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Biodegradability of Municipal Solid Waste Components in Laboratory-Scale Landfills

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The objective of this research was to characterize the anaerobic biodegradability of municipal refuse components by measuring methane yields, the extent of cellulose and hemicellulose decomposition, and leachate toxicity. Tests were conducted in quadruplicate in 2-L reactors operated to obtain maximum yields. Measured methane yields for grass, leaves, branches, food waste, coated paper, old newsprint, old corrugated containers, and office paper were 144.4, 30.6, 62.6, 300.7, 84.4, 74.3, 152.3, and 217.3 mL of CH_4/dry g, respectively. Although, as a general trend, the methane yield increased as the cellulose plus hemicellulose content increased, confounding factors precluded establishing a quantitative relationship. Similarly, the degree of lignification of a particular component was not a good predictor of the extent of biodegradation. With the exception of food waste, leachate from the decomposition of refuse components was not toxic as measured by using an anaerobic toxicity assay.

Introduction

Approximately 62% of the municipal solid waste (refuse) generated in the United States is disposed of by burial in a sanitary landfill (*1*). Methane production from sanitary landfills is well documented (*2, 3*) as is the decomposition of cellulose, the principal biodegradable component of refuse (*4*). Although methane production is well established, there is little information on the biodegradability of individual refuse components and how methane production from landfills might change as the composition of buried waste changes.

Both methane and carbon dioxide are greenhouse gases that contribute to global climate change (*5*). Methane traps about 20 times more infrared energy than carbon dioxide (*5*). Thus, data on the amount of methane that can be expected from refuse already buried as well as methane that will result from the decomposition of refuse buried in the future are needed to better assess the impact of landfills on global climate change. These data are also required to evaluate the effect of various solid waste management strategies on methane production.

The objective of this research was to characterize the anaerobic biodegradability of refuse components by measuring methane yields, the extent of cellulose and hemicellulose decomposition, and leachate toxicity. Although, as a general trend, the methane yield increased as the cellulose plus hemicellulose (carbohydrate) content increased, many confounding factors precluded establishing a quantitative relationship. The degree of lignification of a particular component was not a good predictor of the extent of biodegradation, and there was no evidence for leachate toxicity associated with the decomposition of any component except food waste.

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Experimental Methods

Experimental Design. The components selected for study were the major biodegradable components of refuse (*1*) and included grass (G), leaves (L), branches (B), food waste (F), coated paper (CP), old newsprint (ONP), old corrugated containers (OCC), and office paper (OFF) as well as mixed residential refuse (MSW). Experiments were conducted in quadruplicate in 2-L reactors except for grass. For grass, two more reactors with a second grass sample (G-2) were also monitored. A seed of well-decomposed refuse, henceforth referred to as the seed, was used to initiate the decomposition of each component except MSW. Seed made up 30% by volume of each reactor except for the food reactors in which tests were conducted with 70% seed because initial tests with 30% seed were not successful (*6*). Four control reactors containing seed only (S) were used to measure background methane production. Two additional control reactors (S-2) were initiated with the food reactors that were set up after the other component reactors. Control reactors were operated until all test reactors had been dismantled.

Coated paper, old newsprint, old corrugated containers, and office paper represent 4.2, 6.6, 12.2, and 3.3% of municipal refuse as generated (*1*). Newsprint is a mechanical pulp that contains all of the initial lignin while office paper is a chemical pulp in which most of the lignin has been removed. Corrugated containers and coated paper contain both mechanical and chemical pulp, and coated paper contains a clay coating to provide a smooth, glossy finish. Lignin is at best only slowly degradable under anaerobic conditions and physically surrounds some of the cellulose in refuse components derived from biomass (*7*−*10*). Thus, the papers selected for testing should represent the range of biodegradabilities associated with different types of paper. In addition, these four papers represent the four highest categories of paper discarded (*1*).

Experiments were designed to measure the ultimate methane yield of each component tested under conditions designed to simulate enhanced decomposition in a landfill. This included shredding most components (see following section), seeding, incubation at about 40 °C, and leachate recycle and neutralization. In addition, phosphate and ammonia concentrations were maintained above 5 mg of P/L and 100 mg of N/L, respectively, to minimize the potential for nutrient availability to limit biodegradation. All reactors were monitored until they were no longer producing measurable methane, except the old corrugated container reactors in which the methane yield increased by less than 2% over the final 80 days of monitoring.

Materials. In each case, our objective was to obtain components as they would be discarded prior to contamination with other refuse components. The first grass sample was obtained from a compost facility in Orlando, FL, as grass was not growing in North Carolina during January when this experiment was initiated. The grass was shipped to our laboratory by overnight courier where it was stored at 4 °C for 4 days prior to use. Later, a second grass sample was obtained from a compost facility in Raleigh, NC, for immediate use. Leaves were collected from a compost facility in Raleigh, NC, and stored at 4 °C for 24 days prior to use. Branches less

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TABLE 1. Methane Yield and Initial and Final Solids Composition Data[a]

reactor series	yield (mL of CH_4/ dry g)	cellulose (%)	hemi-cellulose (%)	lignin (%)	volatile solids	MC[b]	MH[b]	ML[b]	methane potential recovery[c]	extent of decom-position[d]	chl/vs[e]
seed	25.5	23.4	4.7	22.5	48.2	0.18	0.36	0.83	43.4 (47.3)	21.8	1.05
SD	5.7					0.02	0.03	0.07	3.5		
seed-2	5.8	18.3	3.7	22.1	42.4	0.34	0.69	0.85	46.6 (49.6)	6.3	1.05
SD	0.6					0.01	0.11	0.01	1.8		
grass	144.4	26.5	10.2	28.4	85.0	0.19	0.42	0.78	89.3 (93.1)	94.3	0.77
SD	15.5					0.01	0.06	0.07	5.5		
grass-2	127.6	25.6	14.8	21.6	87.8	nm[f]	nm	nm	nm	75.5	0.71
SD	21.8										
leaves	30.6[g]	15.3	10.5	43.8	90.2	0.43	0.68	0.90	75.2 (77.7)[g]	28.3[g]	0.77
SD	8.6					0.05	0.10	0.10	5.5		
branch	62.6[g]	35.4	18.4	32.6	96.6	0.52	0.59	0.93	82.8 (85.0)[g]	27.8[g]	0.89
SD	13.3					0.05	0.02	0.08	4.2		
food	300.7	55.4	7.2	11.4	93.8	0.24	0.58	0.80	77.4 (80.7)	84.1	0.99[h]
SD	10.6					0.02	0.04	0.07	4.2		
coated paper	84.4	42.3	9.4	15	74.3	0.54	0.58	1.03	83.7 (85.4)	39.2	0.90
SD	8.1					0.01	0.06	0.03	2.5		
old newsprint	74.33	48.5	9	23.9	98.5	0.73	0.46	0.99	98.0 (99.2)	31.1	0.83
SD	6.8					0.05	0.06	0.06	3.0		
old corrugated containers	152.3	57.3	9.9	20.8	98.2	0.36	0.38	0.93	87.7 (90.9)	54.4	0.90
SD	6.7					0.01	0.01	0.00	1.2		
office paper	217.3	87.4	8.4	2.3	98.6	0.02	0.09	0.95	55.5 (60.3)	54.6	0.99
SD	15.0					0	0.01	0.18	3.5		
MSW	92.0	28.8	9.0	23.1	75.2	0.25	0.22	0.95	87.9 (91.8)	58.4	0.81
SD	4.1					0.03	0.05	0.02	3.2		

[a] Data represent the average for each reactor set. Standard deviations (SD) are presented below the average where data are the average of all reactors in a set. [b] The ratio of the cellulose (MC), hemicellulose (MH), or lignin (ML) recovered from a reactor divided by the initial mass. [c] The methane potential of the cellulose and hemicellulose removed from a reactor plus the measured methane plus the COD of the leachate at reactor takedown; all divided by the methane potential of the cellulose plus hemicellulose added to a reactor initially. The value in parentheses assumes conversion of 5% of the degraded carbohydrates to cell mass. [d] The extent of decomposition is the measured methane yield divided by the yield calculated assuming conversion of 100% of the cellulose and hemicellulose (and protein in the case of food waste) to methane and carbon dioxide. [e] The ratio of the sum of the cellulose, hemicellulose, and lignin concentrations to the volatile solids concentration. [f] nm, not measured. [g] Data exclude L2 and B4. [h] The ratio includes protein.

than 5 cm in diameter were collected from the North Carolina State University (NCSU) compost facility and stored at 4 °C for 16 days prior to use. Food waste was collected by individual graduate students from their houses for the 1-week period prior to initiation of the experiment. This food waste was refrigerated in plastic containers during the week of collection. Coated paper was collected from the Cary, NC, recycling center. Old newsprint was collected from the NCSU library and represented about 50 different newspapers to minimize the influence of different sources of pulp. Old corrugated containers and office paper were collected from the NCSU recycling center. The office paper consisted primarily of used standard white copy paper. MSW was collected in residential areas of Raleigh, NC, as described previously (*11*). The seed was excavated from a landfill known to be in an active state of methane production as described previously (*6*).

Except for grass and coated paper, all components were shredded with a slow-speed, high-torque shredder (Shredpax AZ-7H) to obtain a uniform sample size no greater than about 2 cm wide by 5 cm long. Grass was not shredded because it was already well mixed. Coated paper was not shredded because of concern that the shredded edges of the paper would allow access to uncoated parts of the paper that might be more bioavailable. Instead, magazines were opened, and the center two pages were used in the reactors.

Experimental Equipment, Reactor Operation, and Analytical Methods. The reactor system, including the 2-L reactors, leachate collection and recycling apparatus, and gas collection bag, has been described previously (*11*). Sufficient deionized water was added to each reactor initially to ensure production of about 800 mL of leachate. Additional deionized water was added when the volume of leachate decreased below 500 mL due to sample removal. Leachate was neutralized 6 days/week until the pH stabilized at or slightly above 7. It was recycled 6 days/week throughout the monitoring period. NH_3-N and PO_4-P concentrations were monitored semimonthly, and concentrations were adjusted as necessary to the aforementioned target levels. Reactors were leak-checked monthly by using a water displacement technique, although it was not possible to check the connection between the gas bag and the tubing from the reactor. The methods employed for analysis of gas concentrations and volume, leachate COD and volatile fatty acids (VFAs), cellulose, hemicellulose, and lignin have been presented previously (*6*). NH_3-N and PO_4-P were measured with an autoanalyzer by using the salicylate and molybdate methods, respectively (Lachat Instruments). Metals were analyzed by inductively coupled argon plasma spectroscopy.

Gas volumes were corrected to dry gas at 0 °C and 1 atm (STP). The methane yield attributable to each component was determined by subtracting the methane attributable to the seed from the total methane produced in a reactor. A mass balance was performed on each reactor to provide information on the extent to which cellulose and hemicellulose were converted to methane. The mass balance was performed on the theoretical methane potential added to and recovered from each reactor as described previously (*6*).

Leachate Toxicity. Anaerobic toxicity assays (ATAs) were conducted on the leachate from each reactor 3−4 times during the monitoring period. ATAs were conducted on neutralized leachate (pH 7) to evaluate whether factors other than pH were responsible for leachate toxicity. The ATA procedure has been described previously (*6*).

Results

The methane production rate and yield for each component tested are presented in Figure 1 and Table 1, respectively. The average pH for each reactor set is presented in Figure 2. Methane production rates for the control reactors (S, S-2) are

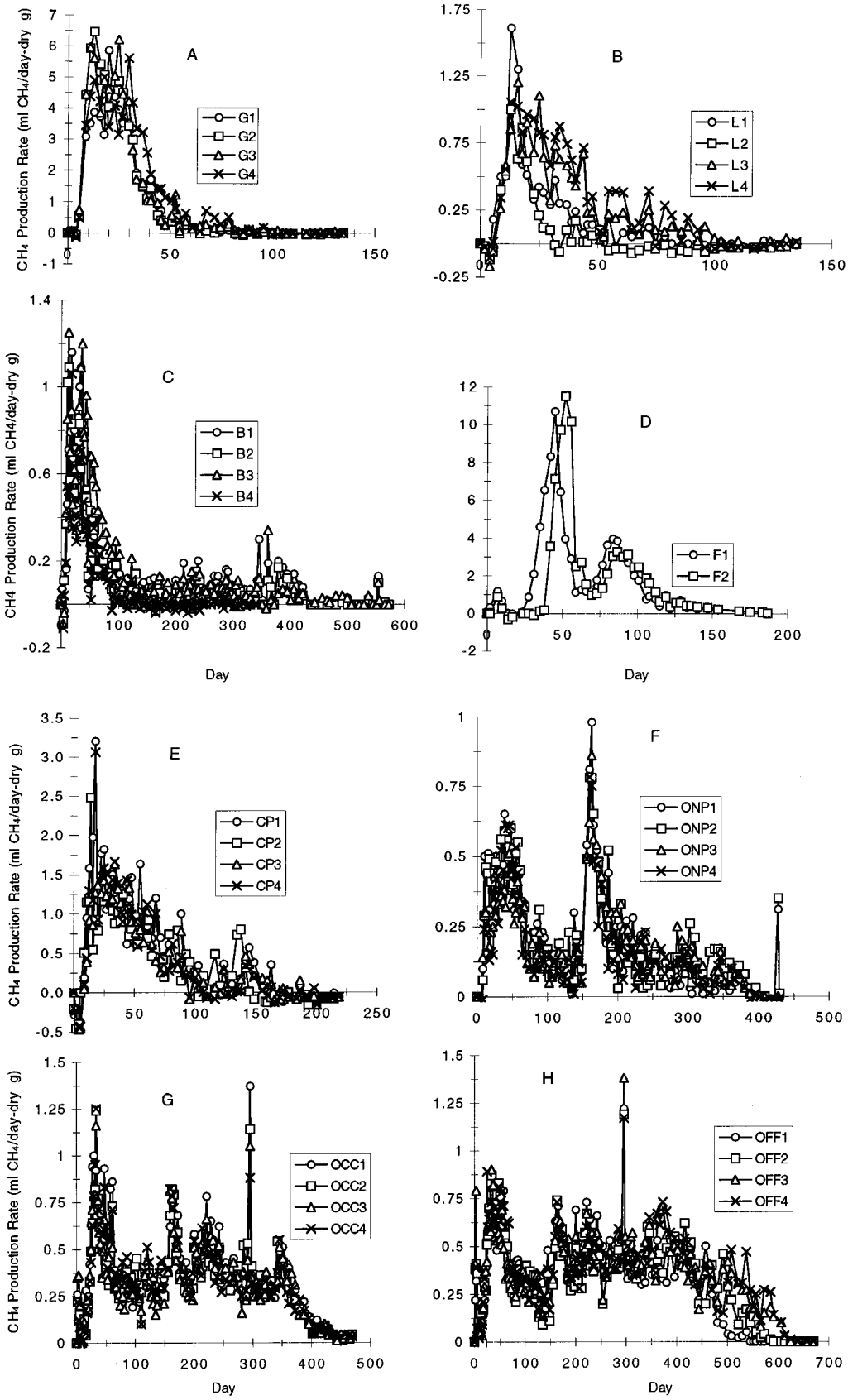

FIGURE 1. Methane production rate for each refuse component.

not presented because they followed the same trend as the component reactors but exhibited relatively low methane production rates. All component rate and yield data have been corrected for methane production attributable to the seed. In some cases, a negative methane production rate is reported. This suggests that less methane was produced in a component reactor relative to the amount of methane that could be expected from the seed. This generally occurred at the initiation of the experiment and once methane production in a reactor was no longer measurable. Reported methane yields do not include "negative methane production" from the end of an experiment.

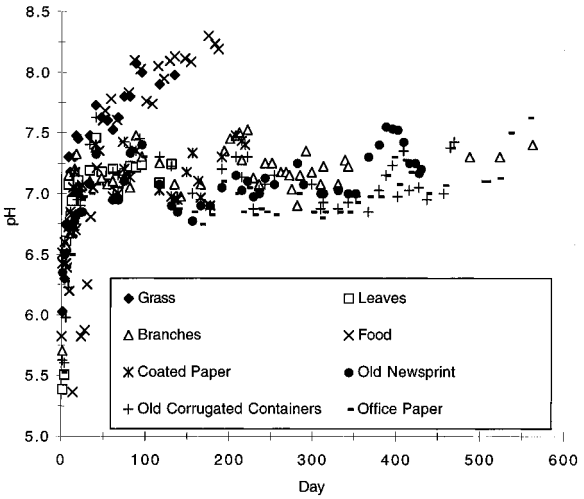

FIGURE 2. Average pH during decomposition of each refuse component

The refuse used to fill the control reactors was excavated at the same time, but that used to fill the S-2 reactors was stored in a drum for over 100 additional days. This accounts for the lower yield in these reactors and is consistent with the lower initial carbohydrate concentration of the refuse added to the S-2 reactors (Table 1).

There was no significant difference in methane yield ($P = 0.95$) between the two sets of grass reactors (Table 1), and the rate trend exhibited by the G-2 reactors was similar to that of the G reactors (G-2 data not shown). Leachate neutralization was not required after the first week in either set of grass reactors, and the pH increased rapidly to 7.5−8. In the grass reactors, the average leachate COD decreased from 7080 (day 15) to 1680 mg/L at reactor dismantling (day 135). COD concentrations at the last seven sampling points (days 40−135) were nearly constant, suggesting that the remaining COD represented recalcitrant carbon (data not shown). Similar trends were measured in the G-2 reactors, although the final COD was considerably higher (4920 mg/L). Eighty-one percent and 58% of the initial cellulose and hemicellulose, respectively, were degraded by the end of the 135-day monitoring period in the grass reactors, and the average methane potential mass balance recovery was 89.3% (Table 1). Final solids analyses and mass balances were not conducted on the G-2 reactors. Although cellulose concentrations were similar between the two sets of grass reactors, lignin concentrations were more variable (Table 1). There is no apparent explanation for the higher extent of decomposition for the grass reactors relative to G-2.

The methane production rate and yield in the leaf reactors are presented in Figure 1B and Table 1, respectively. Leachate neutralization was not required after day 12, and the pH increased rapidly to 7−7.5. Average leachate COD decreased from 3100 (day 15) to 1165 mg/L at reactor dismantling (day 135), and the COD was nearly constant after day 105 (data not shown). Fifty-eight percent and 32% of the initial cellulose and hemicellulose, respectively, were degraded by the end of the 135-day monitoring period, and the average methane potential mass balance recovery was 82.8%. Several lines of evidence suggest gas leakage in reactor L2: (1) positive or net methane production was only measured for 53 days; (2) its methane yield (11.9 mL/dry g) was substantially below that of the other leaf reactors (21.4 to 38.4); and (3) cellulose and hemicellulose decomposition were similar in all leaf reactors. Thus, L2 was excluded from the average yield and methane potential recovery (Table 1).

The methane production rate and yield in the branch reactors are presented in Figure 1C and Table 1, respectively. Leachate neutralization was not required after day 16, and the pH increased rapidly to 7−7.5. The leachate COD decreased slightly from initial values of 350−600 to 200 mg/L by day 350. The COD was nearly constant after day 200 (data not shown). Forty-eight percent and 41% of the initial cellulose and hemicellulose, respectively, were degraded by the end of the 573-day monitoring period, and the average methane potential mass balance recovery was 82.8%. As in the case of L2, similar evidence suggested gas leakage in reactor B4: (1) there was no methane production in reactor B4 after day 343 but B1−B3 produced methane for considerably longer; (2) the methane yield in B4 (26.1 mL/dry g) was substantially below that of B1−B3 (47.4 to 71.9); and (3) cellulose and hemicellulose decomposition were similar in all branch reactors. Thus, B4 was excluded from the average yield and methane potential recovery (Table 1).

Methane production, leachate pH, carboxylic acid concentrations, and solids decomposition data for the food waste reactors have been presented elsewhere (*6*), and key data are summarized in Figure 1D and Table 1. Reactors F3 and F4 leaked, and their methane production rates are not reported.

The methane production rate and yield in the coated paper reactors are presented in Figure 1E and Table 1, respectively. Leachate neutralization was not required after day 12 in these reactors, and the pH remained between 6.8 and 7.5 throughout the experiment. Average leachate COD decreased from 1969 (day 10) to 300−400 mg/L by day 120, after which it remained constant. Forty-six percent and 42% of the initial cellulose and hemicellulose, respectively, were degraded by the end of the 219-day monitoring period, and the average methane potential mass balance recovery was 83.7%.

The methane production rate and yield in the old newsprint reactors are presented in Figure 1F and Table 1, respectively. Methane production was near zero in these reactors after day 388. To verify that substrate availability, as opposed to toxicity or a nutrient limitation, was limiting methane production, cellobiose was added to ONP1 and ONP2 on day 425. Cellobiose recovery as methane was 103% and 96% in ONP1 and ONP2, respectively. The increase in methane production rates at the end of the experiment for ONP1 and ONP2 (Figure 1F) was a result of the cellobiose addition, and this methane was not included in the reported yield. These results confirmed that substrate availability was limiting methane production and that there was not an accumulation of an inhibitory byproduct. Leachate neutralization was not required after day 16, and the pH remained between 6.8 and 7.5. On a few occasions, the leachate pH exceeded 7.5, and there was some concern that the pH was too high for optimal methane production. However, pH neutralization with phosphoric acid had no discernible effect on methane production. Average leachate COD decreased from 1744 (day 9) to 300−430 mg/L by day 62, after which it remained constant (data not shown). Twenty-seven percent and 54% of the initial cellulose and hemicellulose, respectively, were degraded by the end of the 430-day monitoring period, and the average methane potential mass balance recovery was 98.0%.

The methane production rate and yield in the old corrugated container reactors are presented in Figure 1G and Table 1, respectively. Leachate neutralization was not required after day 23, and the pH generally remained between 6.8 and 7.5. As for the old newsprint reactors, the leachate pH occasionally increased above 7.5, and neutralization with phosphoric acid had no effect on methane production. Average leachate COD decreased from 8613 (day 11) to 704 mg/L by day 123, after which it remained between 480 and 872 mg/L. Sixty-four percent and 62% of the initial cellulose and hemicellulose, respectively, were degraded by the end of the 470-day monitoring period, and the average methane potential mass balance recovery was 87.7%.

The methane production rate and yield in the office paper reactors are presented in Figure 1H and Table 1, respectively.

Leachate neutralization was not required after day 23, and the pH remained between 6.8 and 7.5. Average leachate COD decreased from 8767 (day 11) to 500 mg/L by day 123, after which it remained nearly constant. Ninety-eight percent and 86% of the initial cellulose and hemicellulose, respectively, were degraded by the end of the 671-day monitoring period. The average methane potential mass balance recovery was only 55.5%. The measured yield in the individual office paper reactors was similar [coefficient of variation (CV) = 6.9%], and repeated checks of all components of the mass balance did not uncover any identifiable errors. Thus, the data do not suggest gas leakage.

Data on MSW decomposition are summarized in Table 1. MSW decomposition has been described in a number of previous studies, and the behavior of the MSW used here was similar to previous reports (*11*, *12*).

Leachate Toxicity. With the exception of food waste, there was no evidence for toxicity from the leachate associated with the decomposition of any waste component (data not shown, *13*). The results of the food waste leachate toxicity assays are presented elsewhere (*6*). Concentrations of Cr, Zn, Cu, Cd, and Pb were always well below 1 mg/L (*13*). These concentrations are well below concentrations that have been reported as inhibitory in refuse and other anaerobic systems (*14*−*17*).

Discussion

Trends in Methane Production Rate. In this section, trends in leachate composition and the methane production rate among the components tested are compared to the behavior previously reported for MSW and to each other. The high COD and C2−C7 VFA concentrations (*13*, data not shown) and the low pHs in each reactor at the beginning of the experiment are indicative of an imbalance between hydrolytic and fermentative behavior and acetogenic and methanogenic activity. Leachate was neutralized to stimulate the activity of the acetogenic and methanogenic bacteria, which convert fermentation intermediates (primarily VFAs) to methane and carbon dioxide. Because there was a population of acclimated bacteria on the seed, as soon as environmental conditions (pH) became tolerable, there was a rapid increase in the rate of methane production with a concurrent decrease in COD and VFAs. The rate of methane production then decreased as soluble substrates were depleted, and methane production became dependent upon carbohydrate hydrolysis.

The yard waste (grass, branches, leaves) and coated paper reactors all exhibited a classical peak in methane production followed by an asymptotic decline. In contrast, the food, old newsprint, old corrugated containers, and office paper reactors exhibited variations on this trend. Two or three maxima in the methane production rate were measured for these reactors, and the office paper reactors exhibited about 300 days of nearly constant methane production. The occurrence of more than one maximum in methane production rate can be explained by the presence of multiple substrates within a refuse component. For example, food waste contains a number of substrates, and some are likely more degradable than others. Another possibility is that as the solid matrix of each component changes because of biodegradation, additional cellulose becomes bioavailable. The long period of constant methane production in the office paper reactors may be due to the near uniform composition of office paper, which is nearly pure cellulose and hemicellulose with little lignin (Table 1).

Relationship between Solids Composition, Methane Production, and Biodegradability. There was substantial variation in the range of methane yields (30.6−300.7 mL/dry g) and the extent of decomposition (28−94%) among the components tested (Table 1). In previous research with mixed refuse, carbohydrates accounted for 91% of the stoichiometric methane potential (*18*). Carbohydrates were the major

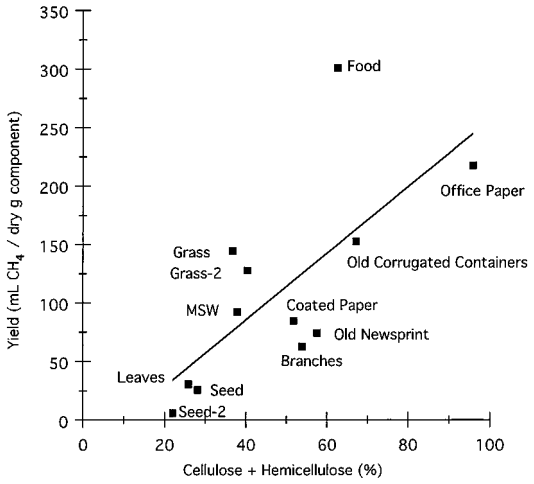

FIGURE 3. Methane yield vs carbohydrate concentration.

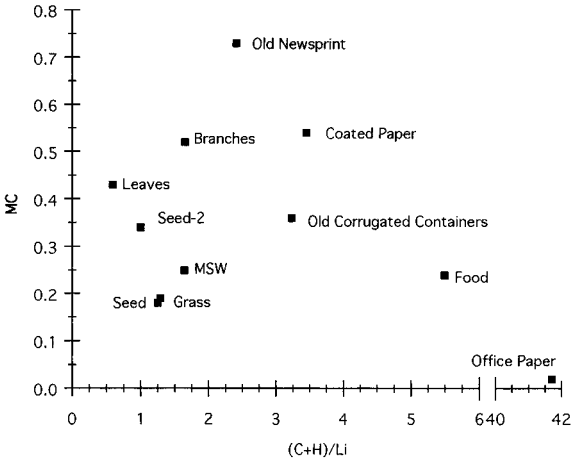

FIGURE 4. Cellulose decomposition vs degree of lignification.

organic compounds analyzed in the waste components tested here, and the relationship between carbohydrate concentration and methane yield is presented in Figure 3. The relatively weak linear relationship ($r^2 = 0.49$) and failure of the regression line to pass through zero suggest that factors in addition to carbohydrate concentration influence methane yield.

As described above, lignin decreases carbohydrate bioavailability and thus would be expected to confound the relationship presented in Figure 3. The components with the lowest yields are the two sets of control reactors and leaves. These are also the components with the lowest carbohydrate to lignin [(C + H)/Li] ratio. The (C + H)/Li ratio is a measure of the degree of lignification. Values of 3−4 have been reported for fresh refuse, and lower values are associated with decomposed refuse (*4*).

There is a general trend of more extensive cellulose biodegradation (MC decreasing) in the less lignified substrates [(C + H)/Li increasing], e.g., food and office paper (Figure 4). However, the quantitative relationship is weak ($r^2 = 0.28$) because office paper has a (C + H)/Li ratio well above any of the other components tested. The trend toward increased cellulose loss with a decreasing degree of lignification is most definite among the four paper components.

There is not a linear relationship between (C + H)/Li and the extent of decomposition (plot not shown, $r^2 = 0.02$). However, it is interesting to note that grass, which is highly lignified, underwent nearly complete decomposition as measured by either MC or the extent of decomposition (Table 1). This suggests that the lignin concentration does not always reflect the degree to which lignin inhibits cellulose bioavailability. Apparently, the lignin in grass is not as restrictive to

microorganisms as the lignin in other components such as branches. This result is consistent with a report by Akin et al. (*19*), who stated that "The chemistry of grass lignocellulose varies considerably from that of wood".

The solids decomposition (MC and MH) and methane yield data document the biodegradability of even the most lignified substrates, leaves and branches, as well as all other refuse components tested. The biodegradation of newsprint measured here contrasts with reports on the excavation of readable newsprint that had been buried in landfills decades earlier (*20*). The reported data do not represent average values but rather observations during an archaeological excavation. The presence of readable newsprint that had not undergone biodegradation may be due to its isolation from other factors required for biodegradation such as bacteria, moisture, and nutrients.

Analysis of Uncertainty in Methane Yield and Methane Potential Recovery. The objective of this section is to evaluate sources of error in the methane yields and mass balances summarized in Table 1. There are a number of potential sources of error in the methane potential mass balances, including (1) the anaerobic biodegradation of organics other than cellulose or hemicellulose, (2) non-methanogenic biodegradation, and (3) carbon converted to cell mass.

The conversion of organics other than cellulose or hemicellulose to methane would inflate the reported methane potential recoveries. The potential significance of non-carbohydrate conversion to methane was evaluated by inspecting the ratio of the sum of the cellulose, hemicellulose, and lignin concentrations to the volatile solids concentration (CHL/VS, Table 1). If cellulose, hemicellulose, and lignin were the only organics present in a component, then this ratio would be 1.0. Although starch was not measured directly, starch present in any component would have been measured as cellulose by using the analytical technique employed here. In the case of food waste, the ratio includes protein.

The CHL/VS ratio is very close to 1.0 for both seeds, branches, food waste, coated paper, old corrugated containers, and office paper. The lowest ratios were measured for grass and leaves (0.77), old newsprint (0.83), and MSW (0.81). Grass and leaves contain waxes and lipids that were not quantified. However, these compounds would not be as degradable as carbohydrates. Old newsprint is mechanically ground wood, so it will contain many of the same trace compounds as branches where the CHL/VS ratio was 0.89. Volatile components of old newsprint that were not quantified include the ink, which comprises 0.5−1% of the dry weight, and various fillers and resins, which might comprise another 2−3% (*21*). The remainder of the unaccounted for organic content is likely due to analytical error. MSW contains a number of unmeasured organics, including rubber, leather, and plastics. However, these unmeasured organics are not anaerobically biodegradable. Thus, they will not adversely affect the methane potential mass balance.

Electron acceptors that could support the non-methanogenic biodegradation of cellulose and hemicellulose include oxygen, nitrate, and sulfate. Oxygen was entrained in the refuse during reactor filling, and some additional oxygen would have entered the reactors during leachate neutralization. Based on the stoichiometry of aerobic cellulose oxidation and estimates of the maximum volume of oxygen that could have entered the reactors, less than 10% of the cellulose added to any reactor could have been oxidized aerobically. The methane potential recoveries in the reactors with the lowest amount of cellulose present initially—grass, leaves, and coated paper—are reported in Table 1. Given the relatively high methane potential recoveries in the grass and coated paper reactors, aerobic oxidation of cellulose would not appear to be a major source of error, although it was undoubtedly a contributing factor.

TABLE 2. Fraction of Methane Attributable to Seed for Each Component[a]

component	fraction (%)
grass	7.9 (0.8)
grass-2	3.0 (0.6)
leaves	25.6 (5.7)
branches	15.1 (3.0)
food waste	6.5 (0.1)
coated paper	21.0 (1.6)
old newsprint	17.7 (1.4)
old corrugated containers	4.7 (0.2)
office paper	3.5 (0.3)

[a] Values exclude reactors L2, B4, F3, and F4 because they leaked. Standard deviations given in parentheses.

Nitrate and sulfate concentrations were not measured regularly. With the exception of food waste, which may contain some nitrate-based preservatives, nitrate would not be expected in refuse or in any of the components tested. Paper excavated from the Fresh Kills landfill was reported to have a reservoir of extractable sulfate (*22*). However, extracts of fresh paper did not contain sulfate, suggesting that the absorbent nature of the paper allowed for sulfate accumulation. To evaluate whether sulfates used in the paper production process remained on the paper, extractions were performed on all four paper types by soaking shredded samples in warm water. The extractable sulfate concentrations in coated paper, old newsprint, old corrugated containers, and office paper were 0.84, 0.95, 0.82, and 0.45 mg of SO_4^{2-}/g, respectively. Based on eq 1, this would support the oxidation of 0.11, 0.11, 0.08, and 0.03% of the cellulose in these reactors, respectively. Thus, the small amounts of sulfate present did not significantly affect the paper mass balances.

$$C_6H_{10}O_5 + 3SO_4^{2-} + 3H^+ \rightarrow 6CO_2 + 3HS^- + 5H_2O \quad (1)$$

Biodegradation of organic carbon is coupled to microbial growth. Thus, some of the degraded carbohydrates were used for cell mass. When methane potential recoveries were recomputed on the assumption that 5% of the cellulose and hemicellullose lost were incorporated into cell mass, recoveries increased by an average of 4.8% (Table 1).

The methane yield of the seed was assumed to be the same, whether it was present in a control reactor or in a reactor with one of the components tested. Nutrients were added to both the seed and the component reactors as necessary to minimize the potential for a nutrient to limit methane production. Nevertheless, this assumption is probably not perfect. To assess the potential impact of the seed on the reported yields, the relative fraction of the total methane produced in each reactor that was attributed to the seed is presented in Table 2. The impact is most significant for those components with low yields, including leaves, branches, old newsprint, and coated paper. However, even in these cases, the total fraction of methane attributed to the seed was never greater than 26%. Thus, the measured methane yields are not overly sensitive to the methane yield of the seed.

In summary, while there are a number of potential errors in the methane potential recovery analyses, there is not one particular problematic procedure. The methane potential recovery was between 90 and 100% in a number of reactors, suggesting that there was no repeatable source of error.

Effect of Recycling on Methane Production. The yield data reported in Table 1 may be used to evaluate the potential impact of changes in municipal refuse composition on potential methane yields from landfills. In addition, these data may be useful to evaluate methane production from other anaerobic treatment processes for refuse (*23, 24*). A

simple model was developed to calculate methane yields as a function of waste composition (*13*). By assuming the composition of refuse buried in landfills to be represented by the EPA waste characterization (*1*), the actual methane yield of refuse buried decreases by only 10% between the base case with no recycling (64.9 L/wet kg) and a case in which 31% of refuse is recycled (58.6 L/wet kg). However, when the decrease in the mass of refuse buried is accounted for, the potential reduction in methane production is 38%. While the yields reported in Table 1 are almost certainly greater than the amount of methane that would be produced under environmental conditions in a landfill, the analysis presented here serves to highlight the potential impact of recycling on methane yields. At landfills where methane is recovered for use as an energy source, additional analyses should be performed to compare the relative benefits of recycling and energy recovery.

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