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Solid-state ^{13}C NMR spectroscopic, chemolytic and biological assessment of pretreated municipal solid waste

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In Central Europe, composting and anaerobic digestion of municipal solid waste (MSW) is used as pretreatment before landfilling to reduce landfill emissions. MSW samples were analyzed before, during, and after pretreatment to assess the stability of the organic matter. Chemolytic, nuclear magnetic resonance (NMR) spectroscopic, and respiration parameters were correlated to evaluate a substitution of the time-consuming respiration analysis by chemical parameters. ^{13}C cross polarization magic angle spinning (CPMAS) NMR spectroscopy showed a preferential biodegradation of O-alkyl carbon (carbohydrates) and a selective accumulation of plastics during all pretreatments, confirming findings from chemolytic analyses. Principal component analysis exhibited a strong association between the respiration rate, the carbohydrate content, and the O-alkyl C content, corroborating that carbohydrates are the most important compounds of MSW with regard to the emission potential. Rank correlation (Spearman) also showed strong relationships between the respiration rate and the content of carbohydrates (r=0.75) and of O-alkyl C (r=0.72). *Journal of Industrial Microbiology & Biotechnology* (2001) **26,** 83–89.

Keywords: solid-state ^{13}C NMR spectroscopy; municipal solid waste; pretreatment; respiration test; principal component analysis

Introduction

Disposal of municipal solid waste (MSW) has been a major environmental issue since the industrial revolution [20]. To reduce the adverse ecological effects of landfilling untreated MSW, i.e., methane and leachate emissions [14], German legislation will require a pretreatment before landfilling, starting in 2005. A pretreatment by composting or anaerobic digestion can substantially decrease the landfill emission potential of MSW [6]. The biodegradation processes during these biological treatments are not easy to control. Consequently, parameters are needed that describe the stability of the treatment product with respect to further biodegradation in the landfill.

Biological stability parameters such as aerobic respiration rate or anaerobic gas production are preferred over chemical parameters because they reveal the actual availability of biodegradable compounds [7,8]. However, it takes 4 days for the aerobic, and 21 days for the anaerobic, stability to be determined. Chemical parameters may reveal further information about the chemical composition of the pretreated MSW and they can be measured quickly. Cellulose and raw fat content, as determined by gravimetric methods [17], correlated well with the respiration rate of MSW after different composting times [8].

It was shown previously that solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy reveals important information about the chemical composition of MSW [11]. The chemical composition is a major controlling factor for the biodegradability and stability of pretreated MSW. The correlation of respiration data with data on the composition of MSW, therefore, is the major objective of this paper. Data from ^{13}C NMR spectroscopic and chemolytic analyses of carbohydrates, proteins, lipids, and lignin were used to check whether chemical parameters provide further information on MSW stability that is responsible for the respiration rate. A principal component analysis (PCA) was performed to discover correlations among all parameters measured.

Materials and methods

Waste materials, pretreatment systems and sample preparation

All waste materials were residual wastes from regions with separate collection of biowaste and other recyclables. These were subjected to a number of different aerobic, anaerobic or alternating aerobic/anaerobic pretreatments that are supposed to stabilize the MSW materials. Table 1 gives an overview of the different pretreatment systems. Before composting or anaerobic digestion, the MSW was shredded and sieved to obtain a higher specific surface for biodegradation. Samples were taken after this mechanical preparation, i.e., before beginning the pretreatment, and after different pretreatment times. The number of samples obtained from each treatment is indicated in Table 1. Samples were delivered in a frozen condition. Samples that were too wet for milling were air-dried for 2–4 days.

For further chemical and respiratory analyses samples were homogenized in a multistep shredding and milling procedure. The samples were first shredded to $\leq$1 mm with a cutting mill in two steps (10 mm, 1 mm), and subsequently to $\leq$0.12 mm in two additional steps (0.5 mm, 0.12 mm) with a centrifugal mill. In a previous study [10] it was shown that representative subsamples are obtained from this multistep preparation procedure.

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Table 1 Overview of the pretreatment systems

Type of system	Total treatment time (weeks)	Number of samples	Treated particle size (mm)	Biological treatment
Aerobic 1	17	3	≤180	1 week composting in tunnel reactors with forced aeration, followed by 16 weeks windrow composting without aeration
Aerobic 2	14	9	≤60	3 weeks composting in containers with forced aeration, followed by 11 weeks windrow composting without aeration
Aerobic 3	55	6	≤40	9 weeks windrow composting with forced aeration, 46 weeks windrow composting without aeration
Aerobic 4	61	5	≤40	61 weeks windrow composting without forced aeration
Aerobic 5	18	3	≤40	18 weeks composting in containers with forced aeration
Alternating 1	23	19	≤20	23 weeks alternating aerobic and anaerobic treatment in small bioreactors (200 l), alternation by switching air flow on and off, treatment intervals (1–3 days) controlled by methane content in reactor gas phase
Alternating 2	24	3	≤20	24 weeks of alternating aerobic/anaerobic treatment in 14-m^3 bioreactors, alternation by switching air flow on and off, treatment intervals (1–3 days) controlled by methane content in reactor gas phase
Anaerobic–aerobic	14.5	4	≤40	2.5 weeks of mesophilic (38°C) one-step dry fermentation in a 50-m^3 continuous-flow reactor, followed by 12 weeks of composting in a rotting box (20 m^3) with pressure aeration
Anaerobic	2.5	6	≤7	2.5 weeks two-step thermophilic wet fermentation in the laboratory.

Elemental and chemolytic analyses

Total carbon and nitrogen were determined with an elemental analyzer (Elementar Vario EL elemental analyzer, Elementar Analysensysteme, Hanau, Germany). Total organic carbon (TOC) was calculated as the difference between total carbon and inorganic carbon. Inorganic carbon was measured in the ignition residue. All analyses were performed in duplicate. Medians of the coefficient of variation were 2.9% for total nitrogen, and 2.5% for TOC.

Chemical compound classes were analyzed with a suite of degradative methods which is routinely used for the analysis of soil organic matter (OM) [4]. A detailed description of all chemolytic methods is given in our previous study [10]. In brief, cellulose and noncellulosic carbohydrates were differentiated by acid hydrolysis with 24 N H_2SO_4 and 1 N HCl. The released sugar monomers were reduced to sugar alcohols with KBH_4 and then oxidized to formaldehyde and formic acid with H_5IO_6. The formaldehyde reacted with MBTH (3-methyl-2-benzothiazolinone-hydrazone-hydrochloride) to form a green-colored complex. The concentration of this complex was measured with a UV/VIS spectrophotometer at 635 nm. Cellulose content was calculated as the difference between total and noncellulosic carbohydrates.

Proteins were hydrolyzed with 6 M HCl and the released α-amino acids were analyzed with a photometer after reaction with ninhydrin. Protein content was calculated by multiplying the α-amino-N concentration by 6.25, assuming an average nitrogen content in proteins of 16%.

The content of total extractable lipids was determined gravimetrically after extraction of the sample with a mixture of chloroform and methanol (1:2, v/v).

Lignin was depolymerized with CuO. After silylation, the released phenols were analyzed with a gas chromatograph equipped with a flame ionization detector. The calculation of lignin content in MSW from the yield of individual phenols is explained in detail by Pichler and Kögel-Knabner [10].

All chemolytic analyses were performed in duplicate. Medians of coefficients of variation for the duplicates were 6.2% for noncellulosic carbohydrates, 14.2% for cellulose, 3.6% for proteins, 3.8% for lipids, and 5.2% for lignin.

NMR spectroscopy

Prior to NMR spectroscopy, paramagnetic compounds were removed by extraction with 10% HF [13]. The comparison of NMR spectra before and after HF extraction showed no major changes in the signal intensity distribution (data not shown). This was confirmed by low TOC losses (>4%) during this treatment which were determined by comparison of the carbon content before and after the HF extraction.

A Bruker DSX 200 spectrometer was used to obtain solid-state ^{13}C NMR spectra at a frequency of 50.32 MHz with a commercial Bruker double air-bearing probe and 7-mm o.d. rotors. Chemical shifts were calibrated with glycine and are reported relative to tetramethylsilane (=0 ppm). Table 2 gives a tentative signal assignment for MSW samples. CPMAS ^{13}C NMR spectra were recorded at a spinning speed of 6.8 kHz. Between 1000 and 10,000 scans were accumulated with a pulse delay between 8 and

Table 2 Tentative signal assignments for ^{13}C NMR spectra of municipal solid waste [7]

Chemical shift range (ppm)	Assignment
220 to 160	carbonyl C from aldehydes, ketones, (poly)amides, esters, carboxyl groups
160 to 110	aromatic C from polystyrene and lignin
110 to 50	O-alkyl C from carbohydrates, lignin side-chains, C_α in amino acids
50 to 0	alkyl C from plastics, lipids, proteins

15 s and a contact time of 1 ms. In order to circumvent spin modulation of Hartmann–Hahn conditions, a ramped ^{1}H pulse from 100% down to 50% was used during the contact time [9]. Line broadening was adjusted to 30 Hz.

Respiration rate

An automatic system [2] was used for hourly recording of the CO_2 release rate. In preliminary experiments we determined that the water content for highest respiration rates was 450 g kg^{-1} (water/total weight). Recording was started when the release rate was nearly constant. The cumulative oxygen uptake after 4 days of recording (AT_4 in milligrams O_2 per gram dry matter) is usually used as a stability parameter for pretreated MSW [7]. Therefore, O_2 uptake was calculated from the CO_2 evolution. This was done by the respiratory quotient, assuming a molar respiratory quotient of 1 for aerobic respiration [15,16]. Measurements were carried out in duplicate. The median of the coefficient of variation of the duplicates was 4.3%.

Results and discussion

Respiration rate during composting

Figure 1 demonstrates the decrease of the respiration rate during composting in the Aerobic 3 system. The initial 9 weeks with forced aeration had the greatest effect on stabilization and reduced the respiration rate by 90%. This is demonstrated in both the TOC-normalized and in dry-matter-normalized units. During the following 46 weeks without forced aeration, the overall reduction of the respiration rate was further increased to 96%. This reflects the intensive biodegradation of easily available carbon sources, particularly of carbohydrates [10]. It also indicates that the composted MSW after pretreatment is composed mainly of refractory compounds which are not expected to be a source of relevant emissions after landfilling.

Table 3 gives the respiration rates before and after treatment for all systems. In Germany, 5 mg O_2 (g dry matter)$^{-1}$ (4 days)$^{-1}$ is discussed as a limit value for MSW before landfilling [5]. Generally, all pretreatment systems lead to a considerable reduction in respiration rate. The respiration rate already dropped below the limit value after 9 weeks of composting for the Aerobic 3 system (Figure 1). However, some treatments still had a rather high respiration rate (Aerobic 1, Aerobic 4) and did not meet the requirement for landfilling. Regarding Aerobic 1, we explain this by the huge particle size ($\leq$150 mm, Table 1) of the MSW, which delays microbial attack. Aerobic 4 did not involve forced aeration, and is thus missing the stimulating effect of high oxygen availability with respect to biodegradation.

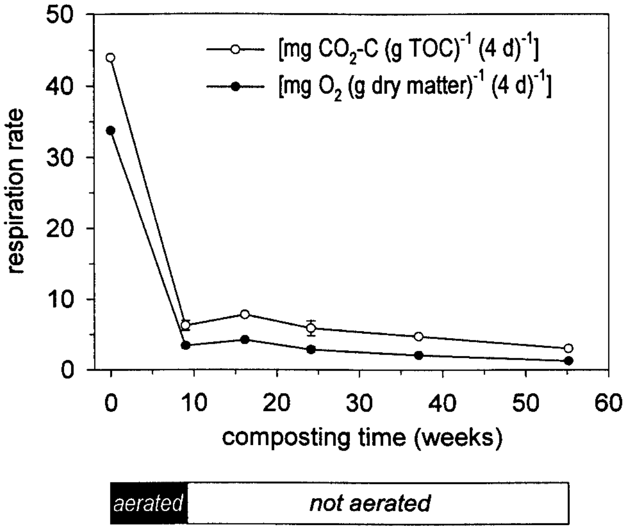

Figure 1 Respiration rate during composting of municipal solid waste (Aerobic 1). Error bars after 9 and 24 weeks represent standard deviations of four sampling replicates.

Table 3 Respiration rates before and after treatment

Type of system	Treatment time (weeks)	Respiration rate, mg O_2 (g dry matter)$^{-1}$ (4 days)$^{-1}$	
		Before treatment	After treatment
Aerobic 1	17	16	7.4
Aerobic 2	14	18	3.3
Aerobic 3	55	34	1.2
Aerobic 4	61	34	6.0
Aerobic 5	18	34	1.4
Alternating 1	23	n.d.	2.6
Alternating 2	24	n.d.	4.9
Anaerobic –aerobic	14.5	27	1.1
Anaerobic	2.5	n.d.	3.6

^{13}C NMR spectra of MSW

NMR spectra of the anaerobic–aerobic treatment are presented as an example representative of most of the pretreatment systems (Figure 2). In a previous study, it was shown that CPMAS ^{13}C NMR spectra represent the chemical composition of MSW samples in a quantitative way [11]. The cross polarization magic angle spinning (CPMAS) technique provides ^{13}C NMR spectra of MSW with representative intensity distribution, whereas carbon is underestimated in the single pulse excitation experiment. The presence of plastics in MSW was confirmed by dipolar dephased (DD) and proton spin relaxation editing (PSRE) ^{13}C NMR spectra.

Signals in the O-alkyl C region (50–110 ppm) dominate the spectrum of fresh MSW (Figure 2). These signals are assigned to carbohydrates such as cellulose, starch, or hemicellulose. The maximum at 72 ppm is explained by C-2, C-3, and C-5 in carbohydrates. The weaker signals at 65, 88, and 105 ppm can be attributed to C-6, C-4, and C-1 in carbohydrates, respectively. The dominating signal in the alkyl C region at 32 ppm is tentatively assigned to methylene groups in plastics (polyethylene, polyisoprene) and lipids. After the anaerobic digestion stage, the intensity of signals in the alkyl C and aromatic C regions increased relatively, while the intensity of the O-alkyl C region decreased. Signals at 22 and 26 ppm, appearing more prominently after anaerobic digestion, are attributed to methyl groups in polypropylene and to methylene groups in polyamide. The two signals in the aryl C region at 128 and 147 ppm, together with the small ones at 40 and 43 ppm, most probably arise from polystyrene [11]. This trend of a relative increase of signals in the alkyl and aromatic region continued during the following composting period. This effect is

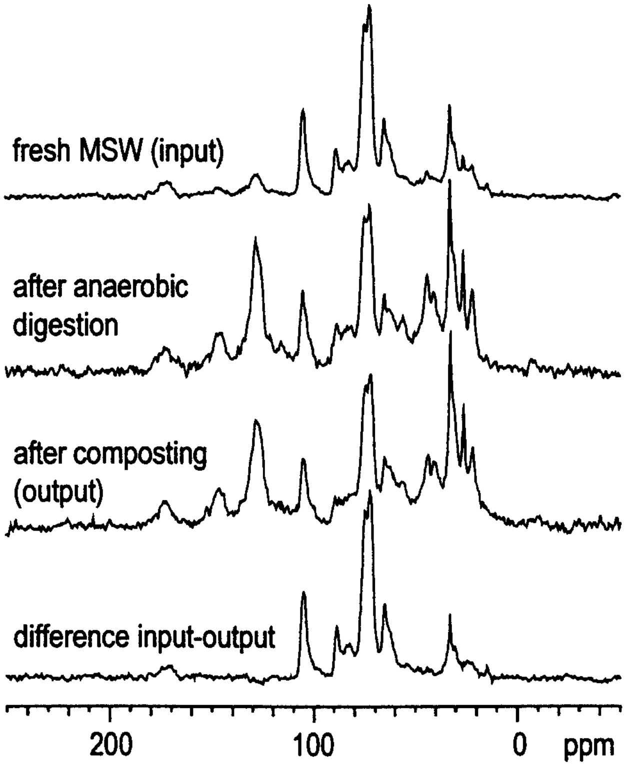

Figure 2 ^{13}C CPMAS NMR spectra of municipal solid waste after different treatment stages in the anaerobic–aerobic system.

best explained by a preferential biodegradation of carbohydrates and an accumulation of plastics during the pretreatment.

Similar changes were also found in all other treatment systems (Table 4). Compositional changes in the ^{13}C NMR spectra are also indicated by an increase of the alkyl C/O-alkyl C ratio (Table 4). This ratio is known to increase with an increasing degree of biodegradation of OM [1]. Fresh waste exhibits ratios of 0.4 to 0.6, except for the anaerobic system. The high ratio of 1.45 for the anaerobic system is due to a low paper content in the waste material, caused by sieving the input material to $\leq$7 mm. After treatment, the ratio ranged between 0.7 and 1.9.

Table 4 shows the mass loss of O-alkyl C during the treatments. This parameter allows the assessment of the intensity of degradation for the various treatment systems with respect to the fraction most relevant for landfill emissions [19]. Mass loss values of O-alkyl C between 51% and 82% were obtained. The highest mass loss of 82% was achieved with the Aerobic 3 system, which also needed the longest treatment time with a total of 55 weeks of composting. The anaerobic treatment demonstrated the highest degradation rate, i.e., mass loss per time unit. Insufficient degradation was obtained with the Aerobic 1 system. In summary, most of the systems accomplished a substantial reduction of O-alkyl C and hence, carbohydrates.

Chemolytic data

Carbohydrates are the most relevant compounds identifiable by the chemolytic methods applied in the MSW input material (Table 5). Proteins, lipids, and lignin accounted for smaller amounts of the OM in the input materials. Carbohydrates exhibited the highest mass losses (71% to 88%) during treatment. Protein and lipid losses were lower due to microbial resynthesis and recalcitrance. Lignin was degraded only to a minor extent. Large amounts of the OM, between 28% and 55% in the input materials and between 39% and 58% in

Table 4 Changes in chemical composition of MSW before and after treatment as determined by solid-state ^{13}C NMR spectroscopy

Type of system	Treatment time (weeks)	% of total signal intensity				TOC loss	% Mass loss[a]				Alkyl C/ O-alkyl C
		Alkyl C	O-alkyl C	Aryl C	Carbonyl C		Alkyl C	O-alkyl C	Aryl C	Carbonyl C	
Aerobic 1	0	30	56	11	3	24	−1	51	−34	−7	0.53
	17	39	36	20	5						1.08
Aerobic 2	0	23	59	13	5	63	49	74	41	59	0.39
	14	32	43	20	5						0.75
Aerobic 3	0	23	62	10	4	57	35	74	6	61	0.37
	16	35	39	22	4	68	50	82	22	56	1.05
	55	36	34	24	6						
Aerobic 4	0	23	62	10	4	53	42	68	−10	28	0.37
	61	28	41	24	7						0.68
Aerobic 5	0	23	62	10	4	59	44	76	1	40	0.37
	18	32	37	25	7						0.85
Alternating 1	0	30	55	12	3	75	61	84	69	64	0.55
	23	46	35	15	5						1.53
Alternating 2	0	19	53	20	8	73	65	77	70	78	0.37
	24	26	45	22	7						0.57
Anaerobic–aerobic	0	23	62	10	5	58	45	71	10	57	0.36
	2.5	30	43	21	5	61	42	76	7	64	0.69
	12	34	38	24	5						0.89
Anaerobic	0	50	34	7	9	60	59	69	28	55	1.45
	2.5	51	26	13	10						1.93

[a] Percent mass loss of the NMR regions was calculated as: 100 − [(% of signal intensity after treatment)/(% of signal intensity before treatment) × (100 − % TOC loss)].

Table 5 Changes in chemical composition of MSW before and after treatment as determined by chemolytic methods

Type of system	Treatment time (weeks)	Mass loss (% OM)	C/N	% of OM mass				
				Total carbohydrates	Proteins	Lipids	Lignin	OM not identified
Aerobic 1	0	26	45	50.2	3.8	10.7	7.1	28.2
	17		28	25.7	4.6	14.5	12.1	43.0
Aerobic 2	0	64	24	42.3	7.7	11.6	9.2	29.2
	14		15	26.2	12.1	9.9	12.8	39.1
Aerobic 3	0	61	27	44.9	6.9	14.1	3.7	30.4
	16	70	18	24.6	8.1	12.7	7.9	46.8
	55		14	17.5	9.5	12.0	8.4	52.7
Aerobic 4	0	53	27	44.4	6.8	14.0	4.8	30.1
	61		17	21.8	8.7	12.1	11.0	46.4
Aerobic 5	0	60	24	44.6	8.1	14.9	4.8	27.7
	18		14	19.8	8.3	12.7	10.1	49.1
Alternating 1	0	75	35	41.9	5.2	11.0	6.4	35.4
	23		21	26.2	6.7	6.3	14.0	46.8
Alternating 2	0	75	24	26.1	7.3	5.8	6.1	54.6
	24		14	19.9	8.5	9.1	5.0	57.5
Anaerobic–aerobic	0	68	24	44.3	7.8	14.5	4.9	28.6
	14.5		24	21.2	8.5	18.3	10.9	41.2
Anaerobic	0	51	23	30.7	8.2	18.5	2.7	40.0
	2.5		15	20.5	13.3	19.8	4.7	41.7

the output materials remained unidentified by chemolytic methods. According to the data from ^{13}C NMR spectroscopy these can mainly be attributed to plastic materials [11].

Correlation of respiration and chemical data

To check which chemical parameter best describes the stability of MSW, data from CPMAS ^{13}C NMR spectroscopy and from chemolytic analyses were correlated with the aerobic respiration rate (Table 6). Not all parameters followed a normal distribution. Therefore, Spearman's nonparametric rank correlation was calculated [12]. Since not all parameters were determined for every sample, the number of data pairs is not the same for every correlation analysis. For the evaluation of MSW stability, the lower range of respiration rates is of greatest relevance. Hence, an additional correlation was calculated using only the data pairs with a respiration rate <15 mg O_2 (g dry matter)$^{-1}$ (4 days)$^{-1}$.

The highest correlation coefficients were obtained with the chemolytic cellulose content and the NMR spectroscopic O-alkyl C content. This confirms the relationship between carbohydrates and the landfill emission potential.

As mentioned in the introduction, correlations were found in another study between raw fat content and the respiration rate [8]. The analysis of the raw fat content is comparable to that of lipids. But for the data obtained in the present study no correlation was found. The same is true for lignin, alkyl C, carbonyl C, and the C/N ratio, based on a significance level of 0.05. Proteins, aromatic C, and the alkyl C/O-alkyl C ratio are significantly correlated with the respiration rate, but exhibit only a low correlation coefficient.

Taking into account only the respiration rate range <15 mg O_2 (g dry matter)$^{-1}$ (4 days)$^{-1}$, all correlation coefficients are lower than for the entire data range. In the final stages of pretreatment, the cellulose content, which exhibits the strongest correlation with the respiration rate, explains only 48% of the variance of the respiration data. This indicates that at this stage factors other than chemical

Table 6 Spearman's rank correlation of respiration rate data with chemolytic and ^{13}C CPMAS NMR spectroscopical data

Parameter[a]	All data pairs			Only pairs with respiration rate <15 mg O_2 (g dry matter)$^{-1}$ (4 days)$^{-1}$		
	n[b]	r[c]	p[d]	n	r	p
C/N ratio	68	0.27	0.02	59	0.15	0.27
Noncellulosic carbohydrates	68	0.74	<0.01	59	0.62	<0.01
Cellulose	68	0.75	<0.01	59	0.69	<0.01
Proteins	68	0.53	<0.01	59	0.48	<0.01
Lipids	53	0.15	0.28	46	−0.12	0.43
Lignin	37	−0.15	0.38	31	−0.04	0.85
Alkyl C	66	0.16	0.21	58	0.12	0.35
O-alkyl C	66	0.72	<0.01	58	0.62	<0.01
Aromatic C	66	−0.34	<0.01	58	−0.29	0.03
Carbonyl C	66	0.40	<0.01	58	0.25	0.05
Alkyl-C/O-alkyl C ratio	66	−0.55	<0.01	58	−0.34	<0.01

The respiration rate was used in terms of mg O_2 (g dry matter)$^{-1}$ (4 days)$^{-1}$.

[a] All parameters were used as percent contents of dry matter, except for ratios.

[b] Number of data pairs.

[c] Spearman's rank correlation coefficient.

[d] Significance level.

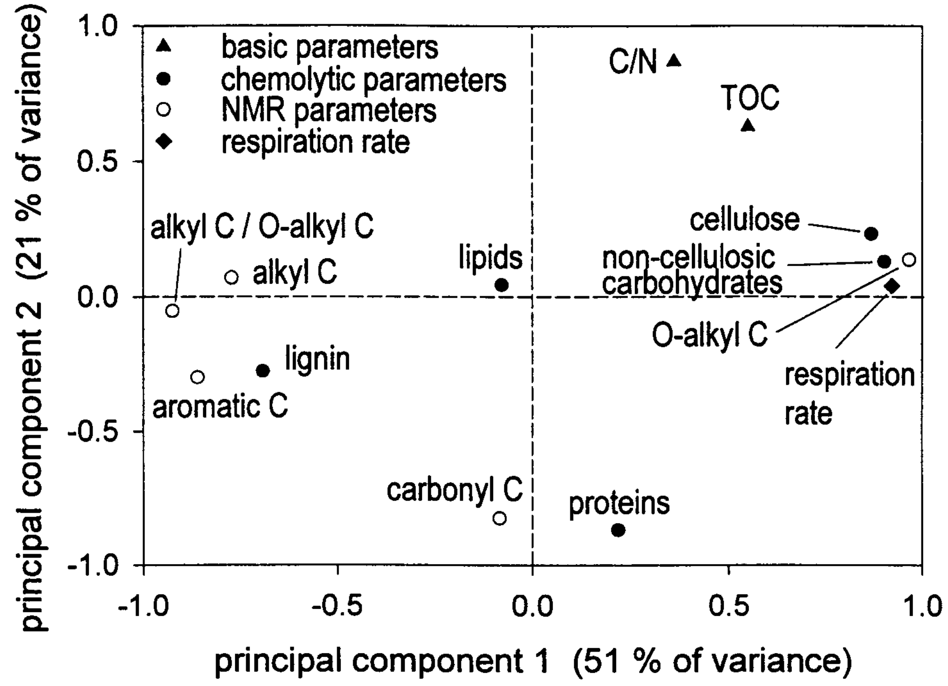

Figure 3 Principal component loads of chemical and biological parameters ($n = 35$). All parameters were normalized to TOC and log-transformed.

composition of the MSW are additionally controlling respiration rates.

Principal component analysis (PCA)

The multivariate PCA was used to reveal relationships between all parameters at the same time. All parameters were normalized to TOC in order to detect relations with respect to the composition and stability of TOC. High numerical values have a great influence on results of the PCA. Therefore all data were log-transformed [18]. Two principal components were extracted and subjected to a varimax rotation, i.e., they were rotated to reveal high correlations with some variables and low correlations with others [3].

Figure 3 shows the principal component loads, i.e., the correlations of the parameters with the two principal components. Principal component 1 explains 51% of the total variance of all data. It is determined by carbohydrates, O-alkyl C, and the respiration rate on the positive scale, and by the alkyl/O-alkyl C ratio, alkyl C, aromatic C, and lignin on the negative scale. This principal component is associated with the biodegradability or stability of MSW. It is again clearly that carbohydrates are the most relevant compounds with regard to the stability and hence the emissions of MSW in the landfill. Principal component 2 explains 21% of the total variance. The C/N ratio on the positive scale, and the protein and carbonyl C content on the negative scale are the best correlated parameters. This indicates an association of this principal component with the fate of nitrogen compounds during treatment. Since the principal components are statistically independent from each other, it is assumed that the transformation of carbon and nitrogen during pretreatment is also independent. However, the total variance is influenced mainly by parameters that indicate the stability of TOC.

Conclusions

^{13}C CPMAS NMR spectroscopy confirmed that carbohydrates (O-alkyl C) were preferentially biodegraded in all treatment systems, while at the same time, plastics were selectively accumulated. Chemolytic and ^{13}C spectroscopic analyses provide relevant information on the compositional changes during pretreatment of MSW. Parameters describing the chemical composition of MSW by using chemolytic and ^{13}C NMR spectroscopic parameters are correlated to the respiration rate and thus to the stability of pretreated MSW. PCA confirmed the strong relationship between respiration rate, carbohydrate and O-alkyl C contents. It also revealed that the transformation of nitrogen is independent of that of carbon.

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