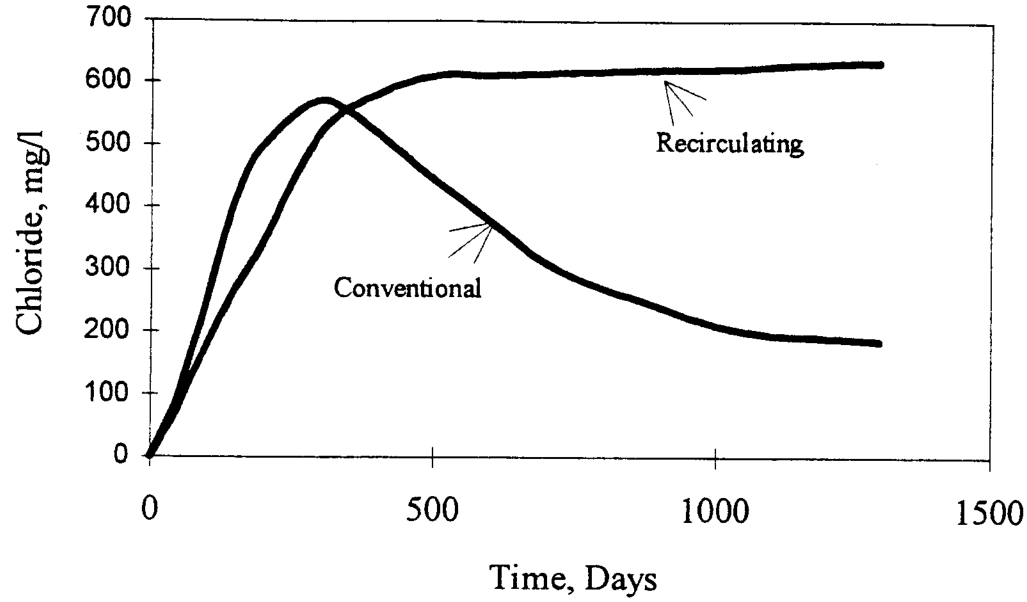

Figure 6-4. Typical Behavior of chloride in conventional and recirculating landfills.

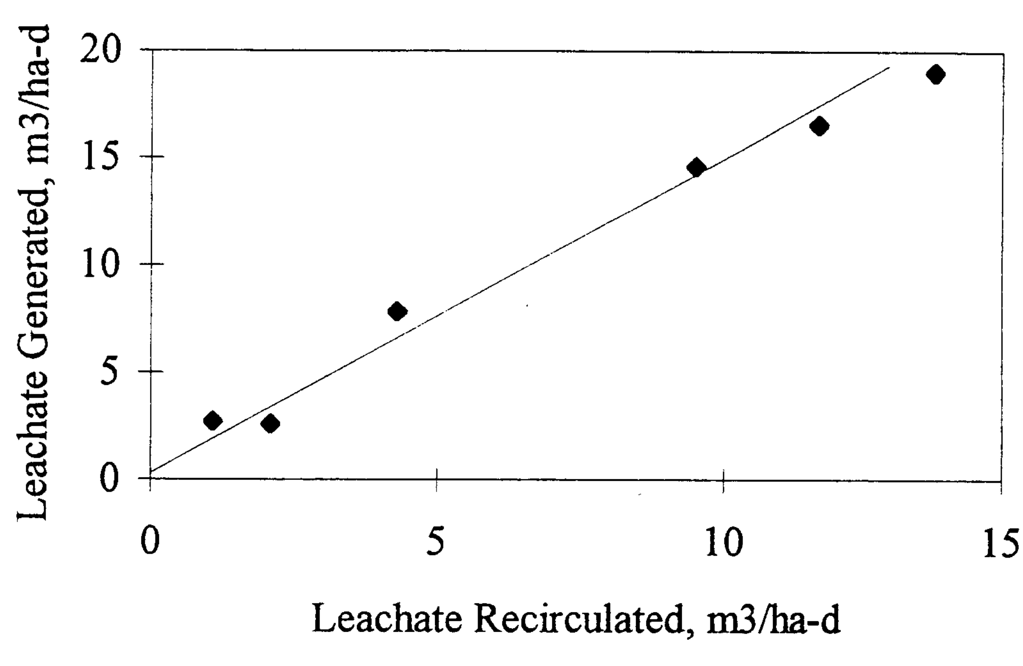

Figure 6-5. Effect of leachate recirculation on leachate generation.

was required for long periods of time). It was also observed that sites with relatively little storage were compelled to recirculate leachate at much higher rates than those with large storage volumes.

Gas Production

While gas production is relatively easy to determine from laboratory lysimeters, full-scale measurement of gas emissions from active sites is more difficult to achieve. Limited data suggest that, as in lysimeters, gas production is significantly enhanced as a result of both accelerated gas production rates as well as the return of organic material in the leachate to the landfill for conversion to gas (as opposed to washout in conventional landfills). Parallel 2.5-ha (one-acre) cells operated by the Delaware Solid Waste Authority comparing conventional operation and leachate recirculation showed a twelve-fold increase of gas production in the recirculating cell relative to the conventional cell (5400 std m^3 vs 480 std m^3 (190,000 std ft^3 vs 17,000 std ft^3), DSWA, 1993).

Gas emission measurements were made by University of Central Florida (Orlando) researchers at a recirculating landfill in Alachua County, Florida using a patented device, the Flux Tube (a variation on the flux chamber used to measure surface emissions). These tests revealed a doubling of gas production rates from waste located in wet areas of the partially recirculating landfill relative to comparably aged waste in dry areas (0.0236 std m^3/kg-yr vs. 0.0096 std m^3/kg-yr (750 std ft^3/ton-yr vs 300 std ft^3/ton-yr, Palumbo, 1995). This fact was corroborated by measurements of biological methane potential (BMP) from samples obtained in wet and dry areas of the same landfill (Miller, et al, 1994). A 50 percent decrease in BMP was measured in wet samples (46 percent wet basis) over a one year period. Negligible decreases in BMP were observed in dry samples (29 percent wet basis) over the same period.