Investigation of 15-year-old municipal solid waste deposit profiles by means of FTIR spectroscopy and thermal analysis

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Five profiles of a 15-year-old bank containing over three weeks composted municipal solid waste were characterized by means of different parameters habitually applied in waste management (loss on ignition, total organic carbon, total nitrogen, NH_4–N, pH), and in addition by humic acid determination, FTIR spectroscopy and thermal analysis. Stabilization processes are revealed by humic acid contents. Over the 15 year period organic matter had developed in various ways. Highest humic acid contents were found at 0.5 m below the surface. Below 1.0–1.5 m anaerobic conditions dominated causing a strong decline of humic acid concentrations. Despite similar contents of organic matter at 0.5 m and at 3.0 m organic matter quality differed. These differences were verified by infrared spectroscopic investigations and thermal analyses (differential scanning calorimetry DSC). The spectral pattern of 15-year-old profile samples (municipal solid waste including the biogenic fraction) was compared to current municipal solid waste and abandoned landfill materials. Current municipal solid waste samples comprised different degradation stages from fresh materials to stabilized waste, suitable for landfilling according to Austrian standards. Municipal solid waste originating from abandoned landfills closed in the seventies represented stable material. Principal component analysis was performed to detect similarities and differences. It is evident that the profile samples constitute a particular group in between municipal solid waste and abandoned landfill material. Some differences can be attributed to the divergent composition of municipal solid waste in the eighties when the organic fraction was not separated. Otherwise, landfill materials from the seventies with the same composition regarding the organic fraction were deposited together with construction waste. Heat flow curves (DSC profiles) of municipal solid waste, representing different decomposition stages, illustrate the development of enthalpies and reveal the status of the profile samples. It is evident that mechanical–biological pretreatment leads to a faster stabilization of waste organic matter.

Introduction

The regulated management of waste collection, separation, treatment and disposal emerged only over the last two decades in several European countries. In the past no attention was paid to waste pretreatment or barrier systems. Negative environmental effects originating from abandoned landfills and deposits stimulated the development of waste management strategies. The ongoing discussion concerning gaseous emissions and their contribution to global warming has become a crucial issue in waste science. Whereas in the past research focused on the environmental impact, especially on gaseous emissions and leachate, interest in the waste material itself, its properties and behavior, has now come to the fore. The long-term behavior of landfilled or deposited waste organic matter is an important issue in terms of the emission potential. Waste materials that contain a considerable amount of biodegradable organic matter contribute to gaseous and liquid emissions in landfills. Biological treatment before landfilling aims at reduction of reactivity. Due to the complex composition of the material manifold processes and interactions between organic and mineral compounds take place. According to environmental conditions either humification or mineralization are favored.[1] Humification contributes to carbon sequestration, therefore producing a positive environmental effect. Deposited waste materials from the past subjected to a similar transformation and stabilization are suitable objects for investigation.

The application of innovative analytical tools for waste characterization and monitoring parallels the increasing interest on waste matter, being an analytical challenge due to its complexity. Infrared spectroscopy[2–6] and thermal analysis have proven useful analytical tools with which to describe biological processes of municipal solid waste and composts.[7–12] In landfill research FTIR spectroscopy was applied for successful remediation control.[13,14]

Multivariate data analysis supports evaluation of huge data sets generated by infrared spectroscopic and thermal investigations.[15,16] Hidden structures and underlying features of huge data sets are revealed by principal component analysis (PCA). The latter has been used in many fields of waste

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management for treatment evaluation and process control. Ecological assessment of landfills was performed by means of multivariate analysis.[14,17] Carbonate stabilization of fly ash originating from municipal solid waste incineration intended for landfilling,[18] process control during composting[19,20] and anaerobic treatment[21] were investigated using PCA. Chemometric methods were applied to study the effects of chemicals on cellulose pyrolysis, indicating the usefulness of these evaluation methods to extract more information from huge data sets generated by thermal methods.[22]

The objective of the present study was to shed light on the long-term behavior of waste organic matter by means of profile investigations of a 15-year-old bank of piled municipal solid waste that had undergone a 3-week composting process. Emphasis was placed on stabilization processes, especially on humification, that had taken place under local environmental conditions. Samples were compared to current municipal solid waste, undergoing mechanical–biological treatment (MBT), and to abandoned landfill sites from the seventies in terms of infrared spectroscopic and thermal characteristics.

Materials and methods

Deposit description, sampling and sample preparation

All samples originated from five 3-metre-deep profiles of a 15-year-old bank of piled municipal solid waste mixed with sewage sludge. Municipal solid waste from the period concerned comprised all fractions that are separated nowadays by both biowaste collection and mechanical treatment in the MBT plant (especially plastics). The last part of the bank was cut by an excavator to obtain a vertical surface for profile sampling. At the basis the distance to the surface was 1.5 m, the interval between the profiles was 80–100 cm. A schematic design of the sampling site is shown in Fig. 1. According to information provided by the company the waste material had been rotted for 3 weeks before being piled up. A uniform mixture of waste material had been deposited, a prerequisite for the intended investigations to avoid zoning by layers of different materials. Herbaceous plants covered the surface of the sampling area. Annual precipitation in the region is 1000 mm.

In total 50 samples ($\sim$3 kg each) were collected from different depths (0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 m) of the five profiles (10 $\times$ 5). The sample name is assigned to the profile number (P1, P2, P3, P4, P5) and to depth, indicated in m (*e.g.* P3-0.5).

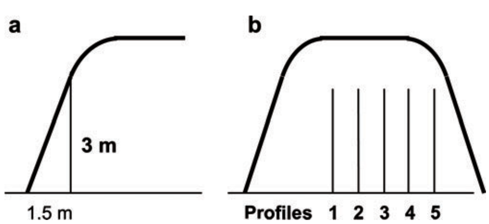

Fig. 1 Side view (a) and front view (b) of the sampling site (15-year-old bank of municipal solid waste).

NH_4–N was determined from the fresh sample. For all other analyses the waste material was air-dried, ground in an agate mill and sieved < 0.2 mm.[23] MBT materials were ground in a cutting mill first.

Samples for comparison (humic acid contents, FTIR spectroscopy and thermal analysis)

Ten composite samples originated from a 3-metre-deep peat bog profile in Lower Austria.

Sample set 1 (85 samples) represents current municipal solid waste from 12 different MBT-plants, covering diverse degradation stages from fresh to landfilled material (120 weeks). The sample name indicates the material (MBT) and the age (weeks = w, year = y), *e.g.* MBT-3w. If further details are needed in some cases they are explained in the text.

Sample set 2 (58 samples) originates from an abandoned landfill operated and closed in the seventies. At this time neither liners nor covers were used. The landfill surface was covered with annual and perennial plants. The sample name indicates the material (LF) and the age, *e.g.* LF-30y.

Chemical investigations and pH value

Humic acids were extracted according to Gerzabek *et al.* using a 0.1 molar Na-pyrophosphate (pH 10.5) solution and precipitated with 37% HCl.[24] Extracts of different fractions were measured photometrically and quantified by gravimetric calibration. Loss on ignition (LOI), total organic carbon (TOC), total nitrogen (N_t), NH_4–N, and pH were determined according to Austrian Standards ÖNORM S 2023.[25] Two replicates were performed.

Infrared spectroscopic investigations

Two milligrams of the prepared sample material were pressed with 200 mg of KBr (FTIR grade) to a pellet and measured immediately in the mid-infrared area (4000–400 cm^{-1}) using the transmission mode. Thirty two scans were recorded, averaged and corrected against ambient air as background (Instrument Bruker Equinox 55, OPUS Software). Two to three replicates were performed. Reproducibility of waste spectra has been described previously.[26]

Relative band heights were calculated as described by Smidt *et al.*[27]

For average spectra and principal component analysis (PCA) spectra were vector normalized.

Thermal analysis

Simultaneous thermal analysis comprising thermogravimetry (TG) and differential scanning calorimetry (DSC) was carried out with an STA 409 CD instrument (Netzsch GmbH, Proteus Software). Combustion parameters: 16 mg of the prepared sample material, heating rate 10 K min^{-1} in the temperature range from 30–950 °C, gas flow 120 ml min^{-1} (80% He/20% O_2), Al_2O_3 pan. DSC curves were corrected in that the DSC curve of the empty pan was subtracted. Energy contents were calculated by integration of the area below the DSC curve and a horizontal baseline from 30 °C to 650 °C.

Three samples (0.1, 0.5, 3.0 m) of profiles 1 and 2 were compared to current MBT waste from the same plant. After 3 weeks of biological treatment the material is dried and sieved through 25 mm. The fraction (fr1) >25 mm (MBT-3w-fr1) containing more organic matter is intended for combustion. The fraction (fr2) <25 mm (MBT-3w-fr2) that is rich in inorganic compounds is intended for landfilling. In addition landfilled MBT material (120 weeks = MBT-120w) and landfill material from an abandoned landfill (~30 years = LF-30y) complete the series.

Data evaluation

Data evaluation was performed by Bruker Software (OPUS 4.0) and Camo 9.2 (Unscrambler)).

Results and discussion

Visual inspection of the profiles indicated anaerobic conditions below 1 m in profiles 1–3, indicated by the dark color. In profiles 4 and 5 the dark colored section was below 1.5 m and 2.0 m, respectively. Due to the location at the outer border area these profiles seemed to be increasingly influenced by penetrating air.

Several parameters are displayed in Table 1. Averages of two replicates are indicated. The deviation complies with the required limits of Austrian Standards.[25] For comparison humic acid contents and loss on ignition of a peat bog profile are included. Humic acid contents of the waste bank profile are highest at 0.5 m, especially in profile 3. Humic acid contents decrease to a low level below a depth of 1 m. These results are in accordance with observations of humification processes in composts.[28] Although aerobic conditions are necessary to provide aromatic building blocks such as lignin, excessive aeration promotes increased mineralization. A depth of 0.5 m seems to have favorable conditions for humification. Organic matter contents (LOI) increase up to a depth of 0.5 m, decrease and increase further. TOC and total nitrogen contents display a similar behavior. The layer between aerobic and anaerobic conditions (1 to 1.5 m) features the lowest organic matter contents. It can be hypothesized that such intersection areas provide favorable conditions for anaerobic and aerobic microbial communities. Changes of all parameters are less distinct in profiles 4 and 5. The pH value is 7.5–7.8 in all depths and profiles, with the exception of profiles 1–3 where the pH value reaches 7.9 and 8.0 at 2.5 m and 3.0 m. In these profiles considerable concentrations of NH_4–N (1344–9924 mg kg^{-1} DM (dry matter)) were found at 3.0 m, likely caused by dammed leachate. In all other samples only minor concentrations (0.4–5.2 mg kg^{-1} DM) were determined.

Compared to humification in a peat bog profile the different genesis becomes evident as shown in Fig. 2. Entrance of air from the surface influences development in the bank profile. By contrast, humification progresses evenly in the peat bog profile with growth from the bottom to the top. It should be emphasized that the composition of municipal solid waste in the eighties differs from current municipal solid waste due to the presence of the biowaste fraction. The ingredients of biowaste improve humic substance synthesis. Therefore relatively high concentrations of humic acids are found in the profiles.

Fig. 2 displays data (profile 3) of humic acid contents (HA) compared to HA concentrations in a peat bog profile, the loss on ignition (LOI) and the ratio of relative band heights (2920/1640 cm^{-1}). The results shed light on the considerable transformation that had taken place. Although the organic matter content is the same at 0.5 m and 3.0 m the properties of organic matter have changed in that the material was increasingly humified at 0.5 m. These findings are confirmed by the band height ratio displaying a minimum at 0.5 m, indicating a decrease of aliphatic substances in favor of aromatic

Table 1 Data (average of 2 replicates) of humic acid contents (HA), loss on ignition (LOI) in bank and peat bog profiles, total nitrogen (N_t), and total organic carbon (TOC) referring to organic dry matter (ODM) and dry matter (DM); P1–P5 = sample names assigned to profiles

Depth/m	P1 HA contents (% ODM)	P2	P3	P4	P5	Peat	P1 LOI (% DM)	P2	P3	P4	P5	Peat
0.1	5.7	7.3	7.1	4.2	4.7	4.4	24.3	26.0	23.1	22.4	21.2	99.2
0.2	6.2	7.4	7.3	3.4	4.7	3.7	25.6	26.9	24.4	22.8	24.1	99.2.
0.3	7.2	8.1	7.2	3.5	4.0	3.6	25.1	26.0	24.9	21.2	22.8	99.2
0.4	7.7	11.6	10.5	3.3	3.5	2.8	27.0	27.4	27.7	20.0	21.4	99.3
0.5	9.4	12.2	19.5	7.1	3.3	2.6	27.9	27.4	30.8	22.5	22.9	99.6
1.0	4.3	4.7	6.0	6.9	7.0	2.7	22.6	22.6	21.4	20.3	25.3	99.3
1.5	3.2	4.5	5.0	8.4	5.9	3.0	20.9	18.1	21.6	21.6	20.8	99.2
2.0	2.6	2.5	3.1	5.3	6.8	4.1	27.3	25.8	24.3	23.9	24.8	98.9
2.5	3.6	3.1	2.5	3.0	5.0	3.9	30.3	29.3	26.5	25.4	22.4	98.1
3.0	2.5	2.4	2.2	2.3	3.2	3.9	34.8	32.9	30.8	30.0	26.7	97.6

	N_t (% DM)					TOC (% DM)				
0.1	0.88	0.98	0.87	0.68	0.65	14.6	14.5	11.8	12.5	12.2
0.2	0.93	0.93	0.88	0.72	0.73	13.8	14.3	15.0	12.7	12.7
0.3	0.90	0.85	0.90	0.62	0.71	15.2	18.4	13.7	13.6	14.5
0.4	0.89	0.88	0.95	0.56	0.63	17.2	15.4	15.8	12.0	11.9
0.5	0.96	0.93	1.06	0.69	0.67	16.5	16.6	17.2	12.3	13.4
1.0	0.63	0.65	0.63	0.68	0.77	12.1	12.4	13.2	11.4	15.7
1.5	0.58	0.55	0.69	0.68	0.68	12.6	12.9	14.8	13.3	12.4
2.0	0.78	0.74	0.68	0.76	0.81	17.5	14.5	14.9	15.3	16.0
2.5	0.86	0.78	0.75	0.77	0.67	17.9	16.9	16.9	15.7	12.9
3.0	0.99	0.96	0.89	0.86	0.81	19.7	20.5	17.7	17.8	16.5

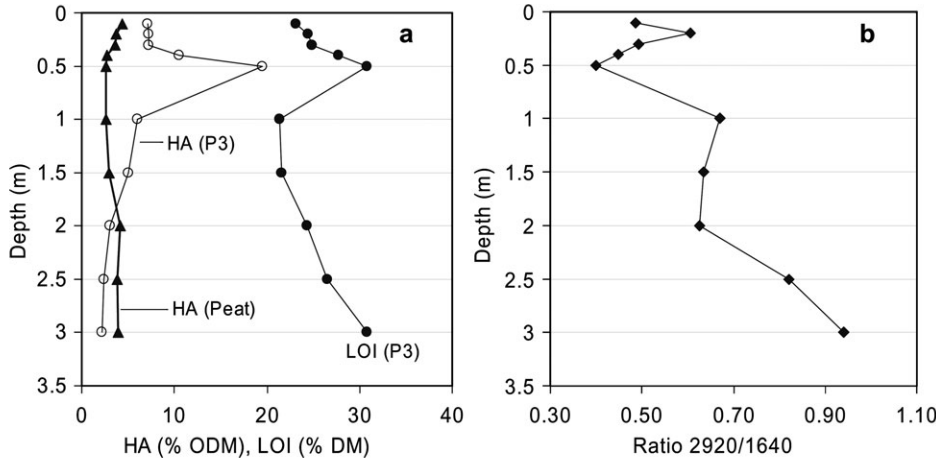

Fig. 2 (a) Humic acid (HA) contents (%) referring to organic dry matter (ODM) in profile 3 (P3), the peat bog profile and LOI of P3; (b) relative band height ratio (2920/1640) of P3.

compounds. Band height ratios of each profile sample are compiled in Table 2.

The intensity of the aliphatic methylene band at 2920 cm^{-1} (Fig. 3) correlates with the stability of the sample.[4,13,14,26] 'Stability' in this context signifies a stage of low biological reactivity and turnover rates. It corresponds to a specific chemical composition that is reflected by the spectral pattern. Indicator bands of metabolic products are no longer visible and band intensities become nearly constant. The Austrian Landfill Ordinance defines this stage by limit values regarding biological parameters.[29] At the base of the waste bank the maximum value can be ascribed to the aliphatic character of organic matter that did not undergo substantial degradation. Laboratory reports from the eighties state LOI values of 29–31% DM for 3-week composted municipal solid waste.

Infrared spectroscopic investigations and principal component analysis

In order to identify similarities with current municipal solid waste (MBT fraction) and abandoned landfill materials spectra and thermal characteristics were compared. Average spectra of each sample set are presented in Fig. 3. Band assignment, matrix effects and interpretation of waste spectra have been described in previous studies.[4,6] With respect to organic matter development it is evident that profile samples are in between landfills and MBT waste. The aliphatic methylene bands at 2920 and 2850 cm^{-1} and the 1640 cm^{-1} band (assigned to C=O vibration of amides, CO_2 vibration of carboxylates and C=C of aromatics and alkenes) are much weaker in the profiles than in MBT waste. The 1320 cm^{-1} band, an indicator of immaturity, is no longer observed in the profile samples. This band can be assigned to (aromatic) amines. It decreases during the biological treatment and disappears when the material is stable. Strong bands that can be attributed to inorganic compounds are found in all spectra (carbonates: C–O stretch vibration and C–O out-of-plane bend at 1425 and 875 cm^{-1}, clay minerals: Si–O–Si stretch at 1030 cm^{-1}). Due to the geological background in Austria carbonates are invariably part of municipal solid waste. The intense carbonate bands in the landfill spectrum can be traced back to the higher portion of construction waste deposited together with municipal solid waste in the seventies.

In order to extract more information from spectral characteristics principal component analysis (PCA) was calculated. Using the overall wavenumber range from 4000 to 400 cm^{-1} grouping of each sample set is visible in the scores plot (Fig. 4a). Profile samples are closer together due to the 'homogeneity' of the piled material. Nevertheless, differences in terms of degradation stages cause distances between the samples. The sample group of the landfill material (LF) and

Table 2 Band height ratio 2920/1640 of profile samples

Depth/m	2920/1640				
	P1	P2	P3	P4	P5
0.1	0.41	0.43	0.49	0.61	0.41
0.2	0.41	0.41	0.61	0.47	0.43
0.3	0.39	0.48	0.49	0.45	0.42
0.4	0.52	0.38	0.45	0.55	0.47
0.5	0.37	0.32	0.40	0.48	0.47
1.0	0.49	0.48	0.67	0.45	0.46
1.5	0.61	0.60	0.63	0.54	0.41
2.0	0.50	0.61	0.63	0.59	0.42
2.5	0.75	0.81	0.82	0.61	0.45
3.0	0.78	0.88	0.94	0.77	0.61

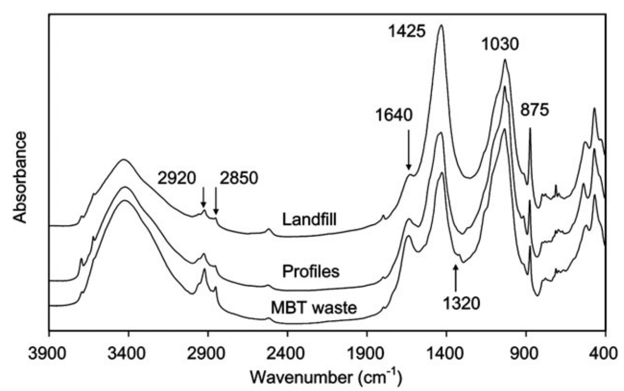

Fig. 3 Average spectra of the sample sets 'Landfill', 'Profiles', 'MBT waste'.

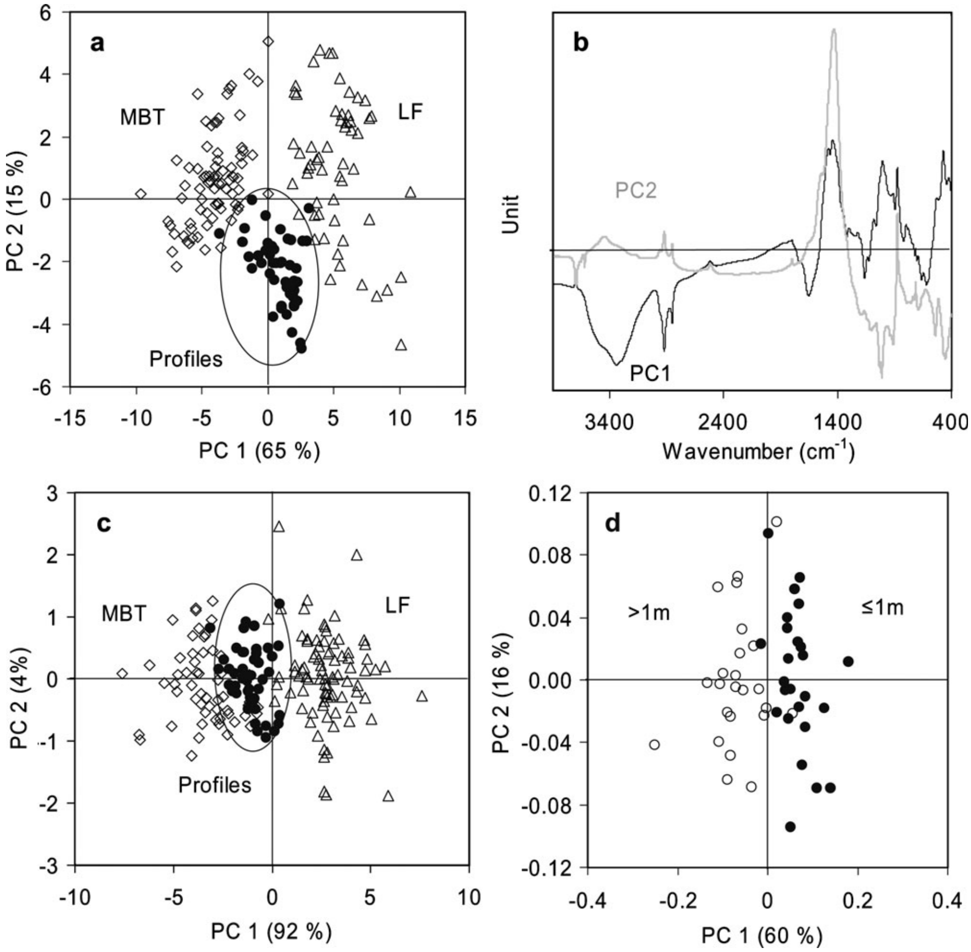

Fig. 4 Scores plot (a) and loadings plot (b) of the sample sets 'Landfill (LF)', 'Profiles', 'MBT waste (MBT)' based on a PCA of spectral data (range 4000–400 cm^{-1}); (c) PCA of these samples using the range 4000–2770 cm^{-1}; (d) PCA of profile samples using the range 4000–400 cm^{-1}.

the MBT waste (MBT) are more widely spread according to the heterogeneity of the material composition and different stages of degradation. The first principal component (PC) explains 65% of the variance, the second PC 15%. The loading plot (b) reveals the responsible regions in the spectrum that contribute to the variance: the broad band of bonded and non-bonded O–H groups (water) at about 3400 cm^{-1}, the aliphatic methylene bands (–CH_2 stretch vibration at 2920 and 2850 cm^{-1}), the 1640 cm^{-1} band and the strong bands of inorganic compounds, mainly carbonates at 1425 cm^{-1} and clay minerals at 1030 cm^{-1} (Fig. 4).

The PCA calculated with data from the selected wavenumber region 4000–2770 cm^{-1} also leads to separation of the sample sets, demonstrating the discrimination power of the aliphatic methylene bands that serves as a relevant indicator of organic waste stability (c).[14,30,31] 92% of the variance is explained by the first PC. According to the scores plot degradation of the material is reflected along the *x*-axis from the left to the right: current MBT material-profile samples–abandoned landfill material. The PCA of the profile samples over the total wavenumber range (4000–400 cm^{-1}) enables samples to be distinguished in the mostly aerobic zone from 0.1 to 1.0 m and samples from 1.0 to 3.0 m that are influenced by anaerobic conditions.

Thermal analysis

The thermal behavior in dependence on temperature reflects the physical properties of the material. Thermal characteristics of waste subsume physical properties of all compounds present in the mixture and thus provide information on the chemical composition in a general way. Chemical changes caused by degradation are paralleled by changes in thermal features. Due to decomposition of organic matter the heat flow of the material decreases corresponding to the decreasing enthalpy. However, referring to organic dry matter an increase of enthalpies can be observed due to enrichment of recalcitrant substances, stabilization and humification processes (Table 3). Organic matter contents were determined by means of the mass losses between 30 and 650 °C (TG curves not shown). Fig. 5 displays the heat flow curves (DSC) of several MBT materials representing different stages of degradation. Three profile 3 (P3) samples from 0.1, 0.5, and 3.0 m are compared to current MBT waste originating from the same plant (two different 3-week-old fractions (fr1 and fr2): MBT-3w-fr1 and MBT-3w-fr2), deposited MBT material (120 weeks = MBT-120w) and landfill material (30 years = LF-30y).

The DSC pattern displays two prominent exothermic peaks, corresponding to the oxidative combustion of organic matter

Table 3 Enthalpy of MBT-, profile- and landfill samples referring to dry matter (DM) and organic dry matter (ODM)

Sample	Enthalpy J g^{-1} (DM)	Enthalpy J g^{-1} (ODM) (30–650 °C)	Mass loss %
P3-0.1	4433	17 446	25.41
P3-0.5	5200	17 497	29.72
P3-3.0	4490	15 123	29.69
P2-0.1	4885	17 642	27.69
P2-0.5	5314	20 438	26.00
P2-3.0	5144	13 925	36.94
MBT-3w-fr1	7556	14 816	51.00
MBT-3w-fr2	5455	19 440	28.06
MBT-120w	5488	27 661	19.84
LF-30-y	3448	49 612	6.95

fractions and an endothermic peak between 700 and 800 °C assigned to the decay of carbonates.[11] Due to organic matter decomposition peak intensities decrease and give way to a flattened elongated exothermic curve.

In the profile sample P3-3.0 the second exothermic peak is still present, indicating that degradation did not progress very fast under anaerobic conditions. The corresponding enthalpies of the samples are compiled in Table 3. Sample MBT-120w demonstrates the efficiency of the biological treatment before landfilling as the decrease of enthalpy can be achieved much faster. According to the Austrian landfill ordinance a limit of the calorific value is required before landfilling (6600 kJ kg^{-1} DM).[29] Apart from sample MBT-3w-fr1 all samples comply with this regulation. This fraction is intended for combustion and therefore higher calorific values are not disadvantageous. With regard to the profile samples it can be concluded that the 3-week composted municipal solid waste was similar to this fraction and, from the current point of view, not sufficiently stabilized when it was piled up. However, over the fifteen years the mineralization and stabilization processes have slowly continued depending on environmental conditions and air supply.

The landfill material (LF-30y) with a low organic matter content that is stable with regard to all relevant parameters becomes similar to soil samples regarding the enthalpy of the remaining organic matter.[12]

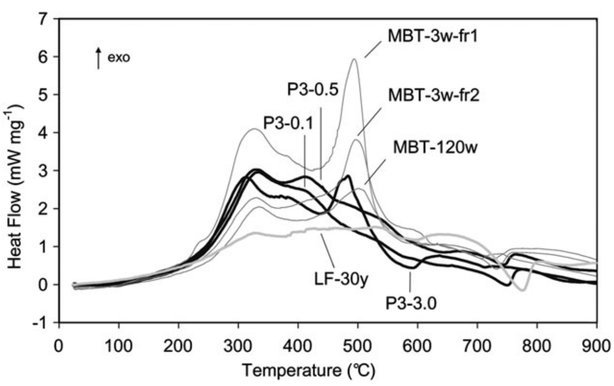

Fig. 5 Thermal pattern (DSC) of profile P3 representing three depths (0.1 m = P3-0.1, 0.5 m = P3-0.5, 3.0 m = P3-3.0) compared to different decomposition stages and fractions (3 weeks, fraction >25 mm = MBT-3w-fr1; 3 weeks, fraction <25 mm = MBT-3w-fr2; 120 weeks = MBT-120w) of MBT waste and abandoned landfill material (30 years) (LF-30y).

Conclusions

Abandoned landfills and deposits are well suited to the investigation of the long-term behavior of waste organic matter. Humification took place preferentially in the 0.5 m layer under aerobic conditions, where mineralization or retarded degradation did not prevail. The biogenic fraction that was not collected separately in the past seems to improve the humification process. FTIR spectroscopy combined with multivariate data analysis and thermal methods are useful tools to assess organic matter properties in deposited waste materials and to compare them with current materials. The investigations performed have shown that biological treatment before landfilling is a useful measure in achieving the desired quality at a much faster rate. 'Quality' of municipal solid waste primarily means 'stability' of organic matter with regard to biological parameters to avoid emissions, especially methane. Thus stabilization is not delayed and left to chance.

The analytical methods applied are promising for use in the assessment of waste matter in abandoned landfills and deposits due to their comprehensive information and available evaluation tools based on multivariate statistical methods. For municipal solid waste and landfill materials validated models will be developed that enable biological parameters to be predicted.[26] This procedure provides faster results and more comprehensive information based on infrared spectral and thermal characteristics than many stipulated, time-consuming investigations. The development and establishment of new standards for waste characterization using the interrelation between biological activity and enthalpies are challenging tasks.

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