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Organic compounds in re-circulated leachates of aerobic biological treated municipal solid waste

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Abstract

Biodegradation of organic matter is required to reduce the potential of municipal solid waste for producing gaseous emissions and leaching contaminants. Therefore, we studied leachates of an aerobic-treated waste from municipal solids and a sewage sludge mixture that were re-circulated to decrease the concentration of biodegradable organic matter in laboratory-scale reactors. After 12 months, the total organic C and biological and chemical oxygen demands were reduced, indicating the biodegradation of organic compounds in the leachates. Curie-point pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and pyrolysis-field ionization mass spectrometry (Py-FIMS) revealed that phenols, alkylaromatic compounds, N-containing compounds and carbohydrates were the predominate compounds in the leachates and solid waste. Leachate re-circulation led to a higher thermal stability of the residual organic matter as indicated by temperature-resolved Py-FIMS. Admixture of sewage sludge to solid waste was less effective in removing organic compounds from the leachates. It resulted in drastic higher and more bio-resistant loads of organic matter in the leachates and revealed increased proportions of alkylaromatic compounds. The biodegradation of organic matter in leachates, re-circulated through municipal solid waste, offers the potential for improved aerobic waste treatments and should be investigated on a larger scale.

Introduction

The harmless removal of municipal solid waste (MSW) requires biodegradation of organic matter to decrease the potential for gas emissions, leaching of organic waste water and other environmental contamination. This can be achieved by a combination of mechanical and biological treatments of MSW under aerobic conditions that stabilize the organic matter remaining in MSW prior to landfilling (Pichler 1999). Addition of sewage sludge can accelerate the stabilization of organic matter due to optimized water-balance and nitrogen supply (Updegraff 1972). Leachates from biologically treated MSW are generally highly loaded with organic matter, and these can be strongly reduced by re-circulation through the decomposing waste (Collins & Spillmann 1977, 1980; Jourdan 1983; Jourdan et al. 1982; Spillmann & Collins 1979). For example, decreases in chemical oxygen demand (COD) from 15000 to 500 mg O_2 l^{-1} and in biological oxygen demand (BOD) from 5000 to 10 mg O_2 l^{-1} were reported for a treatment period of 12 months, a time period equivalent to a biological trickling-filter (Collins & Spillmann 1977). Some authors speculated that enrichment of a refractory organic substance was the reason for decreases in bio-degradability of organic matter in leachates (Jourdan 1983; Stegmann & Knoch 1975). The same was described for organic matter of anaerobic landfill leachates (Göbbels & Püttmann 1997; Harmsen 1983; Kettern 1990). These authors suggested that the decreased biodegradability of the organic matter was induced by polymerization reactions of non-biodegradable organic matter.

Infrared spectroscopy indicated carbohydrates, peptides, lipids and lignin compounds in leachates (Artiola-Fortuny & Fuller 1982). Curie-point pyrolysis-gas chromatography/mass spectrometry (Cp Py-GC/MS) of non-biodegradable organic matter fractions from leachates showed predominant signals of phenols, aromatics and N-containing compounds (Göbbels & Püttmann 1997). Similarly, gas chromatography/mass spectrometry (GC/MS) of solvent-extracted organic matter from leachates revealed the most prominent signals for phenols, alkylaromatics and a variety of N-containing compounds (Öman & Hynning 1993; Paxéus 2000; Schultz & Kjeldsen 1986). However, all these mass spectrometric investigations were carried out on leachates from anaerobic landfills. To the best of our knowledge, leachates from aerobic waste treatments and re-circulated leachates have not yet been investigated by modern analytical methods. Therefore, the objectives of the present study were:

(1) to evaluate the composition and changes of organic matter in re-circulated leachates during a long-term aerobic biological waste treatment using two independent mass-spectrometric methods,
(2) to elucidate which organic substances were preferentially eluted from the decomposing MSW, and which changes in composition and stability the remaining organic matter underwent, and
(3) to investigate effects of sewage sludge addition on the total content and composition of organic matter in re-circulated leachates and in the solid waste.

We hypothesize that the re-circulation of leachate through the MSW leads to biodegradation of easily decomposable organic matter and a biological stabilization of recalcitrant organic matter that remains in the leachate and the leached solid waste.

Materials and methods

Aerobic biological waste treatment

Leachate re-circulation through a MSW and a mixture of MSW with sewage sludge were investigated in laboratory-scale reactors under aerobic conditions. The glass column-reactors had a diameter of 0.3 m and a height of 1.5 m and were filled each with 40 kg of waste and a waste + sewage sludge-mixture (ratio 4:1 by weight), respectively. The used sewage sludge was neither anaerobically nor aerobically stabilized, but mechanically dehydrated and conditioned with lime. The reactors were aerated by an oil-free compressor from the bottom of the columns (Degener et al. 2004). To simulate an aerobic biological MSW treatment under field conditions in the laboratory-scale reactors, computational temperature-controlled water jackets were used for the maintenance of the biological processes. The leachates collected at the ground of the columns were re-circulated permanently to the top of the columns by a peristaltic pump.

Samples, sample preparation and chemical analyses

The treatment periods and sample-codes are shown in Table 1. Samples of the leachates of both reactors were taken at their first output after 6 months from the start (L1-MSW and L1-MSW + SS) and after 12 months at the end of the waste treatment process (L2-MSW and L2-MSW + SS). Due to thermophilic conditions prior to the first leachate

Table 1. Sample-codes of the analyzed leachates and solid waste

	Treatment-period (months)	Sample-code	
		Leachate	Solid waste
Municipal solid waste	6	L1-MSW	–
	12	L2-MSW	MSW
Municipal solid waste + sewage sludge mixture	6	L1-MSW + SS	–
	12	L2-MSW + SS	MSW + SS

output, condensed water was generated exclusively and was substituted by tap water for re-circulation. More details of treatment process were described recently (Franke 2004). The chemical oxygen demand (COD) (Deutsches Institut für Normung 1980), the biological oxygen demand (BOD) (Deutsches Institut für Normung 1998) and the concentration of total organic carbon (TOC) (Deutsches Institut für Normung 1997) were determined without pre-treatment to avoid losses of organic matter. The concentration of dissolved organic carbon (DOC) (Deutsches Institut für Normung 1997) was determined after sample filtration at <0.45 μm (cellulose-acetate, Schleicher & Schuell, Einbeck, Germany) (three replicates each). The concentrations of total carbon (total C) were determined by dry combustion using a VARIO EL analyser (Elementar Analysensysteme GmbH, Hanau, Germany).

For mass spectrometric analyses, 0.5 l of each leachate was freeze-dried and stored. The solid waste samples (MSW and MSW + SS) were prepared after 12 months at the end of the aerobic treatment by manual separation of visible pieces of glass, plastics, metals, textiles and stones so that the more decomposed finer-sized components remained. These were sampled, air-dried and milled step-wise to $\leq$0.1 mm particle-size for mass spectrometric analyses.

Curie-point pyrolysis-gas chromatography/mass spectrometry (Cp Py-GC/MS)

The freeze-dried leachates (1.2–4.1 mg) and the milled solid waste (10–13 mg) were pyrolyzed at 500 °C for 9.9 s in a Curie-point pyrolyzer (Fischer 1040 PSC, Germany). The pyrolysis products were separated on a gas chromatograph Varian 3800 (Varian, USA) equipped with a 25 m capillary column BPX 5 (SGE, Australia) that was coated with 0.25 μm film thickness and had an inner diameter of 0.32 mm. Following split injection up to 45 s (splitless) at 300 °C, the split ratio was 1:100 from 45 up to 90 s and 1:5 from 90 s on. The flow rate of the helium carrier gas was adjusted to 2 ml min^{-1}. The starting temperature for the gas chromatographic program was 28 °C (5 min), and heated at a rate of 5 °C min^{-1} to 280 °C (30 min). The gas chromatograph was connected to a double focussing Finnigan MAT 212 mass spectrometer (Germany). Conditions for mass spectrometric detection in the electron impact mode were 3 kV acceleration voltage, 70 eV electron energy, 2.2 kV multiplier, 1.1 s (mass decade)$^{-1}$ scan speed, and m/z 48–450 mass range. Mass spectra corresponding to peaks in the gas chromatograms were identified by comparisons with the Wiley mass spectral library, software edition 6.0.

The identified single compounds were summed into compound classes. The relative composition of the organic matter is based on the proportions of the peak areas of the compound classes to the total peak area of the chromatograms.

Pyrolysis-field ionization mass spectrometry (Py-FIMS)

For temperature-resolved Py-FIMS, approximately 0.17–1.4 mg of the freeze-dried leachate and 1.2–2.2 mg of the solid waste samples were heated in a direct inlet system of the double-focussing mass spectrometer (Finnigan MAT 731, Germany) from 110 to 700 °C at heating steps of 10 °C. During the analysis, 60 spectra were recorded in the mass range m/z 15–900. In former investigations of numerous biogenic substances, marker signals have been identified, which can be assigned to 10 important classes of biomarkers to determine the relative composition of the pyrolyzed organic matter (Schulten 1984; Schulten & Leinweber 1999). The proportions of the 10 structural classes of the averaged replicate runs ($n = 3$) are reported as relative abundance in percent of total ion intensities (% TII), and as absolute intensities normalized to 1 mg sample weight in counts mg^{-1}. The total ion intensities (TII), normalized to 1 mg sample weight, were plotted against pyrolysis temperature, producing Py-FIMS thermograms. The experimental set-up for Py-FIMS has been described in detail (Schulten 1987; Schulten et al. 1998).

Results and discussion

Oxygen demand and carbon concentrations

Table 2 shows that the COD of 10890 mg O_2 l^{-1} (L1-MSW) decreased to 3550 mg O_2 l^{-1} (L2-MSW) during the leachate re-circulation. The reduction of the COD in the leachate of the variant with sewage sludge from 12400 mg O_2 l^{-1}

Table 2. Sum parameters of the investigated leachates

Leachate origin	Treatment-period (months)	BOD (mg O_2 l^{-1})	COD (mg O_2 l^{-1})	Ratio BOD:COD	TOC (mg l^{-1})	DOC (mg l^{-1})	DOC (% of TOC)
MSW	6	2200	10890	0.2	3890	2640	67
	12	120	3550	0.03	1230	1100	89
MSW + SS	6	1800	12400	0.1	4520	3250	72
	12	130	8600	0.01	2890	2720	94

(L1-MSW + SS) to 8600 mg O_2 l^{-1} (L2-MSW + SS) was lower compared to the variant without sewage sludge (L1, L2-MSW). A possible explanation for that could be the higher proportions of low-biodegradable organic matter in the variant with sewage sludge. This is supported by the higher BOD of 2200 mg O_2 l^{-1} in the variant without sewage sludge (L1-MSW) than in the leachate of the waste + sewage sludge-mixture (1800 mg O_2 l^{-1}) (L1-MSW + SS). However, re-circulation and biodegradation leads to approximately the same BODs (130 mg O_2 l^{-1} in L2-MSW + SS, and 120 mg O_2 l^{-1} in L2-MSW). The ratios BOD:COD of the MSW- and MSW + SS-leachates decreased from >0.1 to ≤0.03 during the re-circulation phase. The low ratio of ≤0.03 indicated a low bio-degradability of the remaining organic matter since a BOD:COD ratio of 0.1 generally is considered as a threshold under which biodegradation is strongly reduced (Kettern 1990).

The TOC and DOC concentrations also decreased during leachate re-circulation but to a lesser extent in the MSW + SS than in the MSW variant. The concentrations of TOC and DOC of the MSW derived leachates showed that 67% of the organic carbon was dissolved after 6 months (L1-MSW) and increased to 89% after 12 months (L2-MSW). The addition of sewage sludge increased the DOC proportion from 72% (L1-MSW + SS) to 94% (L2-MSW + SS) of TOC. Such an increase in DOC proportion as percent of TOC as found in the MSW and MSW + SS variant (Table 2) was previously described as an indicator of largely completed organic matter stabilization in old landfills (Artiola-Fortuny 1982; Christensen et al. 1998). Therefore, the BOD:COD ratio ≤0.03 and the high DOC proportions in the leachates (L2-MSW and L2-MSW + SS) showed the low biodegradability of the remaining organic matter in both variants. This can be explained by the rotting waste acting as a microbial colonized trickling-filter (Collins & Spillmann 1977). However, besides this evidence for basic decomposition processes, insight into the biodegradation reactions at the molecular-chemical level remained a challenge for the application of sophisticated analytical techniques.

Pyrolysis-gas chromatography/mass spectrometry

Leachates of municipal solid waste (L1,2-MSW)

Comparison of the chromatograms and proportions of compound classes of the freeze-dried leachates (Figure 1) shows that the organic matter composition changed due to re-circulation in the leachates (compare Figure 1a and b). The initial high proportion of carbohydrates (17%) decreased to 9.8% ($p \leq 0.01$) whereas proportions of phenols (1–5.3%, $p \leq 0.001$), lipids (0.7–3.2%, $p \leq 0.001$) and alkylaromatic compounds (15–17%, $p \leq 0.01$) significantly increased. The most abundant alkylaromatic compounds were toluene (2), and ethenylbenzene (5). N-containing compounds with the most intensive signals of pyridine (3), 1H-pyrrole, 2-methyl- (4), benzonitrile (6) and 1H-indole, 2-methyl- (8) were abundant at largest and constant proportions during re-circulation (18%), whereas the proportions of the lignin derived 2-methoxyphenol (7) (Bracewell & Robertson 1984; Faix et al. 1987; Sjöström & Keunanen 1990) increased. Chlorinated and sulfur containing compounds were detected in low proportions.

Organic compounds in anaerobic landfill leachates were mainly composed of alkylaromatics, phenols and N-containing compounds, which were identified by Py-GC/MS (Göbbels & Püttmann 1997) and GC/MS (Harmsen 1983; Öman & Hynning 1993). Our results on re-circulated leachates from aerobic waste treatments confirmed the cited studies. However, large proportions of

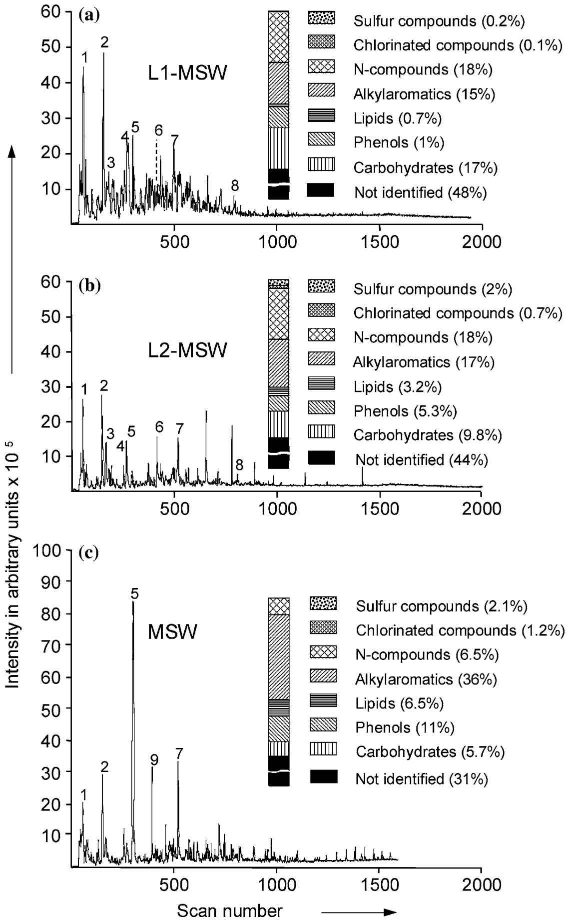

Figure 1. Chromatograms and relative proportions of seven compound classes of the organic matter of freeze-dried leachates (a) L1-MSW after 6 months, (b) L2-MSW after 12 months and (c) municipal solid waste (MSW) after 12 months obtained by Curie-point pyrolysis-gas Chromatography/mass spectrometry.

carbohydrates were detected in the leachates of the present study with the most prominent carbohydrate derived signal of 2-cyclopenten-1-one (1) (Moldoveanu 1998; Schulten et al. 1997). Decreases in carbohydrates proportions as found for re-circulated leachates (Figure 1a, b) were also found during composting (Chefetz et al. 1996; Smidt et al. 2005). This biodegradation of carbohydrates is due to their bio-availability for microorganisms, which can lead to a drastic loss, as described for long-term anaerobic landfills (Göbbels & Püttmann 1997; Harmsen 1983; Öman & Hynning 1993; Sawhney & Kozlosky 1984). The presence of remarkable proportions of alkylaromatic compounds in composts (Chefetz et al. 1996) and in landfill leachates (Schultz & Kjeldsen 1986) was interpreted by their high biological stability. This explains the increased proportions of alkylaromatic compounds after 12 months leachate re-circulation (compare Figure 1a (L1-MSW) with b (L2-MSW)). The detected lipids indicated enrichments of bio-resistant aliphatic substances, as reported for extracts of municipal waste composts (Keeling et al. 1994) and aerobic biological treated waste (Dinel et al. 1996). The determined pyrolysis products of N-containing compounds can be assigned to proteins (Chiavari & Galletti 1992; Munson & Fetterolf 1987; Schulten et al. 1995). Their constant proportion in the re-circulated leachate can be explained by the microbial assimilation and re-synthesis of proteins (Janssen 1996). Furthermore, the proportions of phenols in the leachates of the MSW were significantly enriched during the re-circulation (Figure 1a, b). Such a release of phenols was described for composted organic waste and explained by decomposition of proteins and lignin (Garcia et al. 1992).

Because of the remarkable differences of the non-identified peaks, which made up from 31% (MSW, Figure 1c) to 80% (L1-MSW + SS, Figure 2a) of total peak area, a comparable evaluation for the changing compound class proportions required the calculation of ratios, which express both the state of degradation and stabilization. The ratio of carbohydrates:(phenols + alkylaromatic compounds) decreased from 0.97 to 0.45 ($p \leq 0.01$) and the ratio of carbohydrates:N-containing compounds decreased from 0.84 to 0.55 ($p \leq 0.05$) during the leachate re-circulation. This confirmed the relative enrichment of N-containing compounds due to microbial assimilation at the expense of biodegradable carbohydrates during decomposing of organic material (Janssen 1996).

Municipal solid waste (MSW)

In the chromatograms of the solid waste mainly the same single compounds as in the leachates were generally identified with different intensities. In addition to these signals an intensive polyvinylchlorid (Alajberg et al. 1980; Audisio & Bertini 1992) or polystyrene derived (Alajberg et al. 1980) signal of benzene, (1-methylethenyl) (9) was recorded (Figure 1c). The relative composition showed higher proportions of phenols (11%), lipids (6.5%), and alkylaromatic compounds (36%) and lower proportions of carbohydrates (5.7%)

and N-containing compounds (6.5%) when compared to the leachates. The proportions of carbohydrates and N-containing compounds were lower in the solid waste at the end of the re-circulation treatment than in the leachate. This is explained as a result of the microbial hydrolysis of polymeric carbohydrates and N-containing compounds to water-soluble, low molecular weight compounds (Reinhardt 2000; Schalk 2003). In contrast, a low water solubility of certain organic matter compounds, such as lipids, explains the larger proportions in the solid waste (6.5%) than in leachates. High proportions of aromatic compounds are typical for stabilized biogenic and municipal solid waste (Chefetz et al. 1996). This explains the high intensities of alkylaromatic compounds and phenols in the investigated waste, in addition to the low water solubility. The most intensive signal of the identified phenols was 2-methoxyphenol (7). The predominance of ethenylbenzene (5) in the solid waste was also concluded from ^{13}C CPMAS-NMR spectra of aerobic biological treated waste, and was described as polystyrene derived (Pichler 1999). Based on this finding and the reported high intensities of ethenylbenzene in Py-GC/MS of polystyrene (Alajberg et al. 1980; Audisio & Bertini 1992; Ohtani et al. 1990) we conclude that the ethenylbenzene in MSW is derived from polystyrene. Its clear predominance in the leached MSW can be explained by the low bio-degradability of this substance (Otake et al. 1995).

Leachates of municipal solid waste + sewage sludge-mixture (L1,2-MSW + SS)

The compounds identified in the chromatograms in Figure 2 were similar to those of the MSW without sewage sludge (Figure 1). However, about 51–80% of peak area in the chromatograms in Figure 2 a–c was not identified. This is an effect of the highly complex sewage sludge, which probably added a lot of non-identified, but leachable, substances to the solid mixture. In the leachate after 6 months the ratio of carbohydrates to N-containing compounds was significantly lower in L1-MSW + SS (0.46) than in L1-MSW (0.84) ($p \leq 0.05$, $n = 3$). This is explained by higher proportions of N-containing compounds relative to carbohydrates in the variant with sewage sludge. Such an enrichment of N-containing compounds due to the addition of sewage sludge is in line with previous mass spectrometric investigations of sewage farm soils (Leinweber et al. 1996). Furthermore, the ratio of carbohydrates:(phenols + alkylaromatic compounds) in the leachate with sewage sludge (L1-MSW + SS: 0.61) was also lower than in the leachate without sewage sludge (L1-MSW: 0.97). This indicates an enrichment of alkylaromatic compounds due to the addition of sewage sludge as previously observed in composted MSW + sewage sludge-mixtures (Leinweber et al. 2002).

In the leachates after 6 months (L1-MSW + SS) and 12 months (L2-MSW + SS), the ratio of carbohydrates:N-containing compounds remained constant, indicating an inhibition of the microbial decomposition. This inhibition is also supported by the decrease in total C from 198 g kg^{-1} (L1-MSW + SS) to 156 g kg^{-1} (L2-MSW + SS) during the re-circulation, which was much lower than in the variant without sewage sludge (188 g kg^{-1} in L1-MSW to 107 g kg^{-1} in L2-MSW). Such an inhibition of the microbial decomposition was also reported in aerobic waste-sewage sludge treatment (Pichler 1999). Further evidence for inhibited microbial decomposition are the very intensive signals of starch or pectin derived 2-cyclopenten-1-one (1) (Moldoveanu 1998) and carbohydrate derived furan, 2-methyl- (10) (Bracewell & Robertson 1984), which are easily bio-degradable (Lott-Fischer et al. 2001). The signal of 2-cyclopenten-1-one (1) was more intensive in the solid waste + sewage sludge-mixture (Figure 2c), than in the variant without sewage sludge (Figure 1c).

Municipal solid waste + sewage sludge-mixture (MSW + SS)

The compound classes detected in the solid waste after the leaching period (Figure 1c, 2c) were identical to those of their leachates. An exception was the completely eluted sulfur-containing compounds in MSW + SS. Despite the addition of sewage sludge to MSW + SS, the identified single compounds agreed well with those in the MSW without sewage sludge (not shown). However, this similarity was also reflected by the ratios of compound classes (Figure 1c, 2c). Indices of similarity were used to describe an evolution to more uniform structures during composting of a sewage sludge + grape debris-mixture compared to the organic fraction of a MSW (Garcia et al. 1992). Furthermore, such an evolution was described as an indicator for stabilization as shown for composted

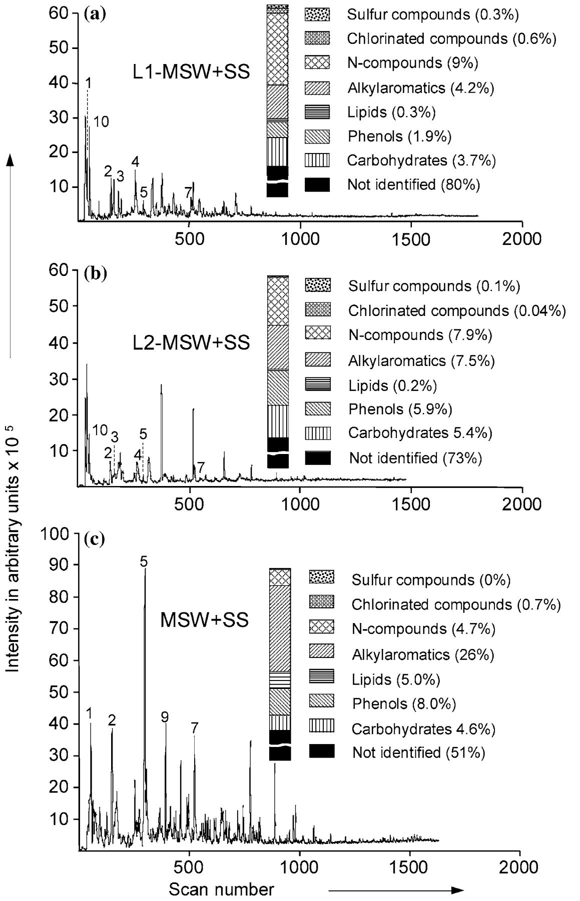

Figure 2. Chromatograms and relative proportions of seven compound classes of the organic matter of freeze-dried leachates (a) L1-MSW + SS after 6 months, (b) L2-MSW + SS after 12 months and (c) municipal solid waste (MSW + SS) after 12 months obtained by Curie-point pyrolysis-gas Chromatography/mass spectrometry.

biowastes from different plant materials, sewage sludge and mechanically biologically pretreated wastes (Smidt et al. 2002). Additionally, the evolution to uniform structures of the MSW and MSW + SS is supported by the elution of the sewage sludge derived organic compounds due to leachate re-circulation that led to highly loaded leachates with COD up to 10000 mg O_2 l^{-1} during composting of waste + sewage sludge-mixtures (Jourdan 1983; Reuß et al. 1975; Spillmann 1989). In the present study, the same effect was observed by the comparison of the leachates after the 12 months treatment (L2-MSW vs. L2-MSW + SS) with higher concentrations of COD (3550 vs. 8600 mg O_2 l^{-1}) and TOC (1230 vs. 2890 mg l^{-1}) (Table 2). The higher loads in the leachate of the waste-sewage sludge-mixture were also supported by higher concentrations of total carbon (110 vs. 190 g kg^{-1}) and total nitrogen (47 vs. 100 g kg^{-1}), as determined in the freeze-dried leachates.

Pyrolysis-field ionization mass spectrometry

Figure 3 shows the thermograms of total ion intensity (TII) (upper right) and the summed and averaged Py-FI mass spectra of the freeze-dried leachates L1-MSW and L2-MSW (Figure 3a, b), and the solid waste (MSW, Figure 3c). In the thermograms the maximum of ion intensity shifted from approximately 350 °C (L1-MSW) to 430 °C (L2-MSW). This indicated an increased thermal stability of the organic matter during the leachate re-circulation. Increasing thermal stabilities have also been reported in decomposing biowastes as direct evidence for the stabilization of organic matter (Smidt et al. 2005). The Py-FI mass spectra of L1-MSW (Figure 3a) and L2-MSW (Figure 3b)

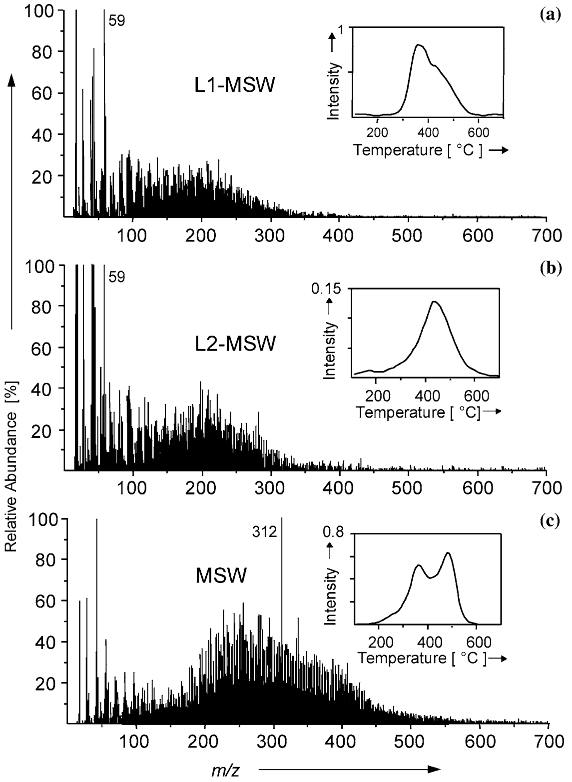

Figure 3. Pyrolysis-field ionization mass spectra and thermograms of the freeze-dried leachates: (a) L1-MSW after 6 months, (b) L2-MSW after 12 months and (c) municipal solid waste (MSW) after 12 months.

displayed intensive signals in the range between m/z 50 and 350. The base peak at m/z 59 (acetamide) could be assigned to N-containing compounds and was described as characteristic pyrolysis product of bacterial cell walls (Bahr & Schulten 1983) and soil microbes (Leinweber & Schulten 1993; Schulten 1993).

In the solid waste sample (Figure 3c) the TII-thermogram shows two peaks of ion intensities at 360 and 490 °C, indicating a more heterogeneous composition of organic compounds than in the leachates. The mass spectrum of the solid waste displayed generally higher ion intensities in the mass range up to m/z 600. This clearly indicated lower molecular weights in the leachates than in the solid waste. The base peak signal at m/z 312 in mass spectra of biogenic organic substances was assigned to lignin dimers, lipids and fatty acids (Leinweber et al. 2002). In the case of the investigated solid waste, the high intensities of m/z 312 in the Py-FIMS spectra indicated the styrene trimer derived from polystyrene (Ohtani et al. 1990). Furthermore, this is supported by the base peak of the chromatogram identified as ethenylbenzene (m/z 104), which was assigned to polystyrene (Figure 1c).

Due to weighing of samples before and after *in-source* pyrolysis, Py-FIMS allows normalization of TII to 1 mg sample weight in counts mg^{-1} and, thus, enables direct quantitative comparisons (Schulten 1999). Figure 4a shows that the TII (counts mg^{-1}) followed the order L1-MSW > MSW > > L2-MSW. The drastic decrease of the ion intensities of L1-MSW (13×10^6 counts mg^{-1}) and L2-MSW (2.3×10^6 counts mg^{-1}) along the re-circulation agreed well with the decrease in concentrations of COD (10890 vs. 3550 mg O_2 l^{-1}) and TOC (3890 vs. 1230 mg l^{-1}) (Table 2). This confirmed the biological reduction of the organic matter in the leachates during the re-circulation, as previously described (Collins & Spillmann 1977, 1980; Jourdan 1983; Jourdan et al. 1982; Spillmann & Collins 1979).

Figure 4b shows the relative abundance of compound classes in % TII. Re-circulation of leachates led to decreased proportions of carbohydrates ($p \leq 0.01$, $n=3$) and of summed proportions of N-containing compounds + peptides ($p \leq 0.05$, $n=3$). Proportions of all other compound classes remained constant. Considering the strong reductions in ion intensities (Figure 4a), this indicates proportional biodegradation of most compound classes, and disproportional decomposition of carbohydrates and N-containing compounds + peptides.

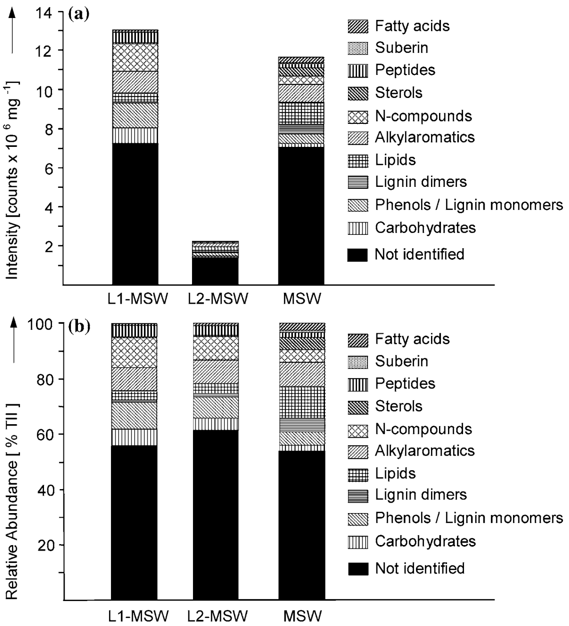

Figure 4. Proportions of 10 structural classes of building blocks of the freeze-dried leachates: L1-MSW after 6 months, L2-MSW after 12 months and the municipal solid waste (MSW) obtained by Py-FIMS: (a) absolute intensities, and (b) relative abundances.

The relative abundance of compound classes from Py-FIMS analyses can be compared with the results of Py-GC/MS. Both methods revealed (1) the order alkylaromatics and N-containing compounds > phenols > carbohydrates, and (2) reduced proportions of carbohydrates during leachate re-circulation (compare Figure 4b with Figure 1a, b). Py-GC/MS indicated increased proportions of alkylaromatic compounds, phenols and lipids (Figure 1a, b) which were not obtained by Py-FIMS (Figure 4b). This difference can be explained by different analytical conditions. Losses of higher-mass organic compounds (1) due to the Curie-point pyrolysis at 500 °C prior to the GC inlet and (2) along the chromatographic separation and the scan range of m/z 48–450 favored the detection of lower molecular compounds in Py-GC/MS. This explains the agreement of reduced carbohydrate-proportions, which were derived from m/z 60 to 162 (Py-FIMS) and m/z 80 to 138 (Py-GC/MS).

Despite some differences in the proportions of the compound classes, the ratios of carbohydrates

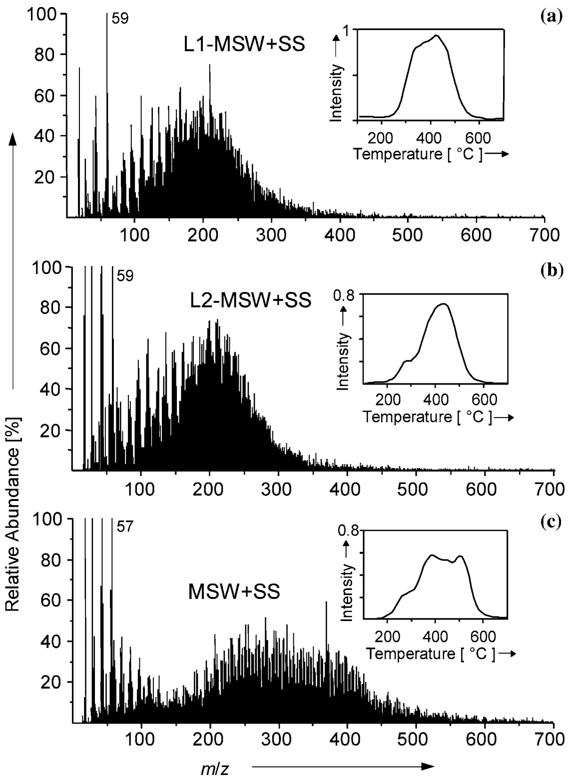

Figure 5. Pyrolysis-field ionization mass spectra and thermograms of the freeze-dried leachates of a municipal solid waste + sewage sludge mixture: (a) L1-MSW + SS after 6 months, (b) L2-MSW + SS after 12 months and (c) solid waste (MSW + SS) after 12 months.

to alkylaromatic compounds ($p \leq 0.01$, $n = 3$) and carbohydrates to N-containing compounds and peptides ($p \leq 0.05$, $n = 3$), derived from Py-FIMS and Py-GC/MS, significantly decreased during the leachate re-circulation. This corresponds to Smidt et al. (2005) who observed decreased proportions of carbohydrates during composting. This agreement, as well as the increased thermal stability (Figure 3a, b), supported the hypothesis of biodegradation of easily decomposable along with biological stabilization of recalcitrant organic matter in re-circulated leachates.

Comparison of compound class proportions of the leachates with the solid waste (MSW) clearly shows that Py-FIMS confirmed the significant differences as determined by Py-GC/MS. After the re-circulation treatment, the solid waste contained high amounts of residual lipids and alkylaromatics at the expense of the microbial degraded and water-soluble carbohydrates and N-containing compounds (Reinhardt 2000; Schalk 2003) which were more intensive in the corresponding leachate L2-MSW (see Figure 4b).

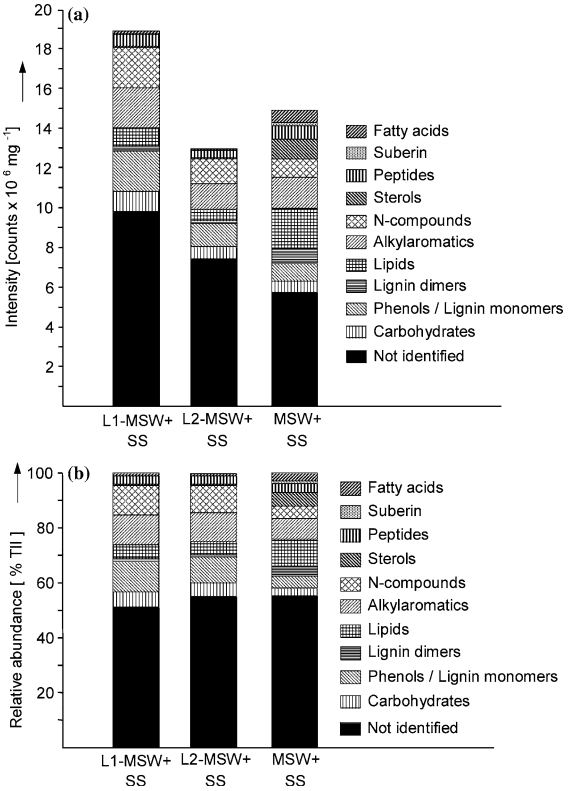

Figure 6. Proportions of 10 structural classes of building blocks of the freeze-dried leachates of a municipal solid waste + sewage sludge mixture: L1-MSW + SS after 6 months, L2-MSW + SS after 12 months and the solid waste (MSW + SS) obtained by Py-FIMS: (a) absolute intensities, and (b) relative abundances.

Py-FIMS was also used to estimate the influence of sewage sludge on the biodegradation of MSW organic matter and the derived leachates (Figure 5). The spectra of L1-MSW + SS (Figure 5a) and L2-MSW + SS (Figure 5b) were intensive in the range of *m*/*z* 50–350 with the base peak at *m*/*z* 59. The influence of sewage sludge was reflected by an initial higher TII of 18.8×10^6 counts mg^{-1} in sample L1-MSW + SS than in sample L1-MSW (13.0×10^6 counts mg^{-1}). After the re-circulation treatment the TII (L2-MSW + SS: $13.1 \times\ 10^6$ counts mg^{-1}) was similar to the initial TII of the variant without sewage sludge (compare Figure 6a with Figure 4a). Furthermore, during the re-circulation treatment, a loss of thermally labile organic compounds (< 400 °C) was observed, whereas the nearly constant maxima of TII at ≈440 °C indicated a higher

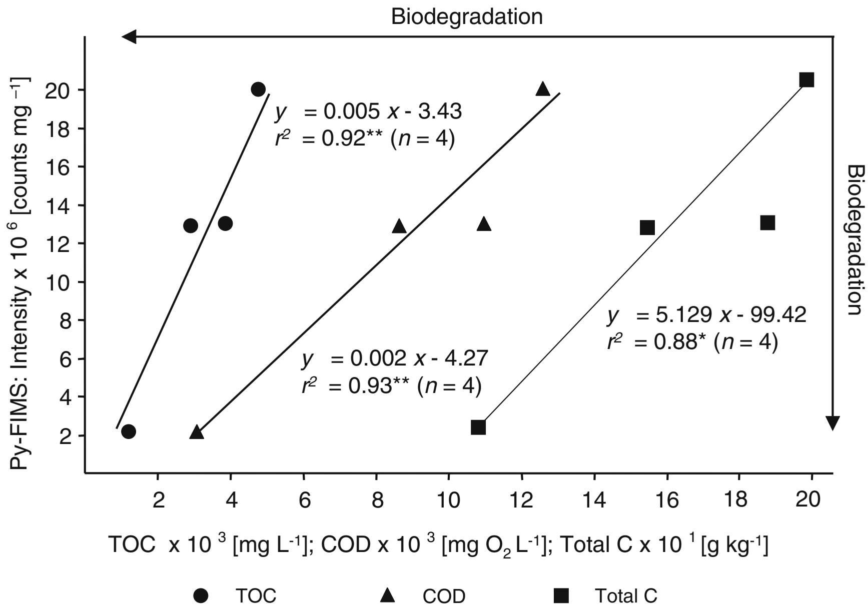

Figure 7. Regression between the total ion intensities (TII) (counts mg^{-1}) as determined by Py-FIMS for the leachates L1-MSW, L2-MSW, L1-MSW + SS and L2-MSW + SS and the (a) TOC (mg l^{-1}) (●) (linear regression $y = 0.005x - 3.43$, where y is TII and x is the concentration of TOC with r^2 for the regression of 0.92 ($n = 4$)), (b) the COD (mg O_2 l^{-1}) (▲) (linear regression $y = 0.002x - 4.27$, where y is the TII and x is the concentration of COD with r^2 for the regression of 0.93 ($n = 4$)) and (c) the total C (g kg^{-1}) (■) (linear regression $y = 5.129x - 99.42$, where y is the TII and x is the concentration of C with r^2 for the regression of 0.88 ($n = 4$)).

stability and lower degradability of organic matter in leachates from solid waste + sewage sludge-mixture than in the variant without sewage sludge (compare Figure 5a, b with Figure 3a, b). Resistance of organic matter to biodegradation can be explained by intramolecular bonds, which appear thermally stable in temperature-resolved Py-FIMS (Schulten & Schnitzer 1993). The heterogeneous composition of organic compounds as indicated by two peaks of TII for MSW (Figure 3c) was also observed for MSW + SS (Figure 5c) with maxima at 380 and 510 °C in the TII-thermograms. The maximum at approximately 380 °C, resembles the maximum at 350 °C that was assigned to lipids and carbohydrates in composts (Smidt et al. 2005).

The mass spectrum of the leached solid waste + sewage sludge-mixture (Figure 5c) revealed a TII (14.8×10^6 counts mg^{-1}) larger than the solid MSW (11.6×10^6 counts mg^{-1}) (compare Figure 6a with Figure 4a). This is explained by the addition of organic matter with sewage sludge, in agreement with previous Py-FIMS investigations of MSW and MSW-sewage sludge composts (Leinweber et al. 2002). The base peak m/z 57 for MSW + SS is derived from peptides, which entered the sample with sewage sludge (Leinweber et al. 1996). Furthermore, the mass range from m/z 15 to 600 in the spectra of MSW (Figure 3c) and MSW + SS (Figure 5c) was larger than in the spectra of the leachates (m/z 50–350) (Figure 3a, b and Figure 5a, b).

Figure 6 shows that the TII per mg sample followed the order L1-MSW + SS > MSW + SS > L2-MSW + SS. These higher ion intensities (counts mg^{-1}) generally exceeded those in the variant without sewage sludge. Furthermore, the ion intensities of the 10 biomarker classes in the leachates derived from the MSW + SS-mixture did not decrease as rigorous with time as in the leachates without the sewage sludge influence (compare Figure 6a with Figure 4a). Thus, the ion intensities confirmed the differently decreased COD and TOC in both leachates along the treatment period (Table 2). Furthermore, the addition of sewage sludge led to a higher content of organic matter and thus required a longer re-circulation treatment for achieving a higher stabilization grade.

Normalization of marker signals to TII showed significantly decreased proportions of N-containing compounds and carbohydrates ($p \leq 0.05$, $n = 3$) after leachate re-circulation (Figure 6b). Proportions of the other compound classes remained constant. This is in agreement with the corresponding Py-FIMS data from the samples without sewage sludge. The comparison of the initial leachates of both variants (L1-MSW and L1-MSW + SS) showed, in agreement with the Py-GC/MS results, significantly lower ratios of carbohydrates:(phenols + alkylaromatic compounds) of 0.24 (L1-MSW + SS) < 0.34 (L1-MSW) ($p \leq 0.01$, $n = 3$). This lower ratio is explained by the addition of alkylaromatics with sewage sludge, which was also described for MSW-composts + sewage sludge mixture (Leinweber et al. 2002). The ratio of carbohydrates:(phenols + alkylaromatic compounds) in the leachates (L1, L2-MSW + SS) remained constant during the re-circulation period. This is explained by the addition of sewage sludge derived organic matter, which inhibited the microbial decomposition (Pichler 1999).

The Py-FIMS analyses of the solid waste (MSW + SS) revealed no distinct sewage sludge effect on the composition of organic matter. Neither proportions of compound classes nor their ratios differed from the variant without sewage sludge (MSW) (compare Figure 6 with Figure 4). Thus, the hypothesis of a preferential elution of sewage sludge derived organic matter obtained by Py-GC/MS is supported by Py-FIMS.

Figure 7 shows significant linear correlations of the total ion intensities (TII) in counts mg^{-1} obtained by Py-FIMS with the concentrations of TOC ($r^2 = 0.92$, $n = 4$), COD ($r^2 = 0.93$, $n = 4$) and total C ($r^2 = 0.88$, $n = 4$) of all investigated leachates. These correlations provide clear evidence that the TII reflect the organic loads of the leachates quantified by TOC, COD, and total C, and the biodegradation along the re-circulation. Similar significant correlations between TII and total organic C were reported in Py-FIMS investigations of a large set of soil samples (Sorge 1995). However, Py-FIMS is a useful complementary analytical method to describe the course of the biodegradation, as well as the stabilization of organic matter during leachate re-circulation, because of (a) higher proportions of identified signals compared to Py-GC/MS, especially for the leachates of the sewage sludge mixture, (b) the estimation of organic matter stabilization during biological treatment by thermograms, and (c) the possibility to establish regressions of sum parameter concentrations with absolute intensities (counts mg^{-1}).

Conclusions

(1) The methodological approach of leachate re-circulation through laboratory-scale reactors filled with municipal waste followed by detailed molecular-chemical investigations of leachates and solids using two independent mass-spectrometric methods was well suited to study organic matter biodegradation in aerobic waste treatment.

(2) The basic chemical characteristics such as COD, BOD, TOC, DOC and total C clearly proved that re-circulation along with the effect of the biological activated trickling filter strongly reduced the organic loads of the leachates, and that this treatment may reduce adverse environmental effects of waste landfills.

(3) The mass spectrometric methods Py-GC/MS and Py-FIMS showed in good agreement that (1) phenols, alkylaromatics and N-containing compounds were the major substance classes in the MSW leachates, and (2) carbohydrates were predominantly decomposed during leachate re-circulation. Moreover, organic matter stabilization during waste treatment was unequivocally verified by the thermal volatilization curves of temperature-resolved Py-FIMS.

(4) Since sewage sludge led to drastically higher loads of organic matter in the leachates therefore sewage sludge addition cannot be recommended to reduce environmental effects of MSW treatments based on current data. However, these organic loads were biologically more resistant to the MSW without sewage sludge.

(5) The clear evidence for biodegradation of organic matter in MSW by re-circulation of leachates, obtained at laboratory-scale, offers a great potential for improved aerobic waste treatments and should be investigated on a larger scale under practical conditions.

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