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EVALUATION OF SERIAL ANAEROBIC/AEROBIC PACKED BED BIOREACTORS FOR TREATMENT OF A SUPERFUND LEACHATE

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Summary

Serial anaerobic/aerobic packed-bed bioreactors were employed to biodegrade organic contaminants in leachate from a high priority Superfund site in the U.S. Steady-state overall Total Organic Carbon (TOC) mass removal rates in excess of 90% were observed. Between 80% and 90% of specific volatile and non-volatile priority pollutants were removed by the bioreactors. Aqueous and gas phase inorganic and organic species were identified and quantified, allowing computation of mass balances for the anaerobic and aerobic subsystems. Species volatilization losses were minimized; losses that did occur were accounted for in the mass balance.

Introduction

Past, present and future releases of hazardous materials from abandoned or inadequate waste disposal sites threaten public health and the environment. This is especially true in highly industrialized states in the U.S., such as New Jersey. In order to clean up the worst of the nation's sites, U.S. Congress enacted the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA), commonly known as "Superfund".

To date, the great majority of remedial actions initiated under Superfund have involved either containment of wastes on-site or removal of wastes to off-site disposal facilities. However, a recent report by the U.S. General Accounting Office indicated a significant risk of containment barrier failure [1]. It also reported that 87% of landfills receiving Superfund wastes are in unacceptable condition; many of these sites may themselves eventually become Superfund sites. It has become apparent that the practices of waste containment and removal constitute an elaborate exchange process wherein the hidden wastes remain hazards.

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In response to this situation Congress enacted the Superfund Amendments and Reauthorization Act (SARA) of 1986, providing new incentives for implementation of innovative, permanent waste destruction technologies. On-site treatment technologies are particularly promising because they avoid the economic costs and safety risks associated with major excavation and/or off-site transportation of hazardous wastes.

The particular site being investigated for this study is an inactive landfill, high on the National Priority List (NPL) established under Superfund. The site is between 10 and 20 acres (40 – 80 km^2) in size, and is known to have accepted various municipal and industrial wastes before closure in the early 1970s. It is estimated to contain several thousand cubic yards of solid wastes and several million gallons of liquid wastes. Several streams, some residences and an active farm are in close proximity to the landfill. The principal threats associated with the landfill are surface and groundwater contamination resulting from off-site migration of the landfill leachate, and secondary air pollution resulting from high concentrations of volatile organic species present in the leachate. Thus, the primary objective of this research was to develop a leachate treatment process effectively addressing these threats.

In November 1985, a 210 gallon (~ 800 l) leachate sample was obtained from a well screened in the landfill. A portion of this sample was assayed for a variety of constituents; important results are summarized in Table 1. There are two major contamination problems associated with the leachate. The first is the presence of high levels of specific organic priority pollutants, including compounds in both the volatile and base/neutral extractable fractions. The second is the gross organic contamination, indicated by the high level of TOC. No pesticides, PCBs or toxic heavy metals are present in excess of method detection limits.

Given these specific leachate characteristics, several pretreatment, primary treatment and post-treatment process steps were screened for applicability. The leachate does not contain dispersed oil phases, excessive turbidity or high levels of toxic heavy metals, which eliminates the need for flocculation, reverse osmosis or ion exchange pretreatment steps. The high levels of organic contamination present in the leachate suggested microbial degradation as an attractive primary treatment process. Treatment processes such as granular activated carbon (GAC) adsorption/regeneration, low temperature oxidation and reverse osmosis are not suited for treating large volumes of concentrated organic wastewaters. However, these processes may be utilized for final polishing of effluent from a microbial treatment process.

The primary treatment process selected for laboratory studies employs consecutive anaerobic/aerobic microbial degradation in packed laboratory columns (LCs). Classical, secondary aerobic treatment was not selected because volatilization of priority pollutants would pose a significant secondary air pollution threat. The selected process can be easily adapted to *in situ* or on-site

TABLE 1

Leachate composition

Constituents	Concentration (ppb)
Volatile organic species	
Methylene chloride	17,000
Trans-1,2-dichloroethylene	570
1,2-dichloroethane	34,000
Trichloroethylene	360
Tetrachloroethylene	73
Benzene	3,800
Toluene	41,000
Total xylenes	9,400
Ethylbenzene	2,200
Base/neutral extractable species	
Bis(2-chloroethyl)ether	34,000
Bis(2-ethylhexyl)phthalate	760
1,2-dichlorobenzene	310
Diethylphthalate	220
Naphthalene	290
	Concentration (ppm)
Volatile fatty acids	*800*
Acetic acid	*175*
Propionic acid	*125*
Butyric acid	*100*
Isobutyric acid	
Other parameters	
Total inorganic carbon	100
Total organic carbon	1,000
Volatile organic carbon	100
Total dissolved solids	2,000
Chemical oxygen demand (mg O_2/l)	1,700
Total Kjeldahl nitrogen (mg N/l)	96
Total phosphorus	<0.2
Sulfate	19
Cyanide	<0.01
Ammonia (mg N/l)	85
Nitrate and nitrite (mg N/l)	<1.0
Calcium	75.7
Magnesium	11.8
Sodium	81.0
Iron	431

operation. Previous packed bed bioreactor experiments have successfully demonstrated treatment of a wide variety of wastewaters containing hazardous substances [2,3]. In addition, experiments have demonstrated that data obtained from laboratory scale investigations can be used to design pilot- and full-scale treatment systems [4]. Organic solute removals in excess of 99% have been obtained in the field.

Experimental design

The experiment discussed (Experiment 0187) employed an experimental design similar to that used in a previous experiment (Experiment 0586) with the same leachate. Experiment 0187 incorporated several design modifications directly resulting form process difficulties experienced during Experiment 0586. Experiment 0586 is described fully in a prior publication [5].

The laboratory column experiment (Experiment 0187) was designed to examine the ability of serial anaerobic/aerobic packed-bed bioreactors to biodegrade the wide variety of constituents in the leachate (Fig. 1). Initially, leachate influent was pumped upward through a column packed with a sandy loam soil. This type of soil was used as it is readily available on-site, and had been used successfully in previous packed-bed biodegradation experiments [2,3]. An upflow configuration was employed as it ensures column saturation, minimizing species volatilization losses as influent passes through the column. Column saturation also minimizes the presence of air, establishing anaerobic conditions throughout the column. This encourages degradation of the several volatile organic species (chlorinated, short-chain alkanes); it has been shown that these compounds are most effectively biodegraded anaerobically [6,7].

The second treatment step involved passing the effluent from the anaerobic column upward through a second column packed with coarse sand. This column was intermittently fed pure oxygen gas to promote aerobic microbial degradation of organic constituents still remaining after anaerobic treatment. The intention was that the larger part of the volatile species present would be biodegraded anaerobically, minimizing subsequent volatilization losses in the aerobic column. Volatile species entering the aerobic column would likely be stripped from solution by the passage of oxygen gas. Non-volatile organic species, which comprise 90% of the organic carbon in the leachate, were exposed to both anaerobic and aerobic treatment in the overall treatment system. The design is sufficiently flexible to allow for several recycle modes.

Sand was used as a packing for the aerobic column in response to operating results from Experiment 0586; 0.63 cm glass beads were used as packing for the aerobic column in Experiment 0586. Treatment efficiencies (i.e. mass of organic carbon removed) for the aerobic columns in Experiment 0586 were lower than expected. It was thought that sand, which has a much greater surface area than glass beads, would support a much larger microbial population.

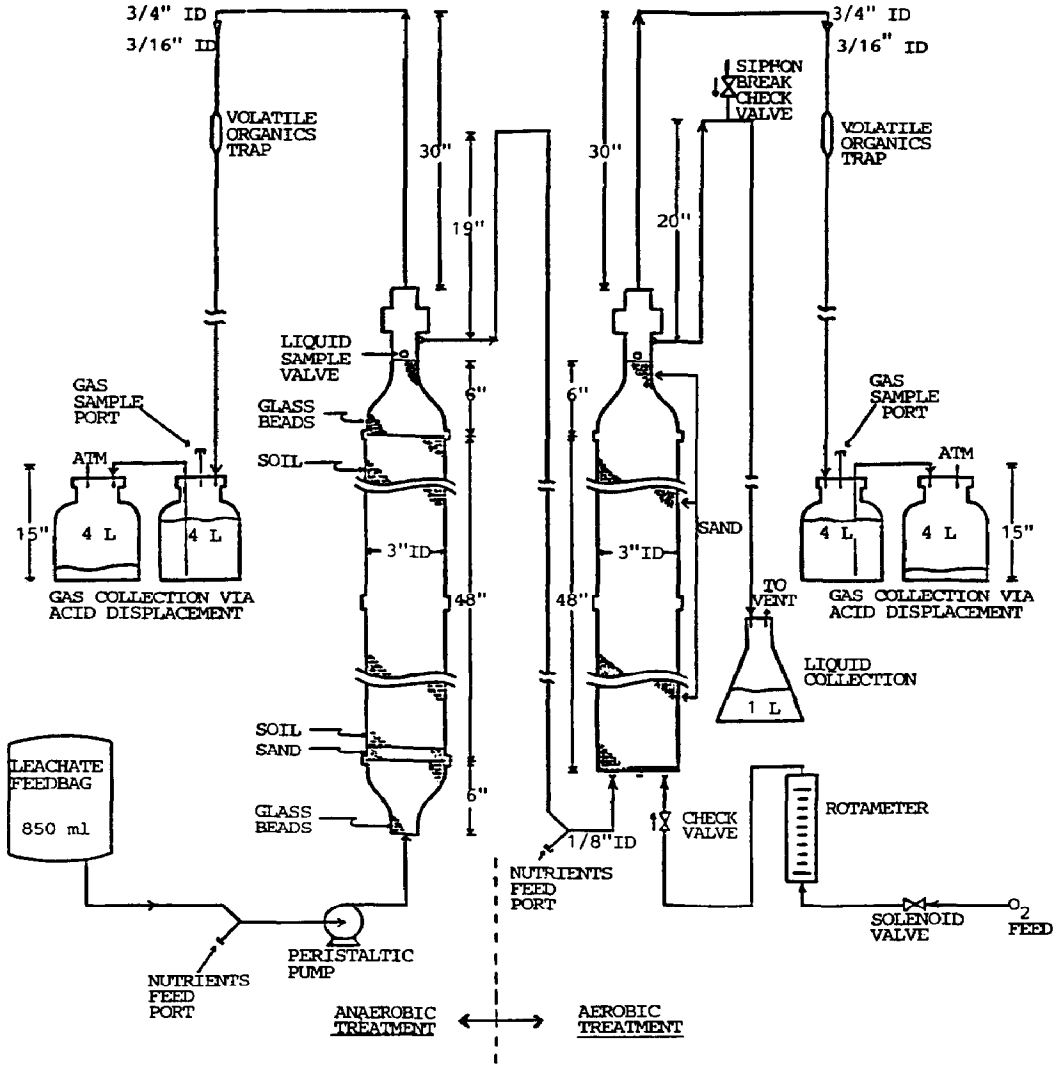

Fig. 1. Experimental apparatus.

Another advantage of the irregular grain size of sand is that gas – liquid contact should be improved, enhancing aerobic growth. Also, the interparticle pores in sand should be large enough to reduce the probability of plugging due to excessive microbial growth. Plugging would likely occur in an aerobic column packed with soil (which has much smaller interparticle pores than sand), since aerobic microbial growth rates are much higher than anaerobic microbial growth rates and accordingly lead to greater biomass.

The experimental design allowed for collection and quantification of gases

produced biologically, as well as entrapment and quantification of non-biodegraded organic species volatilized during operation. Also, the final liquid effluent from the aerobic column was collected in entirety. These capabilities allowed computation of total carbon mass balances over the anaerobic and aerobic subsystems, as well as the combined serial anaerobic/aerobic system. The total carbon mass balance included organic and inorganic carbon in both the liquid and gas phases. The same type of balance can also be performed for total nitrogen. Individual species mass balances for volatile and non-volatile priority pollutants were also possible, but were less accurate, given inherent analytical limitations.

Experiment 0187 employed two serial anaerobic/aerobic bioreactors these were operated as replicates (LC 5 soil/sand and LC 6 soil/sand). Full-strength leachate was used as influent to these columns. The target hydraulic flux rate was 50 l/m^2 day or 5.08 cm/day.

Materials and methods

The leachate was kept refrigerated in 4 liter amber bottles, without headspace, prior to use. Refrigeration was necessary to discourage biodegradation during storage. The leachate also required pretreatment to remove all iron species before it could be used as column influent. during Experiment 0586 it was discovered that iron oxides and hydroxides were precipitated out of the leachate, plugging the interparticle pores in the soil, resulting in greatly decreased hydraulic fluxes. The precipitation process was highly pH dependent, with all iron species precipitating out of solution above pH 8; a large percentage precipitated at pH 7. The pretreatment process employed during experiment 0187 involved adding 6 *M* KOH to the leachate, while it was in the amber bottle, to adjust the pH to 8.5, to precipitate all of the iron species; this was done very quickly, to minimize volatilization losses.

The supernatant from leachate pretreatment was pumped (Fig. 1) by a peristaltic pump into collapsible PVC feedbags, until full; sufficient 1 *M* HCl was added to each feedbag to reduce the leachate pH to 7.0. Specific salts were also added to each feedbag, making the influent 0.1 *M* in calcium chloride and 0.1 *M* in calcium nitrate. Calcium was added to cationically balance the influent, avoiding disintegration of clay particle aggregates. Disintegration of aggregates can lead to plugging of the interparticle pores in the soil packing, resulting in significantly reduced hydraulic flux rates, as has been demonstrated in a previous experiment [8]. Nitrate was added as an electron acceptor for anaerobic respiration. While filling the feedbags, exposure of the leachate to the atmosphere was minimized, reducing volatilization losses. The feedbags were gently squeezed to remove air bubbles before being connected to the bioreactor systems. PVC bags were used as they exhibit the lowest gas permeability of commercially available polymer sheet.

A programmable, timer-controlled, peristaltic pump was employed to draw the leachate from the feedbag. The pump provided the driving force for upward flow of leachate through the serial anaerobic/aerobic microbial treatment system. A liquid sampling port was located after the pump and before the anaerobic column, allowing for leachate sampling and supplemental nutrient addition, if necessary.

Both the anaerobic and aerobic columns consisted of two coupled 122 cm long by 7.6 cm diameter glass process pipes. The soil used to pack the anaerobic columns was obtained from an agricultural area adjacent to the landfill. The soil was classified as a sandy loam (70% sand, 16% silt and 14% clay) with a natural pH of 6.5, a cation exchange capacity of 6.6 meq/100 g, and a soil organic carbon content of 1.6%, by weight. The soil packing was accomplished by compressing 2.5 to 4.0 cm layers of soil until an effective packing depth of 122 cm was achieved.

After being treated anaerobically, partially biodegraded leachate emerged from the top of the column. Gases were produced as a result of anaerobic biodegradation of organic constituents in the leachate. To identify and quantify these gases, a gas separation and collection system was devised. It consisted of a 1.9 cm ID tube extending upward from the top of the column, leading to a 4 liter bottle completely filled with 0.05 *M* sulfuric acid. Gases produced during anaerobic biodegradation (CO_2, CH_4, N_2, H_2, etc.) are negligibly soluble in the acid. As gases were produced, pressure increased, and the acid was displaced into a second 4-liter bottle, calibrated for accurate measurement of gas volume produced. The pressure increase needed to displace the acid was much less than that required for the gases to enter the adjacent aerobic column instead. As a result of separating and collecting these gases, a gas – liquid interface was formed in the tube, possibly allowing volatilization of unbiodegraded organic species. Syringe sampling of the liquid anaerobic effluent was possible via a septum-fitted valve located several inches below the gas–liquid interface. This was important so that liquid samples accurately reflected the character of the anaerobic effluent, prior to possible volatilization losses.

Treated liquid entered the second stage of the process via overflow from the top of the anaerobic column into the bottom of the aerobic column. Supplemental nutrients may be introduced into the aerobic column from an injection port located at the bottom of the column. Oxygen gas entered the column through a port located at the bottom of the column. The gas flow rate was controlled by a calibrated rotameter; a solenoid valve interfaced to a programmable timer turned the gas flow on and off at selected intervals. Each aerobic column was packed with industrial grade coarse sand. For support, the packing in both the anaerobic and aerobic columns was underlain by a thin (0.3 cm) layer of glass wool and a several centimeter thick layer of glass beads.

Finally, aerobically treated liquid effluent excited the top of the aerobic column in a manner similar to the liquid leaving the anaerobic column. The pri-

mary difference was that the aerobic effluent overflowed into a vented one liter graduated cylinder. A gas separation and collection system identical to that of the anaerobic column was employed for identification and quantification of gases produced by the aerobic treatment process. Sampling of the liquid effluent from the aerobic column was done in an identical manner to sampling done from the anaerobic column. All liquid samples were filtered through a 0.45 μm nylon syringe filter immediately after being taken. Samples were stored without headspace at 4°C in 5 ml glass vials equipped with hole caps and teflon-faced neoprene septa, prior to performing specific analyses. Both serial anaerobic/aerobic bioreactor systems were enclosed in black-out cloth, to discourage photosynthetic growth. Both bioreactor systems were kept airtight to prevent contamination due to atmospheric infiltration and losses due to volatilization of organic species.

Start-up procedures

Initially, each of the anaerobic soil columns was saturated, driving off trapped gases (especially oxygen) which might interfere with anaerobic growth. To accomplish this, a cationically balanced feed solution (0.02 *M* calcium nitrate) was pumped through the columns for several weeks.

After saturation was achieved, each of the anaerobic soil columns was fed a nutrient solution to encourage microbial growth. It contained 100 mg/l carbon (as dextrose) balanced with 10 mg/l nitrogen (as ammonium chloride) and 0.5 mg/l phosphorous (as K_2HPO_4). These columns were then inoculated with 50 ml of an active anaerobic culture obtained from the Old Bridge Sewage Authority. Five days later (Day 1), full-strength leachate influent was introduced to the anaerobic columns; supplemental nutrients were discontinued because the leachate contained sufficient nitrogen and phosphorus relative to carbon. It should be noted that the leachate contains a sufficient amount of Total Inorganic Carbon (TIC between 100 mg/l and 200 mg/l) to support methanogenesis, which uses carbon dioxide as a final electron acceptor. The leachate did not contain sulfate, precluding anaerobic respiration by using sulfate as the final electron acceptor. Full-strength leachate remained the influent to the anaerobic columns through the end of the experiment (225 days).

From Day 10 through Day 15, the same nutrients that were added to the anaerobic columns were introduced into the aerobic columns also; nutrient addition was terminated after this interval. Nutrients were added to these columns at this time to account for the mean hydraulic residence time in the anaerobic columns (approximately 12 days at the target flux of 50 l/(m^2 day)). On Day 13, 50 ml of an aerobic, activated sludge culture obtained from the Somerset–Raritan Valley Sewage Treatment plant was added to each aerobic column. Target oxygen flow rates (approximately 100 l/m^2 day)) were greater than twice the stoichiometric amount necessary to convert all of the influent TOC to CO_2, assuming the worst-case, i.e., negligible anaerobic biodegradation.

Results and discussion

Hydraulic flux responses

Average hydraulic fluxes during steady state operation of the bioreactors are presented in Table 2. Hydraulic flux data, compiled as a 5-day moving average, are presented for only one (LC 6) of the serial anaerobic/aerobic laboratory column systems in Fig. 2, since replication was excellent. Typical fluxes of 40–45 l/(m^2 day) were observed. These mean hydraulic fluxes were considerably higher (>60% higher) for Experiment 0187, compared to Experiment 0586, due to pretreatment of the leachate to remove iron species. It appeared that much greater fluxes could have been achieved, if desired. A few isolated incidents of reduced flux occurred; these were generally the result of worn or clogged pump tubing. Flux rates quickly returned to normal after replacement of the tubing.

Effluent carbon responses

Effluent TIC and TOC responses, and influent TOC data are presented together for the anaerobic and aerobic subsystems of one of the bioreactors (LC 6) in Figs. 3 and 4. Once again, replication between the two bioreactor systems was excellent. Effluent TOC concentrations exhibited similar trends for the anaerobic and aerobic columns. Initially for each column, anaerobic or aerobic, effluent TOC concentrations remained close to zero. Subsequently, there was a significant increase in effluent TOC, followed by a decline to a relatively

TABLE 2

Steady-state laboratory column operating results, Exp. 0187

Column	LC 5-Soil	LC 5-Sand	LC 6-Soil	LC 6-Sand
Column packing	Sandy loam	Sand	Sandy loam	Sand
Microbial treatment	Anaerobic	Aerobic	Anaerobic	Aerobic
Influent TOC, mg/l	700–1000	Variable	700–1000	Variable
Mean hydr. flux, l/(m^2 day)	40.7		46.2	
Mean TOC loading, g/(m^2 day)	28.2	5.3	32.1	4.6
Mean TOC removal, g/(m^2 day)	22.9	2.3	27.5	2.2
Subsystem TOC removal, % mass basis	81	44	85	47
Combined TOC removal, % mass basis	90		92	
Mean gas flux, l/(m^2 day)	40.9	137.4	40.9	130.0
Gas composition, mean mol%	41 N_2, 51 CH_4 7 CO_2	94 O_2 6 CO_2	40 N_2 53 CH_4 7 CO_2	93 O_2 7 CO_2

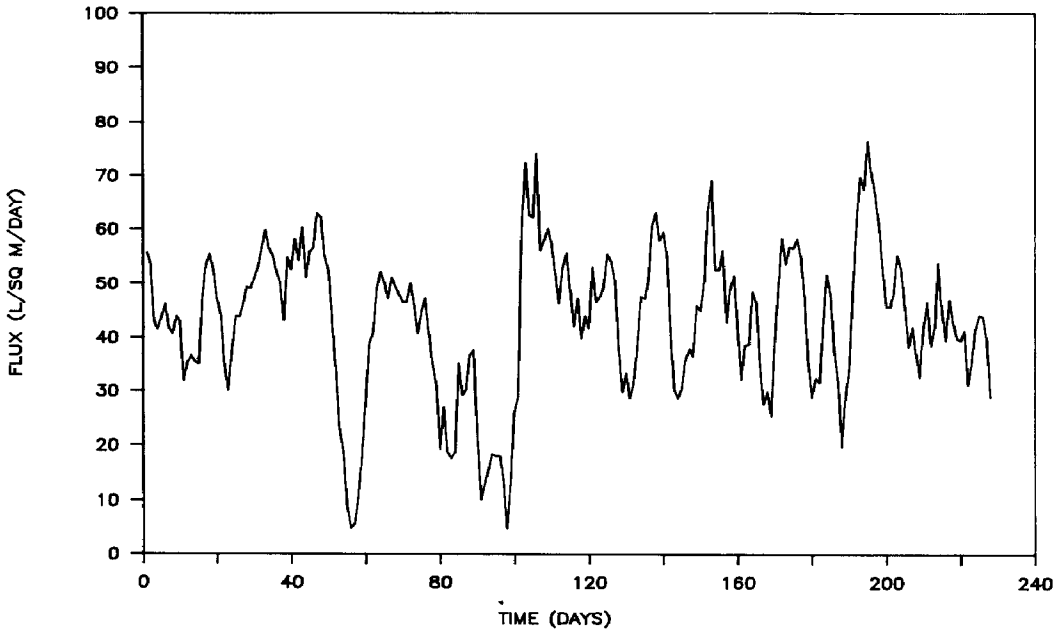

Fig. 2. Hydraulic flux, LC 6 (5-day moving average).

steady state effluent TOC concentration. Similar effluent TOC concentration responses have been observed in previous experiments with other leachates [2,3,8].

Effluent TOC concentration responses are indicated of the physical, chemical and biological status of a column. These responses result from three major competing processes: convective flow with dispersion, adsorption and microbial degradation. A numerical model incorporating these processes has been developed to simulate experimental responses of bioreactor columns [9]. One or more of these processes may control organic carbon removal during different time intervals of operation. In general, effluent TOC concentration responses can be separated into three regimes.

The first regime is a characteristic response delay during which effluent TOC concentrations remain near zero. Microbial populations are small and adsorption and dispersion are the controlling organic mass removal processes. The duration of this response delay is dependent on organic loading, hydraulic flux, extent of axial mixing and the adsorption capacity of the column packing. This response delay was much longer for the anaerobic columns than for the aerobic columns. Effluent TOC concentrations from the anaerobic columns did not begin to increase until 11 days (approximately one full mean residence time) after starting full-strength leachate flow. In comparison, effluent TOC concentrations from the aerobic columns began to rise shortly after the influent TOC concentrations began to rise. This shorter response delay is probably the result

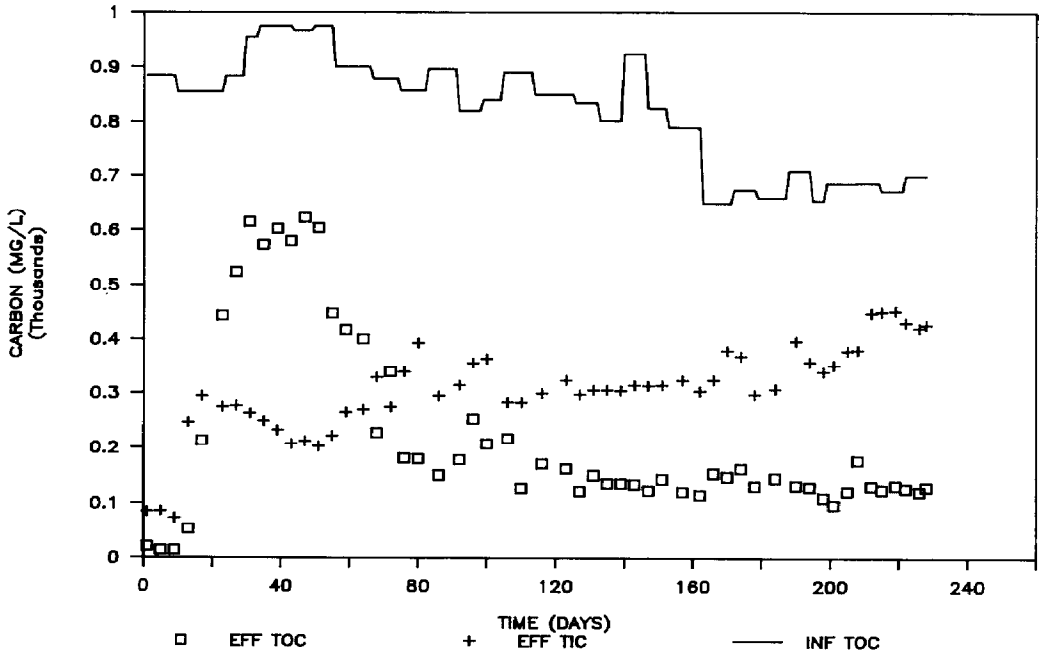

Fig. 3. Carbon responses, LC 6 - anaerobic column.

of greatly increased axial dispersion resulting from oxygen introduction, and minimal adsorptive capacity of the sand packing.

During the second regime, effluent TOC concentrations rise to a peak and then decline to a relatively steady-state level. This regime is observed while the adsorptive capacity of the column packing is being exhausted, and before the microbial community is able to adapt fully to the available organic carbon. This peak was much more pronounced for the anaerobic columns. There are two reasons for this. First, the TOC concentration of the anaerobic column influent was considerably higher – the influent to the aerobic columns had already been partially biodegraded in the anaerobic columns. Second, anaerobic microbial growth is generally much slower than aerobic growth.

The third regime is indicated by establishment of a relatively constant effluent TOC concentration level. At this point the microbial community is fully developed and adapted to the available organic carbon, allowing the microbial community to degrade a large percentage of the influent TOC. Steady-state was attained for the anaerobic columns by Day 140 and by Day 75 for the aerobic columns. Steady-state effluent TOC concentration levels were between 110 mg/l and 150 mg/l for the anaerobic columns, and between 40 mg/l and 80 mg/l for the aerobic columns.

Percent TOC removals (on an integrated mass basis) for each anaerobic and

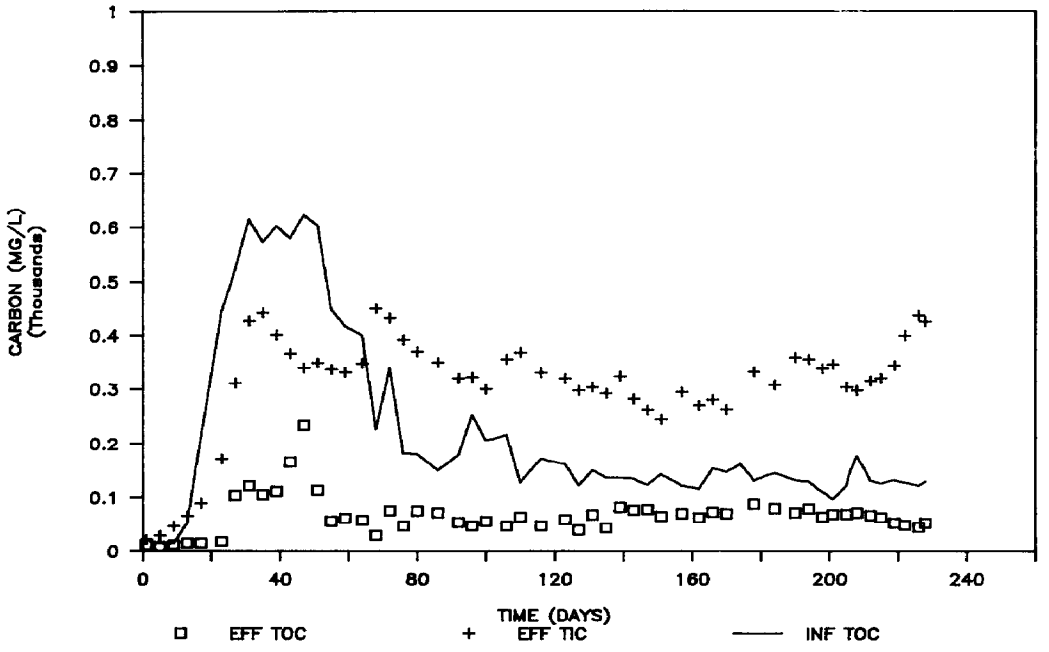

Fig. 4. Carbon responses, LC 6 - aerobic column.

aerobic subsystem, and for the combined anaerobic/aerobic systems are presented in Table 2. These TOC reductions all reflect steady-state operating results, and were computed based on the last 75 days of the experiment (Days 150–225). Steady state percent TOC removals for the anaerobic columns were in excess of 80%, while steady state percent TOC removals for the subsequent aerobic columns were only about 45%. Combined, each serial anaerobic/aerobic bioreactor removed greater than 90% of the leachate organic carbon, at steady-state. It should be remembered that during steady-state operation the primary TOC removal process is microbial degradation.

Steady state percent TOC removals for the aerobic columns were less than expected, although slightly more than observed during Experiment 0586. The use of sand as packing did not seem to substantially increase percent TOC removals, as expected; it seems that the packing was not an important factor in the aerobic biodegradation of the anaerobic effluent. The factors responsible may have been the low levels of available organic substrate and nutrients at steady state, combined with the possibility that the organic species remaining after anaerobic treatment were not easily biodegradable. It is unlikely that there was a problem with the aerobic treatment system *per se*, considering that during unsteady state operation (while anaerobic effluent TOC was peaking)

the aerobic column was able to remove a substantially higher percentage of organic carbon (approximately 75%).

It was thought that addition of an easily degradable carbon source (glucose) and other nutrients (potassium phosphate), might enhance aerobic biodegradation, possibly by cometabolism. This was done by syringe addition to the aerobic columns of 0.03 g of carbon (as glucose) daily for 25 days near the end of the experiment (Days 195–220). Only a slight increase in percent TOC removals was observed. This result probably indicates that the anaerobic effluent contained organic species which were difficult to biodegrade.

A very important measure of process performance is the mean TOC removal rate. It depends on percent TOC removal, organic loading and hydraulic flux rate. Average steady-state (Days 150–225) TOC removal rates for each anaerobic and aerobic subsystem are presented in Table 2. Steady-state mean TOC removal rates were much higher for the anaerobic columns than the aerobic columns. This was due to the much higher influent TOC concentrations to these columns, coupled with a much higher percent TOC removal. TOC removal rates were significantly increased relative to Experiment 0586, primarily due to increased hydraulic flux rates.

Effluent TIC concentration responses show a general increase to a relatively steady-state level for both the anaerobic and aerobic columns. This increase is concurrent with the microbial development and adaptation period for each column. The increase is due to formation of inorganic carbon as a by-product of either anaerobic (fermentation, anaerobic respiration) or aerobic (respiration) microbial growth. The carbon dioxide produced biologically is much more soluble than other biologically produced gases, such as methane and nitrogen.

Effluent pH responses

Effluent pH responses for the anaerobic and aerobic subsystems of one of the bioreactor systems (LC 6) are presented in Figs. 5 and 6. Only one set of responses is presented, since replication was excellent. For each column the effluent pH response was generally flat, fluctuating slightly around pH 7. No obvious relationship between effluent pH and any other system variable was evident, although it would be expected that effluent TIC values would be strongly dependent on effluent pH; as pH decreases, soluble inorganic carbon (carbonate, bicarbonate, etc.) is converted to inorganic carbon dioxide and volatilized. It is significant that the effluent pH was near natural, which is generally an optimum pH for microbial growth. This correlates well with the effluent TIC and TOC responses for each column, which also suggest the existence of healthy microbial communities in each anaerobic and aerobic column. The lack of fluctuations in effluent pH also suggests that the columns were adequately buffered.

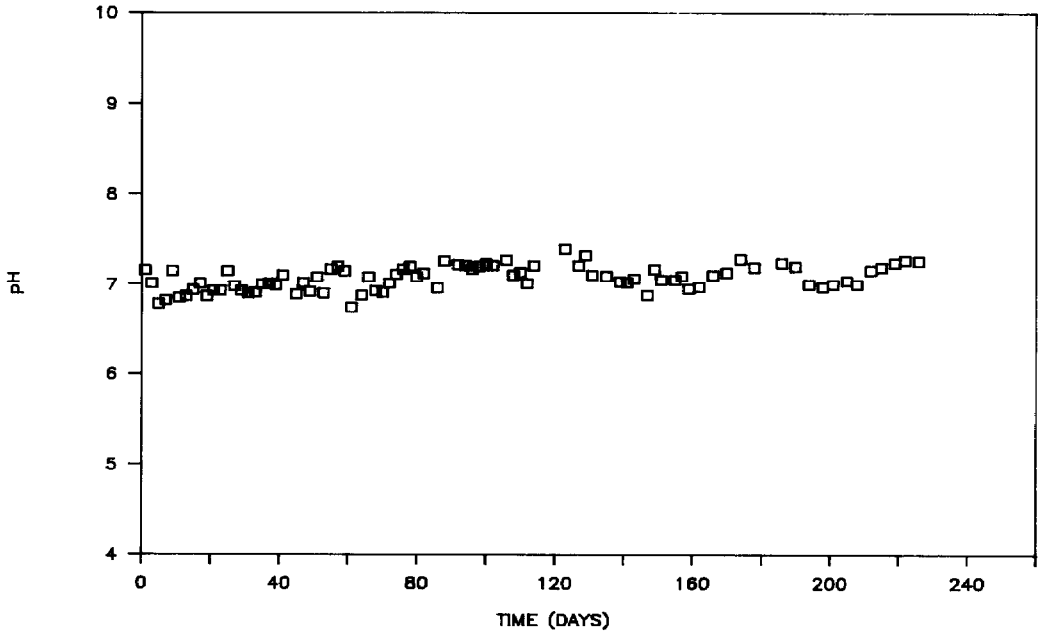

Fig. 5. Effluent pH, LC 6 - anaerobic column.

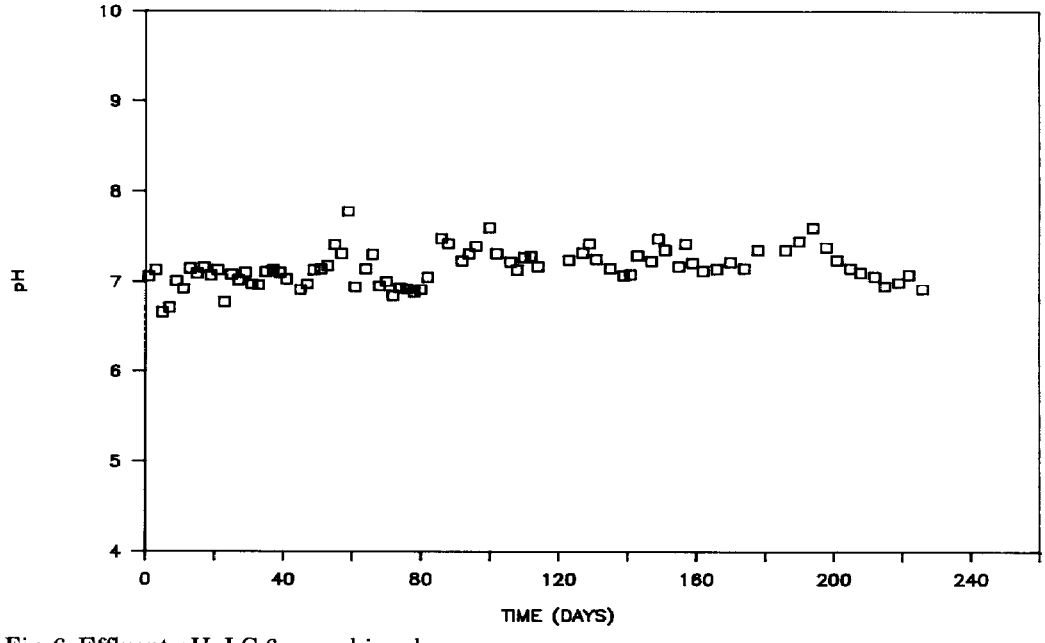

Fig. 6. Effluent pH, LC 6 - aerobic column.

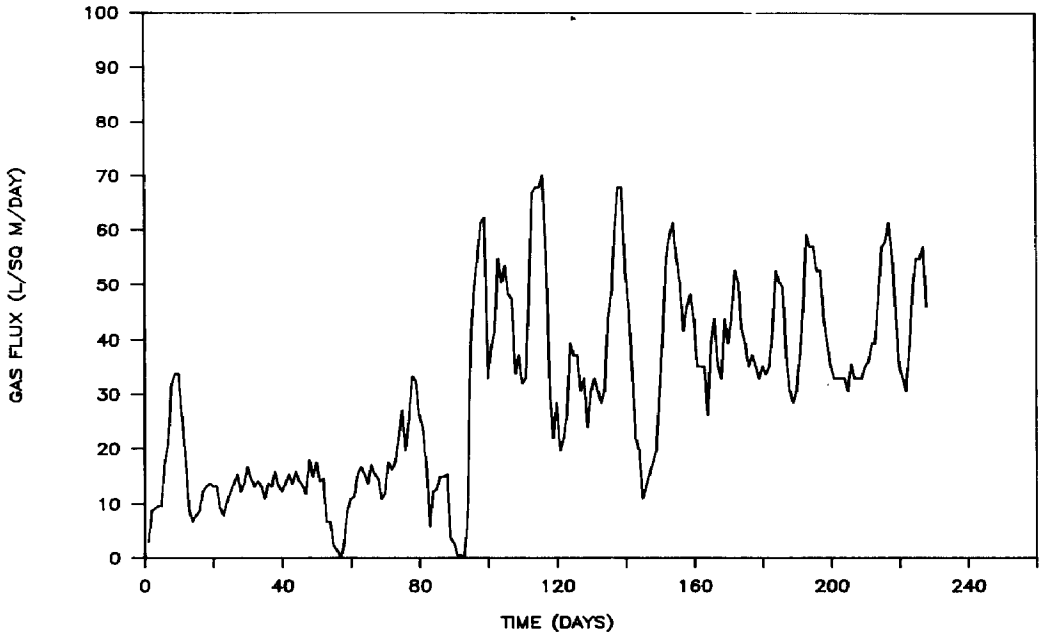

Fig. 7. Gas flux, LC 6 – anaerobic column (5-day moving average).

Biological gas production and composition

Steady-state (Days 150–225) mean gas fluxes and mean molar percent composition data for each anaerobic and aerobic subsystem are compiled in Table 2. Gas flux data as a 5-day moving mean, and molar percent compositions data for the anaerobic and aerobic subsystems of one of the bioreactor systems (LC 6) are presented in Figures 7–8, and 9–10, respectively. Replication was generally excellent.

Gas fluxes from all of the columns were lower than expected and very erratic during the first 100 days of the experiment. Also, up to this point methane collection from the anaerobic columns was low. At this time, it was discovered that the gas collection systems had minute leaks. These leaks were not large enough to preclude gas collection entirely, but it appears that identification and quantification of gases produced was significantly impaired. The leaks were repaired by applying silicone cement to all leaking connections. After these repairs, gas fluxes increased significantly and fluctuations decreased somewhat, for all of the columns. Also, measurement of methane production from the anaerobic columns increased dramatically, probably due to an actual increase in methane produced coupled with elimination of methane losses from the gas collection systems.

In general, gas fluxes from the aerobic columns were much higher than from the anaerobic columns. This was expected, considering oxygen gas was added

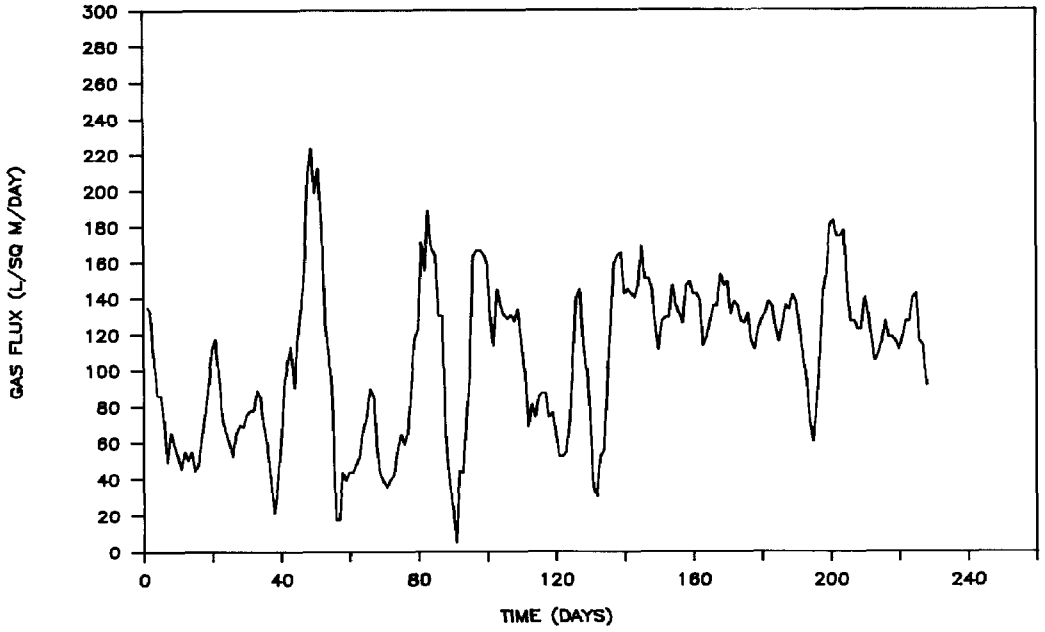

Fig. 8. Gas flux LC 6 – aerobic column (5-day moving average).

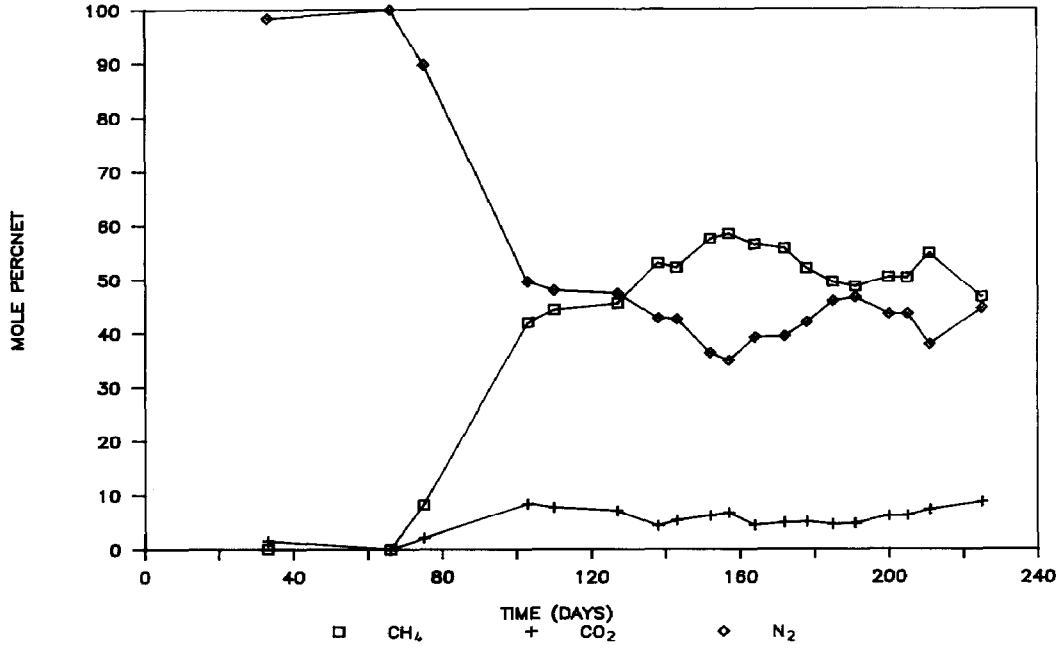

Fig. 9. Gas composition, LC 6 – anaerobic column.

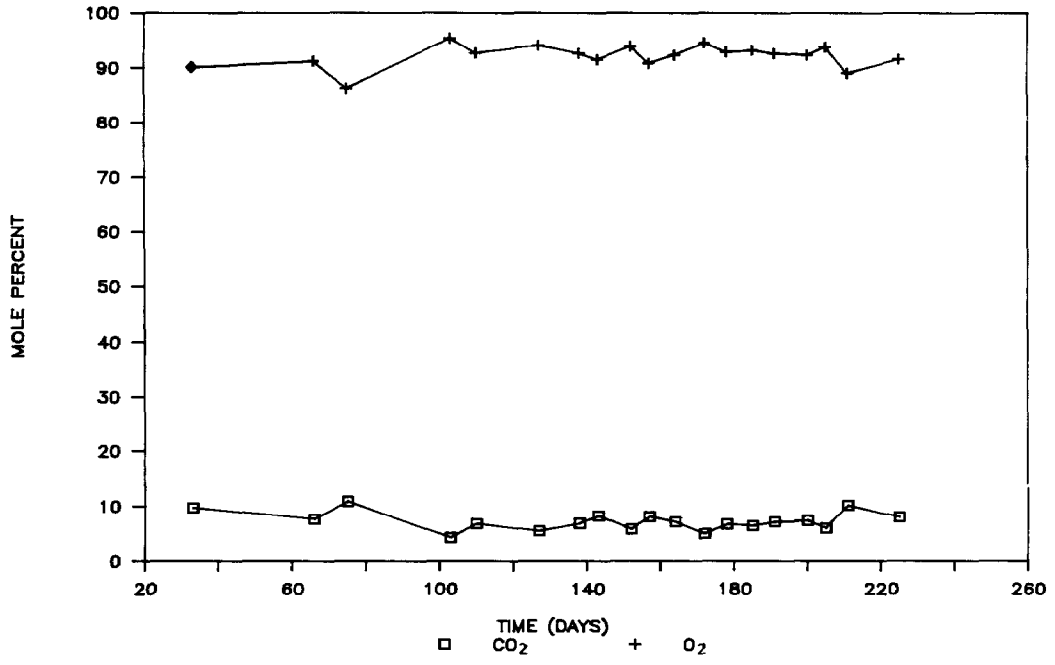

Fig. 10. Gas composition, LC 6 – aerobic column.

to the aerobic columns daily, in excess of saturation levels. As such, oxygen constituted a large mole percentage of the gas collected from the aerobic columns. At steady-state, oxygen comprised between 90 and 95 mol% of the total gas collected; the balance was carbon dioxide, with trace amounts of methane. The amount of carbon dioxide produced was significant, indicating substantial microbial activity in the aerobic columns. It was likely that carbon dioxide entered the gas phase, as a result of the liquid phase being saturated with soluble inorganic carbon (TIC), given the particular effluent pH, and the high levels of total dissolved solids.

At steady-state, methane and nitrogen comprised most of the gas collected from the anaerobic columns; hydrogen was below detection level. A small amount of carbon dioxide gas was collected, also; once again, it was likely that inorganic carbon, as carbon dioxide, entered the gas phase as a result of the liquid phase being saturated with TIC. The production of methane and nitrogen indicated the presence of substantial methanogenic and denitrifying populations in the anaerobic columns. The production of liquid and gas phase inorganic carbon (TIC and CO_2) indicated a substantial amount of fermentation occurring. These data correlate well with the data showing large amounts of organic carbon biodegraded in the anaerobic columns. Methanogenesis followed denitrification after a lag of 60–70 days; stable, slightly rising pH indicated rapid conversion of volatile fatty acids produced by acetogenic organisms.

Carbon balances

Steady-state (Days 150–225) carbon mass balances were computed for each anaerobic and aerobic subsystem, and for each combined bioreactor system. This was done to investigate the accuracy of experimental liquid and gas phase measurements and to test the integrity of the experimental design.

The steady-state mass balance states that the sum of the mass of carbon entering the system (column) must equal the sum of the mass of carbon leaving the system. At steady-state, carbon accumulation terms, including aspiration, liquid hold-up and bioaccumulation, were assumed to be zero. The mass of carbon entering the system includes the sum of the liquid-phase inorganic carbon (TIC) and the sum of the liquid-phase organic carbon (TOC). The sum of the carbon leaving the system also includes the sum of the liquid-phase TIC and TOC as well as the sum of he gas-phase carbon dioxide and methane. Volatile organic carbon was not included in this balance due to analytical limitations; this should not significantly affect the carbon balances since volatile organic carbon accounts for less than 10% of the TOC in the leachate. These sums were computed for each anaerobic and aerobic system over the 75 day steady-state period selected. Then, for each subsystem the percent difference between sums of influent and effluent carbon was computed by subtracting the sum of the influent carbon from the sum of the effluent carbon and dividing the difference by the sum of the influent carbon. Carbon sum data and percent differences are presented in Table 3.

The percent difference data indicate that overall steady-state carbon mass balances can be computed with a reasonable degree of accuracy (less than 20% error in all cases) for the anaerobic and aerobic bioreactors. In all cases the sum of the effluent carbon was less than the sum of the influent carbon. There are two likely sources of error to account for this difference.

The first is that system carbon losses were much more likely from the gas

TABLE 3

Summary of steady-state carbon mass balance data (values in grams)

Sums	LC 5-Soil	LC 5-Sand	LC 6-Soil	LC 6-Sand
Inf. TOC_{liq}	9.68	2.41[a]	10.96	2.36[a]
Inf. TIC_{liq}	2.49	5.14	2.82	5.71
Eff. TOC_{liq}	1.86	1.04	1.61	0.85
Eff. TIC_{liq}	5.14	4.53	5.71	5.01
Eff. CO_2–C_g	0.47	1.24	0.42	1.50
Eff. CH_4–C_g	3.20	0.08	3.44	0.10
Inf. C	12.17	7.55	13.78	8.07
Eff. C	10.67	6.89	11.23	7.46
Difference %	−12.3	−8.65	−18.51	−7.56

[a]Includes 0.75 g carbon added as glucose.

phase; counterdiffusion would result in elevated nitrogen concentrations and reduced carbon dioxide and methane concentrations. This appears to have occurred, as the sum of the mass of nitrogen gas produced exceeded the sum of the mass of available nitrate-nitrogen (including possible conversion of leachate ammonia to nitrate) fed to the anaerobic columns during this steady-state period.

The second possible source of error is the assumption that organic carbon accumulation was negligible during steady-state operation. It is possible that some organic carbon, especially products of cell lysis, was still being incorporated into the humus fraction of the soil packing. It is also possible that bioaccumulation of organic carbon was still occurring if cell growth rates still exceeded cell death rates.

Priority pollutant analyses and mass balances

Volatile organic priority pollutants comprise more than 90% of the total volatile organic carbon (VOC) present in the leachate. Identification and quantification of these compounds at key steps in the biodegradation process is important. To accomplish this, a method employing purge and trap concentration followed by capillary column gas chromatographic separation with FID detection was developed [10].

These compounds were monitored daily for a 26 day period during steady-state operation of the serial bioreactor system, LC 6. Samples of the leachate influent, anaerobic effluent and aerobic effluent were taken for analysis every day during this interval. Results indicated the presence of only trace amounts of toluene and methylene chloride in the anaerobic effluent; the other compounds (benzene, 1,2-dichloroethane and ethylbenzene) were not detected in the anaerobic effluent. The minimum detection limit for each of these compounds was approximately 50 μg/l (ppb). None of the volatile priority pollutants, as anticipated, was ever detected in the aerobic effluent. Daily sampling

TABLE 4

Steady-state volatile species mass balances[a] for the anaerobic column LC 6-soil

Compound of interest	Influent mass (μg)	Effluent mass (μg)	Removal percent
Benzene	1491	310[b]	80
Toluene	12000	431	96
1,2-Dichloroethane	30000	310[b]	99
Ethylbenzene	2000	310[b]	85
Methylene chloride	36000	1592	96

[a]Balances were compiled over a 26 day period during steady-state operation.
[b]These compounds were never detected above the minimum detection limit of 50 μg/l; sample concentrations were assumed to be 50 μg/l in these cases.

TABLE 5

Steady-state priority pollutant levels at selected stages of the treatment process[a]

Priority pollutant	Concentration (μg/l)			
	Leachate[b] influent	Anaerobic[c] effluent	Aerobic[c] effluent	Reverse osmosis permeate[d]
Benzene	2660	15	ND[e]	ND
Toluene	38600	109	ND	ND
1,2 Dichloroethane	58600	ND	ND	ND
Ethylbenzene	1420	ND	ND	ND
Methylene chloride	22000	ND	ND	ND
Bis(2-chloroethyl) ether	26900	8210	3800	23
Phenol	12500	ND	ND	ND

[a]All analyses were performed by a certified commercial lab.
[b]Leachate influent data are an average of three separate analyses from three leachate bottles used during steady-state operation; data do not include losses due to volatilization.
[c]Anaerobic and aerobic effluent samples were taken during steady-state operation of bioreactor LC 6; the anaerobic data are for a single analysis set, while the aerobic data are an average of two separate analyses.
[d]The reverse osmosis permeate was taken while operating in maximum recovery mode.
[e]For the volatile priority pollutants ND means not detected, with minimum detection limits of approximately 10 μg/l; for phenol the minimum detection limit was 1.5 μg/l.

of the leachate influent indicated significant volatilization losses from the PVC feedbag, especially for the aromatic compounds, before the leachate entered the anaerobic column. However, anywhere from 10% to 50% of the volatile organic species still entered the anaerobic system.

Mass balances were computed for each priority pollutant, for the anaerobic subsystem operating at steady-state. The sum of the leachate influent mass, the sum of the anaerobic effluent mass and the mass removal percent are compiled for each compound of interest in Table 4. These balances take into account the wide fluctuations in species concentrations observed for the leachate influent. Results indicated that between 80% and 99% of specific compounds were removed by the anaerobic column. It is possible that volatilization and/or diffusion losses from the anaerobic column accounted for some of this removal. However, losses should have been minimized, since the system was airtight as indicated by steady gas collection, and liquid samples were taken nearly 30 cm below the liquid–gas interface where volatilization would occur. By considering this, it is very likely that anaerobic biodegradation was the primary volatile priority pollutant removal process.

On occasion, samples were taken from specific points in the process during steady-state operation, and from permeate produced from reverse osmosis treatment of the final aerobic effluent. These samples were then submitted to

a certified laboratory for a full priority pollutant analysis, including volatile and non-volatile compounds. A summary of samples submitted and results obtained is presented in Table 5.

For the volatile organic priority pollutants, the results were generally in agreement with internal laboratory results. Only trace levels of toluene and benzene were detected in the anaerobic effluent; none of the other compounds were detected. None of the volatile compounds was detected in the aerobic effluent. Finally, no volatile compounds were detected in permeate from reverse osmosis treatment of the aerobic effluent. The concentrations of volatile species in the leachate reflect levels before volatilization losses from the PVC feedbags occurred.

The major non-volatile priority pollutant compounds of interest were bis(2-chloroethyl)ether and phenol. Internal laboratory analyses of these compounds were not performed due to analytical limitations. Results from commercial laboratory analyses indicated significant removal of bis(2-chloroethyl)ether by both the anaerobic and aerobic subsystems during steady-state operation. Combined bioreactor system removals were near 90%. All of the phenol present in the leachate was removed by the anaerobic columns operating at steady-state. Considering the much lower volatilities of these compounds, volatilization losses should not account for a significant percentage of removal of these species.

Reverse osmosis post-treatment

The reverse osmosis treatment system employed a proprietary thin-film composite membrane, consisting of a polyester coating with a polyester substrate support, combined with a cross-linked aromatic polyamide membrane, mounted in a plate and frame unit. It was operated in a maximum recovery mode with a mean flux of 13.72 l/(m^2 h). Total dissolved solids (TDS) percent rejection was 99% and TOC percent rejection was 92%; permeate TDS levels were less than 100 mg/l, and permeate TOC levels were approximately 5 mg/l. The reverse osmosis system also removed most of the bis(2-chloroethyl)ether remaining after anaerobic/aerobic microbial treatment. These data indicate that reverse osmosis is an attractive post-treatment process. The design and operation of the reverse osmosis unit are detailed in another publication [11].

Conclusions

Sequential anaerobic/aerobic packed bed microbial treatment is a viable process for renovation of leachate from a high priority Superfund site. Leachate pretreatment, involving pH adjustment to precipitate iron species, significantly improved hydraulic fluxes through the bioreactors, substantially increasing TOC mass removal rates. The serial anaerobic/aerobic bioreactors removed in excess of 90% of the leachate TOC at steady-state. Substantial

percentages of both volatile and non-volatile priority pollutants were also removed at steady-state. Identification and quantification of aqueous and gas phase inorganic and organic species allowed computation of mass balances for the anaerobic and aerobic subsystems. Reverse osmosis is an attractive post-treatment process, eliminating 99% of the TDS and 92% of the TOC remaining after microbial treatment.

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