

Influence of Input Materials and Composting Operation on Humification of Organic Matter

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ABSTRACT

Composts play an important role in the context of resource recovery and soil improvement by increasing soil organic matter. This study focuses on compost quality in terms of humic acid (HA) content which due to its favorable properties provides benefits for soils and plants. A series of Austrian and foreign composts (174 samples) were investigated to find out the level of HAs built up during composting. HA contents from 5.4% ODM to 46.8% ODM were determined. The influence of input materials and process operation on HA formation was demonstrated by monitoring several composting processes. Fourier Transform Infrared (FT-IR) spectroscopy and thermal analysis such as thermogravimetry (TG) and differential scanning calorimetry (DSC) were applied as analytical tools for process and product control. Well-balanced mixtures of biowaste comprising kitchen-, market- and yard waste were found to provide the best conditions for HA formation. In these biowastes not only suitable molecules for humification were available, but microbial activity was also maintained for a longer period due to the diverse degradability of chemical compounds. Moderate aeration favored humification whereas too much air supply promoted mineralization. HAs undergo maturation during composting which was revealed by changes of spectral and thermal patterns and the increase of enthalpy. HAs are a sink for carbon and nitrogen. The nitrogen content in HAs was in the range from 5.11 to 8.91% of HA dry matter. The contribution to the total nitrogen in the composts was found to be 15 to 61%. HA molecules contain 48 to 54% carbon. HAs play an important role in carbon sequestration and will be considered as a key factor for carbon credits in the future.

Keywords: compost humic acids, FT-IR spectroscopy, input materials, multivariate data analysis, process operation, thermal analysis

INTRODUCTION

Composting of organic waste materials is a biotechnological process which currently undergoes a comeback. In the context of resource recovery this technology has gained in significance during the last decade. Biogenic materials from households, markets, gardens, from food industry and agriculture are considered valuable raw materials to produce composts for different purposes (Ahmad *et al.* 2007).

For a long time composting was carried out based on the experience of farmers and gardeners. However, in recent years composting has become a relevant topic in agriculture, horticulture, soil science and waste management, promoting a scientific interdisciplinary approach to composting. The loss of organic matter in agricultural soils (Montanarella 2003; Leifeld and Kögel-Knabner 2005) is an additional reason for research activities in this field, being aware that stable organic matter has to be recycled to maintain soil functions in the long term. The increase of soil organic matter has been considered the main bio-physical strategy for mitigating desertification in Europe (Stroosnijder 2000). In several north-western European countries and in Russia the fertility of poor sandy soils and farmer's prosperity have been increased by continuous compost application that has led to soil formation over the centuries. These anthropogenic soils (Plaggen Soils) are characterized by a higher organic matter and phosphorus content. The latter can be traced back to manure which was a main component of these composts as well as plant materials (Pape 1970; Conry 1974; Hubbe *et al.* 2007).

Composting has a long-standing tradition all over the world due to the fact that it can be performed with marginal technical equipment. Thus composting still represents an appropriate technique to operate organic waste in deve-

loping countries where compost application on poor soils can affect the improvement of soil properties (Puppala *et al.* 2007; Leroy *et al.* 2008). In industrial countries the increasing interest in composting has stimulated the development of composting devices. However, the understanding of the microbial metabolism and the knowledge of material properties play a crucial role in process operation.

The use of biogenic waste materials such as yard, market and kitchen waste provided an incentive in several European countries for a legal frame in terms of input materials and compost quality. However, quality standards need to be improved and current research initiatives are dealing with the definition and the establishment of quality parameters that describe the benefits of composts in a more comprehensive way. Nutrients (Courtney and Mullen 2008) and phytosanitary effects (Bruns *et al.* 1996; Erhart *et al.* 1999) are in the focus of interest. These properties are strongly related to organic matter quality. Therefore compost organic matter deserves closer attention.

The composting process aims at stabilization of organic matter in order to reach maturity which is a prerequisite for plant compatibility (Sellami *et al.* 2008). Stabilization is achieved by mineralization and humification. Mineralization results in degradation of organic molecules to inorganic compounds. Humification comprises degradation to a certain extent and synthesis of stable organic molecules. HAs are synthesized during composting which is the only technological humification process. Humic substances are built up with molecule moieties originating from degraded biomolecules. Aromatic rings constitute the skeletal structure. Depending on the integrated molecules, functional groups vary widely and consequently a stoichiometric formula for a specific molecule does not exist. Determination of humic substances focuses on separation of "fractions" according to

their solubility at different pH values: fulvic acids, HAs and humins. HAs are extracted under alkaline conditions and precipitated at pH 1. HAs in soils represent a stable fraction of humic substances with low turnover rates (Scheffer and Schachtschabel 1998). Compared to humins they are extractable and can be quantified by conventional analytical methods. The chemical composition of HAs, the mechanisms of synthesis, and their functions have been widely investigated in soil science (Tan 2003; Sutton and Sposito 2005). Different analytical approaches were suggested for HA characterization (Adani and Ricca 2004; Adani *et al.* 2007). Due to their well known favorable properties for soils and plants the content of HAs is suggested as a quality criterion for composts.

Besides the synthesis of humic substances leads to reduction of gaseous emissions and therefore provides an additional environmental benefit in that organic compounds are not only mineralized and released as CO₂ but also bound in stable HAs. This process is an effective contribution to carbon sequestration.

The objective of this research was to find out which input materials and process operation can support humification in composts. HAs were used as an indicator of humification. Characteristics of HAs in composts were revealed by FT-IR spectroscopy and thermal analysis and compared to characteristics of soil HAs. Classification of appropriate biogenic waste materials and prediction of HA contents were performed by means of developed models based on FTIR spectroscopy and multivariate data analysis.

MATERIALS AND METHODS

Materials

The materials, bulk materials, number of samples and their origin, details of aeration, windrow systems and composting time are summarized in **Table 1**. The Austrian Compost ordinance defines input materials and quality classes and two types of composts are distinguished: compost from sewage sludge and biowaste. Biowaste comprises kitchen (fruits, vegetables) waste mainly originating from the separated collection. This mixture is called “biowaste” throughout the manuscript.

For nitrogen and carbon determination of HAs 15 out of 20 samples shown in **Fig. 1** were selected, dialyzed and freeze-dried.

Final products of sewage sludge composts from 8 different composting plants were used for classification.

Composting operation

Composting can be operated by various technical systems. The main influence factors on the rotting progress are the input materials and the rotting procedure. Biogenic waste or sewage sludge usually serves as input materials in Austrian composting plants.

Manure compost is generally produced in farms. Processes can be classified according to the input materials and additives, the machinery and process operation. The latter is mainly influenced by the shape of the windrows and the aeration system.

Gas measurement in the plant

CO₂ and CH₄ were detected with the Multigas Analyzer LMSx (MLU[®]). Temperature was measured with the Testo 110 (Testo[®]).

Chemical analyses and HA determination

Carbon and nitrogen were determined by combustion by a CNS analyzer (VarioMax[®]). Loss on ignition (LOI) was determined according to Austrian Standard Methods ÖNORM S 2023 (Austrian Standards Institute 1986). HA analysis was carried out according to Gerzabek *et al.* (1993) based on alkaline extraction with 0.1 molar sodium pyrophosphate solution and precipitation with HCl (37%). Based on gravimetric determination HA contents were calculated from photometrically measured optical densities and referred to as organic dry matter (ODM = LOI). HA determination was also carried out using prediction models based on spectroscopic methods and partial least squares regression (PLS-R), developed by Meissl *et al.* (2007, 2008).

For additional analyses (FT-IR spectroscopy, thermal analysis) precipitated HAs were dialyzed and freeze-dried.

Biological tests

Respiration activity was measured over a 4-day-period (RA₄) or a 7-day-period (RA₇) in a Sapromat (Voith Sulzer[®]) where the oxygen uptake (mg O₂ g⁻¹ DM) was recorded in grams of dry matter (Binner *et al.* 1998).

Fourier Transform Infrared (FT-IR) Spectroscopy

FT-IR absorbance spectra were recorded using a Bruker (Germany) FT-IR spectrometer (EQUINOX 55) equipped with a DTGS detector. Two milligrams of the sample were mixed with 200 mg KBr (Aldrich; 22,186-4; FT-IR grade) and homogenized in a mortar. KBr pellets (diameter 13 mm) were prepared in a standard device under vacuum and at a pressure of 75 kN cm⁻² for 3 min. Thirty-two scans per sample were collected in the wavenumber range 4000-400 cm⁻¹ in transmission mode at a spectral resolution of 4 cm⁻¹ and the spectra collected corrected against air as background.

For multivariate data analysis, the spectra were vector normalized. Vector normalization was used to reduce possible negative effects (e.g. differences in thickness of the pellet and baseline offset). The procedure is described by Smidt *et al.* (2008).

Table 1 Materials and their origin (number of samples used for principal component analysis are indicated in brackets).

Materials	Origin	N ^o of samples	Bulk material	Aeration system	Composting time (days)	Windrow shape
Compost end products	Different Austrian and foreign composting plants	20 (174)	-	-	-	-
Process A	Lab scale experiment	6	wood chips	passive	189	lab scale
Process B	Austrian biowaste composting plant	15	branches, twigs	passive	142	line windrow
Process C	Austrian biowaste composting plant	47	yard waste, sieve separated overflow	passive	260	four weeks line, then table pile
Process D	Austrian biowaste composting plant	20 (121)	yard waste, sieve separated overflow	passive	149	line windrow
Process E	Austrian biowaste composting plant	17 (126)	yard waste, sieve separated overflow	two weeks active pressure	140	two weeks boxes, then table pile
Process F	Austrian biowaste composting plant	(131)	yard waste, sieve separated overflow	passive	140	four weeks line, then table pile
Process G	Austrian biowaste composting plant	(71)	yard waste, sieve separated overflow	six weeks active pressure	40	six weeks table pile, then conic windrow
MBT-material	MBT-waste originating from three Austrian plants	83	-	-	-	-

Thermal analyses

Thermal analyses were performed by means of an instrument for simultaneous thermal analysis STA 409 CD Skimmer (Netzsch GmbH). The heating rate was set to 10 K min⁻¹. Oxidative combustion was carried out with a gas flow of 120 ml min⁻¹ (80% He/20% O₂). A sample amount of 16.00 mg was combusted in an Al₂O₃ pan. Sample DSC curves were corrected by subtraction of the DSC curve of the empty pan.

Enthalpies were calculated by integration of the peak area below the DSC curve drawing a horizontal baseline from 30 to 650°C (between the second exothermic peak of organic matter and the endothermic peak of the carbonate decay).

Multivariate data analyses

Principal Component Analysis (PCA) and Soft Independent Modeling of Class Analogy (SIMCA) were carried out using the Unscrambler 9.6 software (Camo Software AS, www.camo.com). PCA is used to analyze large data sets. The information of the original data matrix *Z* is projected to the smaller number of dimensions needed to describe the relevant information contained in the original observation. The original data matrix *Z* is decomposed into a "Scores matrix (*T*)", a "transposed Loadings matrix (*P*^T)" and an "Errors matrix (*E*)", mathematically explained as $Z = T * P^T + E$. SIMCA provides a procedure for classification by means of PCA class modeling (Brereton 2002). The SIMCA method is a procedure of "soft modeling" often used in chemical pattern recognition. Soft modeling means that two classes can overlap. Therefore it is possible that samples have characteristics of both defined classes, or of neither of the defined classes.

RESULTS AND DISCUSSION

HAs in composts - Development and characterization

Systematic investigations of composts demonstrated that humification and the obtained HA contents did not depend on the amount of organic matter in the input material, but on its chemical composition. **Fig. 1** displays organic matter contents (LOI) and the portion of HAs in 20 selected samples out of 174 composts. LOI and HA contents that were referred to dry matter are not correlated to each other. These findings are supported by the position of the relevant parameters in the correlation loadings plot. The calculation is based on a principal component analysis of these parameters (**Fig. 2**). A good correlation between the parameters is indicated by a small distance. Whereas the distance between the LOI and the HA content in the compost is quite large, the humic acid content and the contribution of humic acid nitrogen (HAN contribution) are closely related. This effect is discussed below in more detail. Nitrogen contents in the compost and in HAs are independent of each other.

HAs are reflected in the infrared spectrum of composts. Both mid and near infrared area are appropriate to predict HAs contents by means of a model based on a partial least square regression (PLS-R). The procedure of model development and validation for HA determination has been described recently (Meissl *et al.* 2007, 2008). This evaluation tool enables a fast determination of compost HAs in practice.

HAs are not only reflected in the infrared spectrum but also in the thermal pattern as they influence the thermal behavior of composts. HAs contribute considerably to the second exothermic peak at about 489°C in the DSC profile of biowaste composts. In sewage sludge composts a distinct peak is missing. However, after alkaline extraction of HAs from biowaste composts the peak is not longer found (**Fig. 3**).

As indicated in **Figs. 1** and **2** HA formation is closely related to the input material and process operation. Due to the randomly synthesized molecules the individual spectral and thermal pattern of HAs differ depending on the origin, although the main characteristics are found in all HA spec-

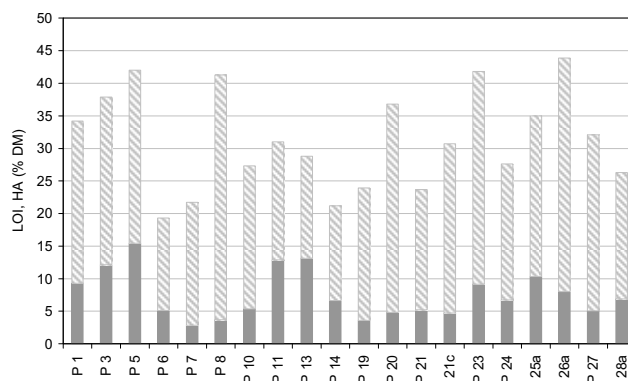


Fig. 1 Organic matter contents (LOI) with the portion of humic acids (HA) in 20 selected composts out of 174, originating from different composting plants (P); data are referring to dry matter (DM).

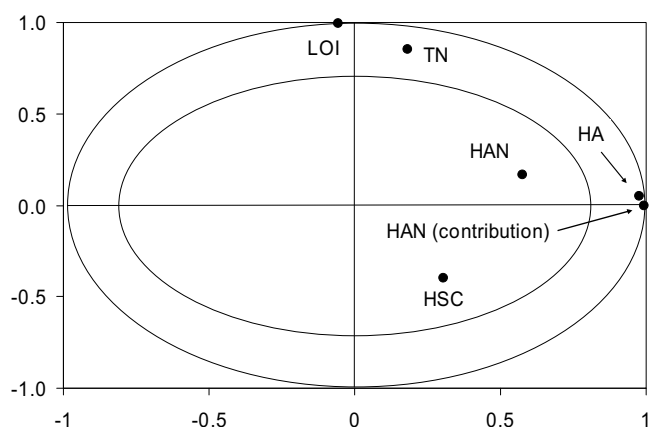


Fig. 2 Correlation loadings plot of several parameters: humic acids (HAs) content in compost, loss on ignition (LOI), total nitrogen in compost (TN), nitrogen content of HA (HAN), contribution of HAN to TN (HAN (contribution)), carbon content of HA (HSC).

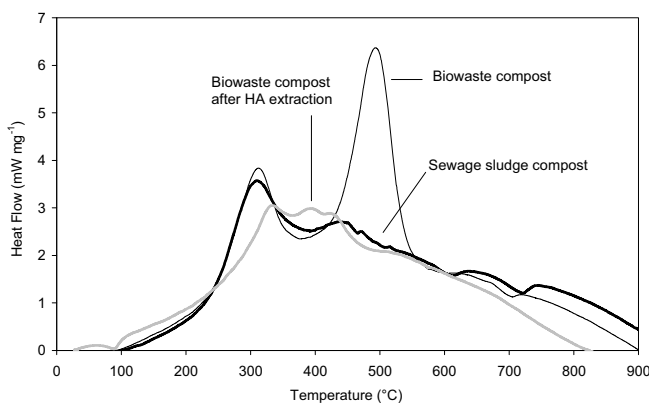


Fig. 3 Heat flow (DSC) profiles of sewage sludge compost, biowaste compost and biowaste compost after extraction of humic acids.

tra: the aliphatic methylene bands at 2920 and 2850 cm⁻¹, the C=O vibration of carboxylic acids, esters, aldehydes, and ketones at 1720 cm⁻¹, the band at 1620 cm⁻¹ that can be assigned to C=O (carboxylates) and C=C (alkenes and aromatics), the band at 1230 cm⁻¹ (C-O, carboxylic acids), and a more or less prominent band at 1030 cm⁻¹ that can be attributed to clay minerals. They are rather an impurity that can not be separated from HAs without chemical treatment. Additional bands are found in the "polysaccharide" region (1170–950 cm⁻¹) in weakly degraded materials at the beginning of the composting process (**Fig. 4**). In the final product HAs are similar to soil HAs. The development leads to stabilization which is important for the evaluation of carbon sequestration.

Changes in the infrared spectral pattern of HAs during

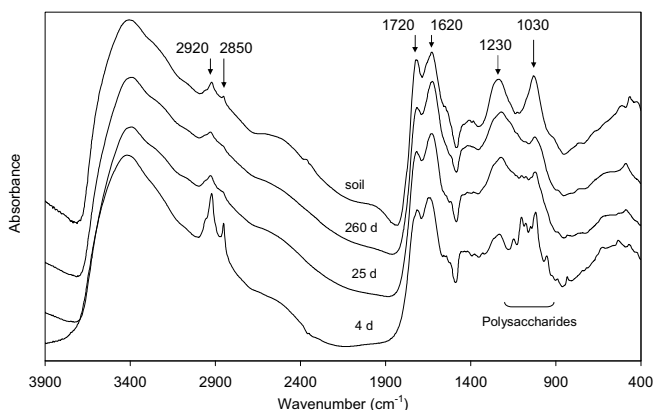


Fig. 4 Development of humic acids during composting (sampling day 4, 25, 260) revealed by infrared spectral characteristics (aliphatic methylene bands at 2920 and 2850 cm^{-1} , C=O and C-O vibrations of carboxylic acids at 1720 and 1260 cm^{-1} respectively, aromatic C=C vibration at 1640 cm^{-1} , impurities of clay minerals at 1030 cm^{-1} , several bands of polysaccharides in the wavenumber region 1170-950 cm^{-1}); comparison to a soil spectrum.

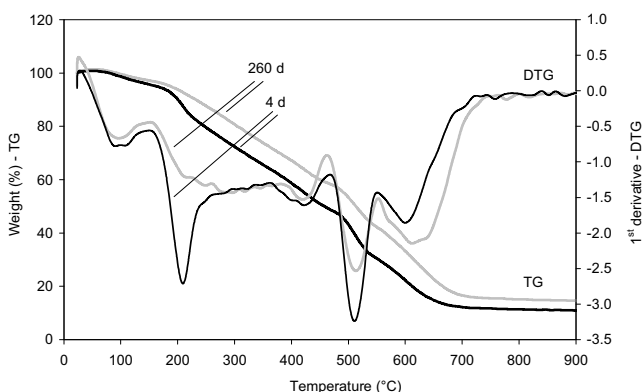


Fig. 5 TG and DTG profiles of humic acids from little rotted biogenic waste (4 d) and compost (260 d)

composting are confirmed by thermoanalytical results. **Fig. 5** illustrates the thermograms (TG curves) and the 1st derivative (DTG curve) of the 4-day-sample and the final sample (260 d). The peak at 210°C in the 4-day-sample can be assigned to cellulosic compounds that are combusted at this temperature. It corresponds to spectral characteristics in the polysaccharide region. The intensity of the peak at 512°C decreases in the compost, whereas the peak at 604°C (4-day-sample) broadens and shifts to 614°C which indicates increasing stability (Dell'Abate *et al.* 2000; Provenzano *et*

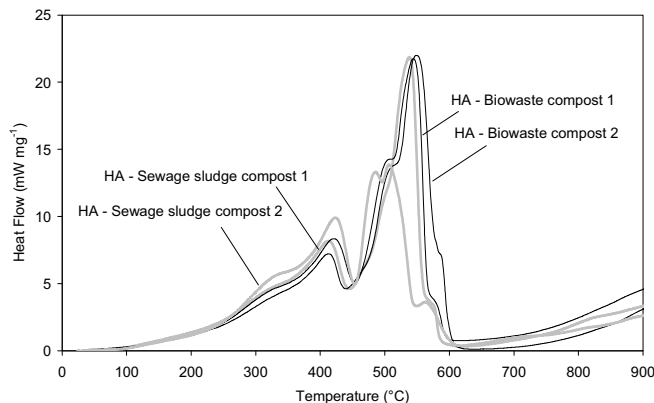


Fig. 6 Individual thermal pattern (DSC profile) of four humic acids isolated from biowaste and sewage sludge composts.

Table 3 Development of enthalpy in humic acids (HA) during composting (biowaste); enthalpy data of wood and degraded wood (enthalpy referring to ODM).

Sample ID	Enthalpy (Jg^{-1} ODM)
HA-4d	12297
HA-25d	16180
HA-260d	17864
wood	11359
wood degraded	10387

al. 2000; Otero *et al.* 2002; Melis and Castaldi 2004; Smidt and Tintner 2007).

Even though all HAs under investigation show an individual thermal behavior similarities are clearly visible. **Fig. 6** demonstrates the DSC profiles of HAs from biowaste and sewage sludge composts.

Several composts (end products) were selected for detailed investigations on HAs. Changes of HA characteristics during composting are paralleled by changes in enthalpies. Enthalpies of HAs isolated from composts are listed in **Table 2**. Enthalpies refer to organic matter. Changes of enthalpy during composting are presented in **Table 3**. For comparison reasons enthalpy data of wood and degraded wood are indicated.

HA contents referring to organic dry matter (ODM) and dry matter (DM) of compost, total nitrogen (TN) in compost, carbon (HAC) and nitrogen (HAN) contents (HAN), contribution of HA nitrogen to total nitrogen of composts (HAN contribution), the portion of HA carbon (HAC contribution) as well as enthalpies of HAs are compiled in **Table 2**. HA formation in sewage sludge composts is in general weaker than in biowaste

Table 2 Humic acid (HA) contents referring to compost organic dry matter (% ODM) and to compost dry matter (% DM); total nitrogen (TN) content in composts, carbon (HAC) and nitrogen (HAN) contents in HAs, contribution of HA nitrogen to total nitrogen of composts, portion of HA carbon, enthalpy of humic acids (sewage sludge composts are highlighted in gray); Samples 5 and 13 originate from processes (E) and (F).

Sample ID	HA (% ODM)	HA (% DM)	TN (% DM)	HAC (% DM)	HAN (% DM)	HAN (contribution) (%)	HAC (contribution) (% DM)	Enthalpy of HA (Jg^{-1} ODM)
1	27.2	9.3	1.53	54.4	5.11	31	5.1	18405
3	32.0	12.1	2.50	53.6	7.64	37	6.5	19526
5 (F)	36.7	15.4	2.96	53.4	8.91	46	8.2	17864
6	26.6	5.1	0.97	54.2	6.48	34	2.8	18205
7	13.2	2.9	1.16	53.1	6.23	15	1.5	16570
8	8.9	3.7	1.86	51.9	8.23	16	1.9	17624
10	19.7	5.4	1.92	53.8	5.56	16	2.9	16628
11	41.5	12.9	1.86	54.4	7.79	54	7.0	19103
13 (E)	45.6	13.1	1.62	54.1	7.50	61	7.1	19505
14	31.3	6.6	1.14	53.9	8.11	47	3.6	18981
19	15.1	3.6	1.25	52.2	6.21	18	1.9	13980
21	22.0	5.2	1.27	47.5	6.43	33	2.5	14913
21c	15.4	4.7	1.36	49.7	6.24	30	2.3	14458
24	24.3	6.7	1.69	48.6	8.42	40	3.3	15840
25a	29.5	10.3	2.35	47.6	7.08	34	4.9	17108

composts due to the facts mentioned below. The contribution of HA nitrogen to the total nitrogen primarily depends on the amount of HAs in the compost. This correlation is also reflected by the correlation loading plot (Fig. 2).

Influence of input materials

In Austria the term “compost” is reserved to biogenic materials that have undergone an aerobic biological process. This definition is not generally valid in other countries where the term “compost” focuses more on the application than on process operation. Therefore digests (residues from anaerobic treatment of biogenic materials) from other countries were included. The HA contents in 174 European composts and digests (Fig. 7) ranged from 5.4% ODM to 46.8% ODM. This wide range underlines that different materials and treatments result in different levels of humification and that the parameter “HAs” seems to be suitable to differentiate the processes.

Classes of end product qualities are established according to the compliance with limit values. Independent of these end product parameters sewage sludge composts only reach lower HA contents as exemplified by 54 end products from Austrian composting plants (Fig. 8). Sewage sludge composting is maintained by addition of bulk materials. In terms of humification sewage sludge composts usually produce smaller amounts of HAs (Table 2). This can be explained by the one-sided composition of the material that has already undergone an anaerobic process (anaerobic stabilization of sewage sludge) and the missing well-balanced mixture. Focussing on humification heterogeneous mixtures of input materials comprising easily, less easily and hardly degradable substances are essential. Sewage sludge mainly consists of microbial biomass. Cuttings from trees and shrubs serve as bulk material. They are hardly degraded during the short rotting phase in a composting plant.

Laboratory experiments with mixtures of various portions of biowaste and sewage sludge as input materials indi-

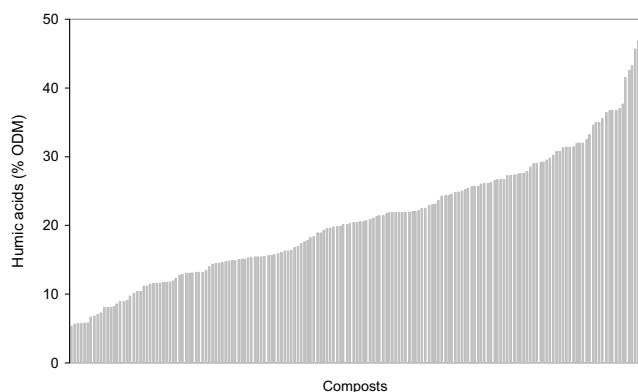


Fig. 7 174 end products of composting plants sorted by their content of humic acids.

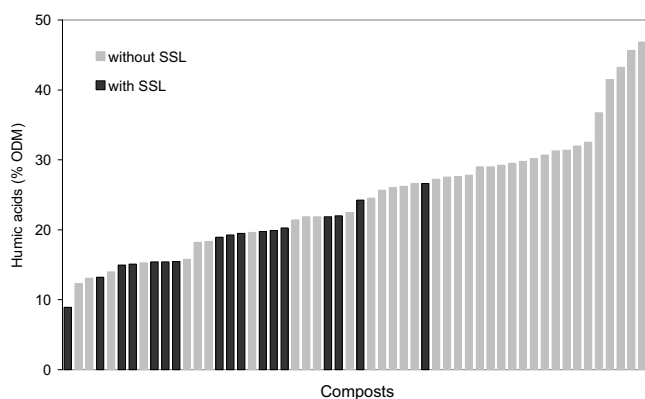


Fig. 8 54 Austrian composts with (black) and without (gray) sewage sludge (SSL) ranged according to their content of humic acids.

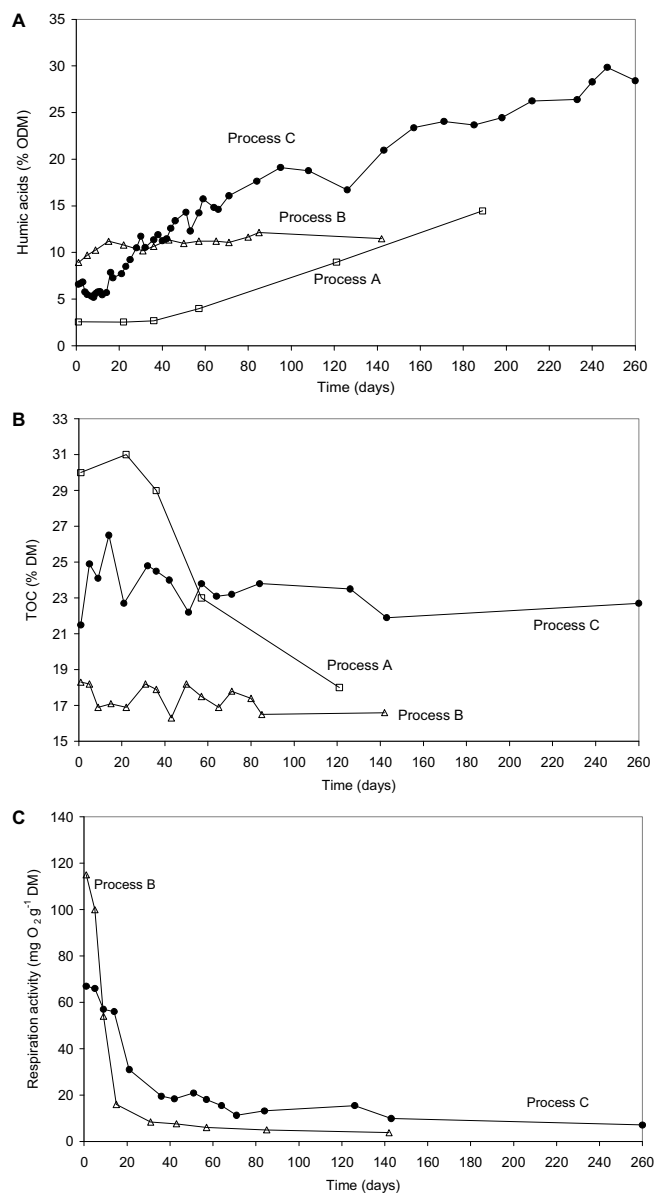


Fig. 9 (A) Humic acid formation (B) development of total organic carbon and (C) development of respiration activity (7 days) in biowaste composting processes. Process A: Lab-scale with an artificial mixture, anaerobic for one week; Process B: mixture of easily and scarcely degradable material, open windrow; Process C: yard and kitchen waste from the separate collection, open windrow.

cated, that even a relatively small amount of biowaste could intensify humification also in sewage sludge composts (Smidt *et al.* 2007).

However, the composition of biowaste mixtures can also be unfavorable for humification. Three different biowaste composting processes were compared to one another (Fig. 9A).

The different input materials led to different humification levels. HA contents in process A remained at a low constant level for 28 days. Due to the change from anaerobic to aerobic conditions mineralization was accelerated which led to an increasing HA portion in the remaining organic matter. It should be emphasized that the rise is relative because of the considerable degradation of organic matter that is visualized by the development of total organic carbon (Fig. 9B). A slight but significant increase of HAs was nevertheless observed indicating the stability of this organic matter fraction.

In process B a slight increase of HA contents was determined at the beginning, followed by settling down at a stable level (Fig. 9A). This behavior can be due to the fast turnover of easily degradable compounds that is indicated

by a high respiration activity (RA₇) at the beginning, followed by a strong and fast decline at the end (Fig. 9C). The moderate decrease of respiration activity as shown in process C is missing. The barely degradable bulk material was not decomposed at all. This fact confirms the well-balanced mixture that provides favorable conditions to maintain the microbiological process for a longer period of time.

In process C the HA content increased continuously to about 27% ODM. Contrary to process B, microbial activity decreased slowly (Fig. 9C), indicating appropriate conditions for humification in terms of material composition and process operation. For the processing basic conditions for microbial growth and activities are important to be maintained: water and air supply. Forced aeration can contribute to cover oxygen requirements, but too much oxygen stimulates mineralization which antagonizes humification. The structure of the material, especially particle size and geometry, and the portion of bulk materials strongly influence these parameters.

Influence of process operation

Basically two systems are applied within the first rotting phase: a closed system (rotting box) and an open window system. In the closed system the material is processed in boxes, where the air supply is controlled managed either by pressing or by sucking. Water is added if necessary. After one to three weeks the composting process is continued in open windrows. The advantage of closed systems is the avoidance of olfactory emissions in the early phase of degradation. No influence on humification is observed by the rotting system applied for the intensive rotting phase as illustrated in Fig. 10.

The shape of the windrows influences the ongoing process. Geometry and size play an important role for convection of air flow from the bottom to the top where the heated air escapes. If the windrow is too high, air supply is limited. In this context the role of suitable bulk materials and particle sizes should be mentioned as the air flow is mainly influenced by these properties. Nevertheless, zones of limited aeration are found, especially in the core of the windrow. With respect to humification natural convection yields the most favorable air supply for this purpose. Turning machines support natural aeration by regular rotation. Forced aeration can provide too much air causing mineralization to dominate which counteracts humification. Fig. 11 demonstrates the gas composition of CO₂ and methane, the temperature profile in the windrows during the composting process (process D), and the HA contents produced. The bio-

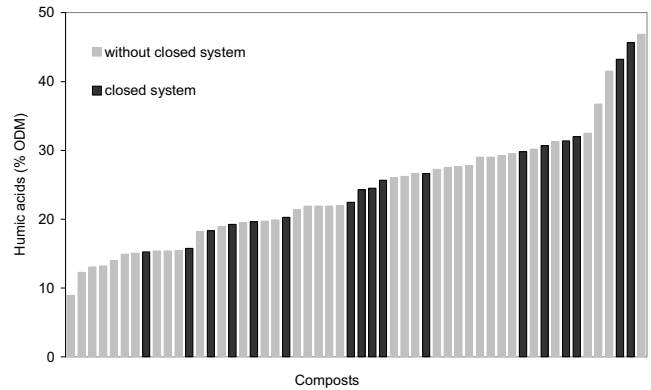


Fig. 10 54 Austrian composts ranged by their content of humic acids; intensive rotting phase in a closed system (black), in an open system since the beginning (gray).

waste material was rotated by a turning machine. It is clearly visible that changing conditions and partial and intermittent oxygen limitation can lead to good results with regard to humification. These findings are in accordance with data reported by Kononova (1975). Highest contents of humified organic matter are found in those regions where mineralization proceeds in a moderate rate.

Process control using FT-IR spectroscopy and thermal analysis

The infrared spectrum is an individual chemical fingerprint of the material under investigation. FT-IR spectroscopy is a common analytical tool for process control and quality assessment in several sectors of industry (Bauer *et al.* 2008; Etzold and Lichtenberg-Kraag 2008; Georget *et al.* 2008; Shim *et al.* 2008). In waste management research FT-IR spectroscopy has been used for process monitoring and product assessment. The characteristic spectral pattern and its changes provide information on degradation, stabilization and chemical composition of the processed material. The approach of qualitative spectra interpretation was presented by several authors (Ouatmane *et al.* 2002; Smidt *et al.* 2002; Zaccheo *et al.* 2002; Smidt and Schwanninger 2005; Smidt and Meissl 2006).

Wavenumber position of relevant bands, their vibration and assignment to functional groups or compounds are summarized in Table 4. The development of these indicator bands during composting is indicated by arrows.

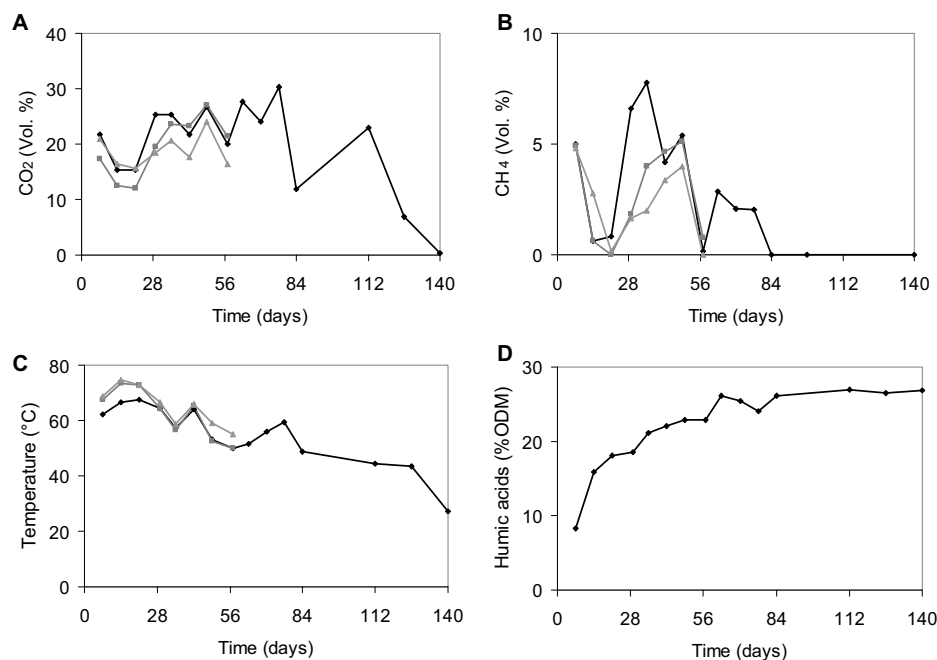


Fig. 11 CO₂ (A) and CH₄ (B) concentrations, temperature (C) and humic acid formation (D) in three windrows of the same age in the biowaste composting process D.

Table 4 Relevant indicator bands, band assignment to functional groups and behavior with time.

Wavenumber (cm ⁻¹)	Vibration	Functional group or compound	Development weeks	
			0-16	>16
3400	O-H stretching	Bond and non bond hydroxyl groups and water	↓	→
2920	Asym. C-H stretch.	Aliphatic methylene group	↓	→
2850	Sym. C-H stretch.	Aliphatic methylene group	↓	→
1740-1720	C=O stretching	Aldehydes, ketones, carboxylic acids, esters	↓	→
1640	C=O stretching	Amide I, carboxylates	↓	→
	C=C stretching	Aromatic ring modes, alkenes	↑	→
1600-1590	C=C	Aromatic skeleton	↑	→
1580-1540	N-H in plane	Amides II	↓	→
1515-1505	Aromatic skeletal	Lignocellulose		
1420	COO ⁻ stretching	Carboxylic acids	↓	→
	C-O stretching	Carbonate	↑	→
1384	N-O stretching	Nitrate	↑	↑(↓)
1320	C-N stretching	Aromatic primary and secondary amines	↑↓	
1260-1240	C-O	Carboxylic acids	↓	
	C-N	Amide III		
1250-900	C-O-C, C-O, C-O-P	Polysaccharides, phosphodiesters	↓	→
1030	Si-O stretching	Clay minerals	↑	→
	Si-O-Si	Silica		
875	C-O out of plane	Carbonate	↑	→

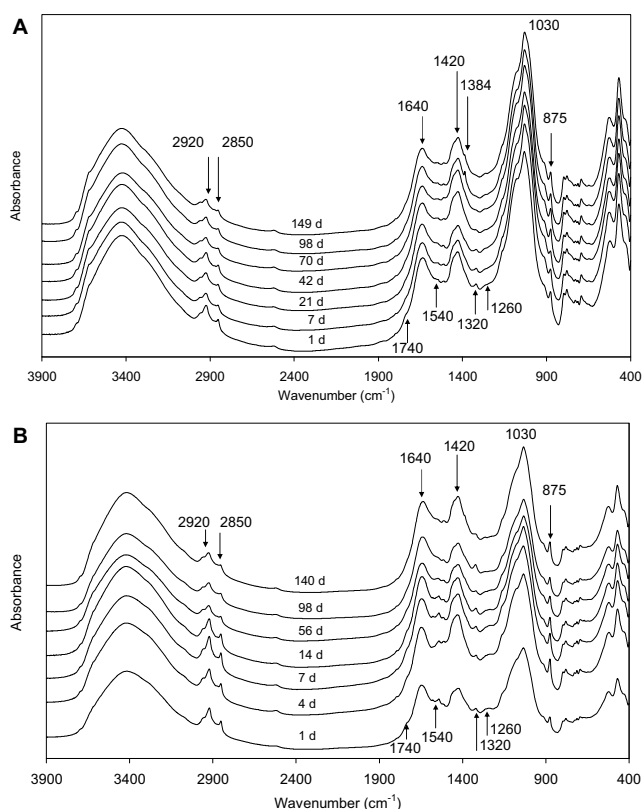


Fig. 12 Changes of infrared spectroscopic characteristics during a composting process for (A) process D (149 days) and (B) process E (140 days).

In **Fig. 12** two biowaste composting processes (process D and E) are presented. Changes of spectral characteristics during composting are displayed. In process D (**Fig. 12A**) earth was added, as indicated by the prominent clay mineral band at 1030 cm⁻¹. In process E (**Fig. 12B**) leftovers were added. The methylene group, reflected by bands at 2920 cm⁻¹ and 2850 cm⁻¹, are part of many biomolecules. Their degradation causes these bands to decrease up to a constant band height, indicating the stabilization of the composting process. The strong broad band at 1640 cm⁻¹ is caused by several functional groups (C=O and C=C). The weak band at about 1540 cm⁻¹ can be assigned to amides. Several materials such as sewage sludge and leftovers display a stronger amide band. The weak band at 1320 cm⁻¹ is a reliable indicator of metabolic activities. Its development reflects process dynamics. The N-O vibration of nitrate is found at

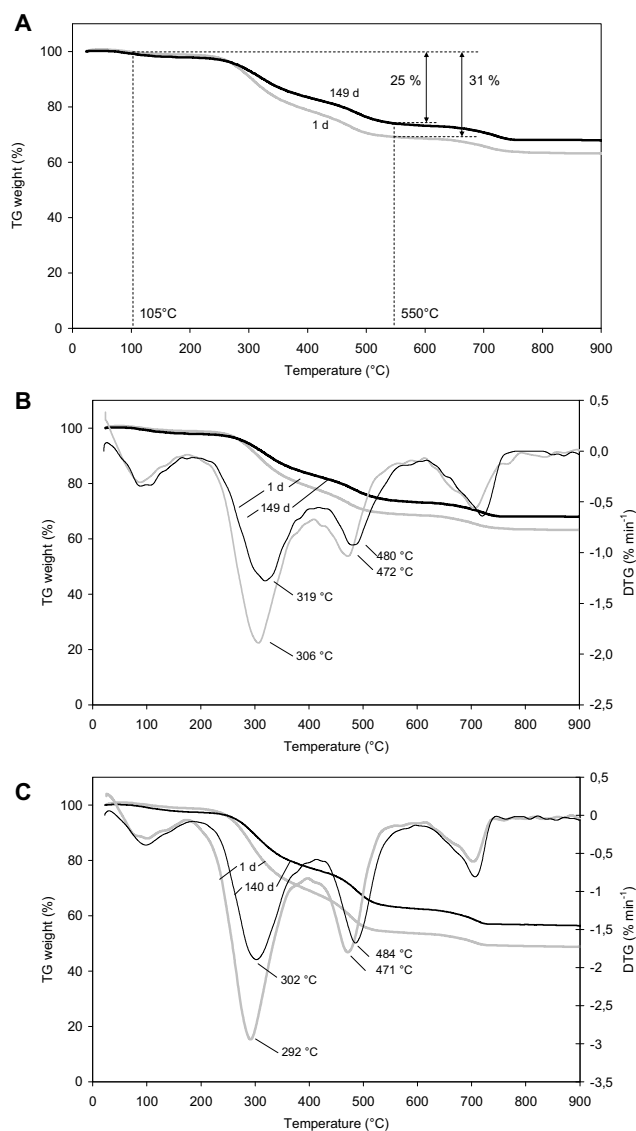


Fig. 13 (A) Thermograms of the initial and the final sample in composting process D, DTG profile of the initial and the final sample in composting (B) process D and (C) process E.

1384 cm⁻¹. Nitrate is a mineralization product of organic nitrogen containing molecules and indicates an advanced stage of composting. However the nitrate band is not necessarily found in all stabilized composts. The bands at 1420

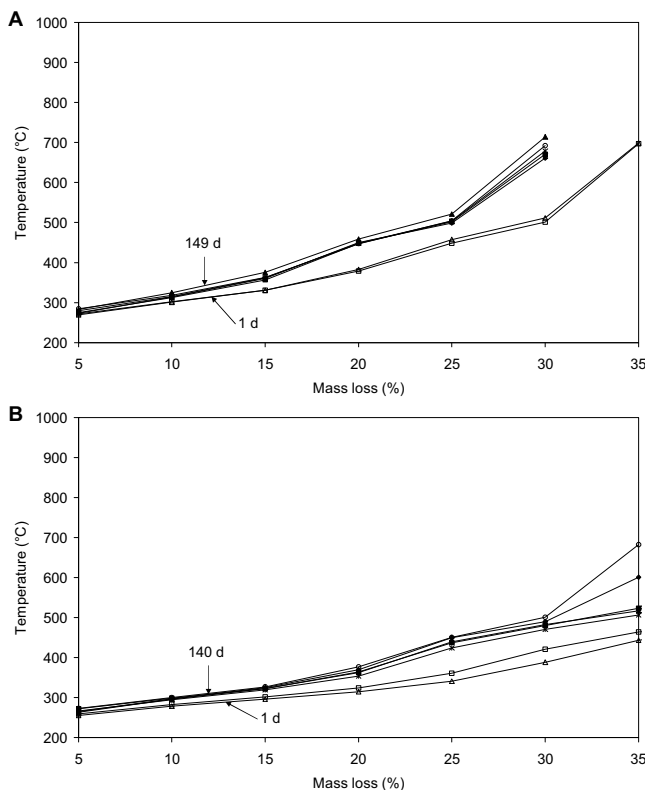


Fig. 14 Mass loss vs. temperature during composting (A) process D and (B) process E.

and 875 cm^{-1} are assigned to carbonates. The main indicator bands are similar in all biowaste composting processes. However, individual spectral characteristics of the input mixture are revealed by principal component analysis that emphasizes tiny differences as shown in **Fig. 16**.

In addition to infrared spectroscopy, thermal analysis was applied. Thermal characteristics of waste subsume physical properties of all compounds present in the mixture and thus provide information on the chemical composition in general. The thermal behavior changes with progressing stabilization and therefore provides information on compost maturity. The thermogram (TG) displays the weight loss during combustion, whereas the DSC curve illustrates the heat flow. Stabilization is reflected by a curve shift to higher temperature ranges. Thermograms of the input material (1 d) and the final product (149 d) are illustrated in **Fig. 13A** (process D). Organic matter contents are reflected by the mass loss between 105 and 550°C (**Fig. 13A**). The increased stabilization process during composting becomes clearly visible by the peak shift to higher temperatures, as illustrated by the DTG curves (**Figs. 13B, 13C**). The 1st peak represents the mass loss by water evaporation, the 2nd and 3rd peak are assigned to the mass losses of organic matter fractions, the 4th peak to the carbonate decay. Due to increased degradation of organic matter, peak intensities decrease with time.

Fig. 14 displays the mass loss vs. temperature. The evaluation of the data demonstrates the additional required temperature for stabilization (Smidt and Lechner 2005). Mass losses of 10-30% are obtained at lower temperatures for the input material (1 d) than for the final product (149 d).

Organic matter combustion generates two prominent exothermic peaks in the DSC profile (**Fig. 15**) caused by the two organic matter fractions mentioned above. The endothermic peak between 700 and 800°C is assigned to the decay of carbonates. The area below the heat flow curve corresponds to the enthalpy. The DSC curves also shift to higher temperatures with increasing stabilization. Heat flow and enthalpy decrease in the whole system with organic matter degradation. Heat flow and enthalpy increase if they refer to organic dry matter (ODM), which indicates the change of

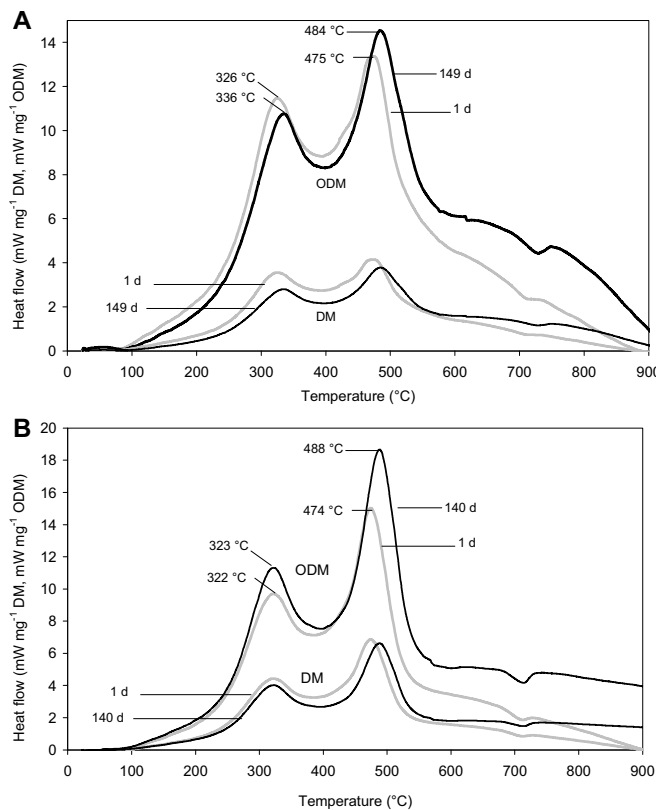


Fig. 15 DSC profiles of the initial and the final sample referring to DM and ODM (A) process D and (B) process E.

organic matter properties. Apart from other factors such as enrichment of barely degradable compounds humification contributes to this effect observed in both composting processes (D and E).

Identification of biowaste composts – separation from municipal solid waste compost and other materials

Biowaste composts that are produced from yard waste, kitchen waste and market waste from the separate collection differ from other materials due to their specific spectral characteristics. Individual features of specific biowaste mixtures that remain throughout the whole process, are reflected by a principal component analysis of their spectra. **Fig. 16** displays the scores plot of the principal component analysis based on spectral characteristics of biowaste samples during the rotting process.

Contrary to other countries biologically treated municipal solid waste (MSW) is not allowed in Austria for use in agriculture and horticulture. Mechanically-biologically treated

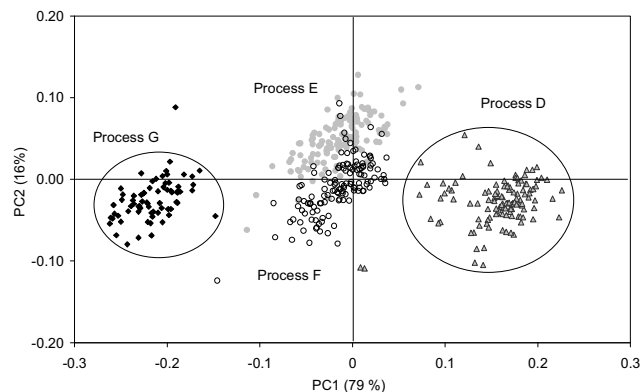


Fig. 16 Principal component analysis of biowaste composting processes based on infrared spectral characteristics.

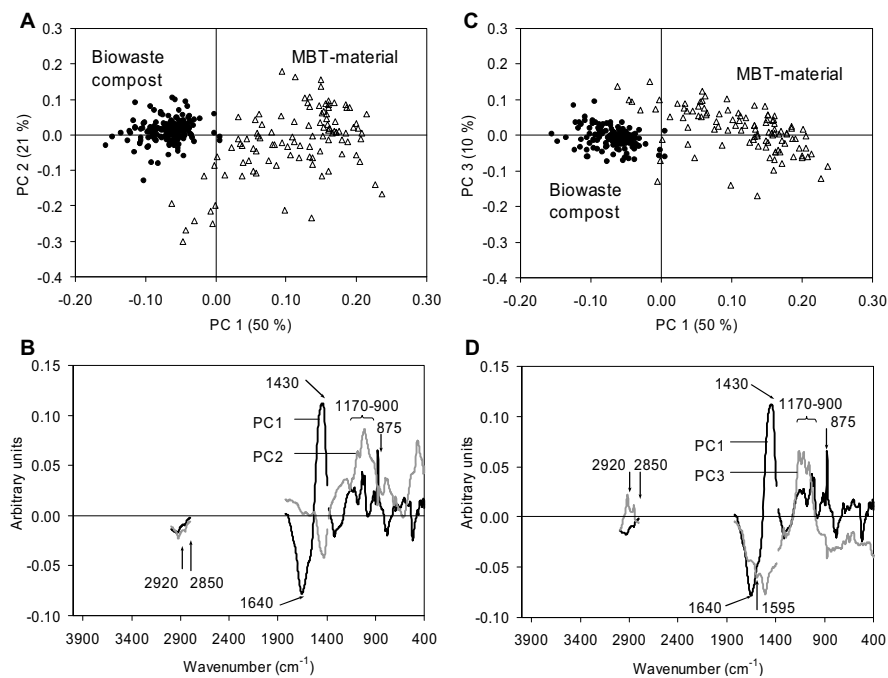


Fig. 17 PCA using wavenumber regions 3000–2800 cm^{-1} , 1800–1535 cm^{-1} , 1346–890 cm^{-1} , and 860–400 cm^{-1} . Scores (A) and loadings (B) of composts ● and MBT-waste △ obtained by plotting the first vs. the second PC; scores (C) and loadings (D) of these materials obtained by plotting the first vs. the third PC (explained variance by a single PC in brackets)

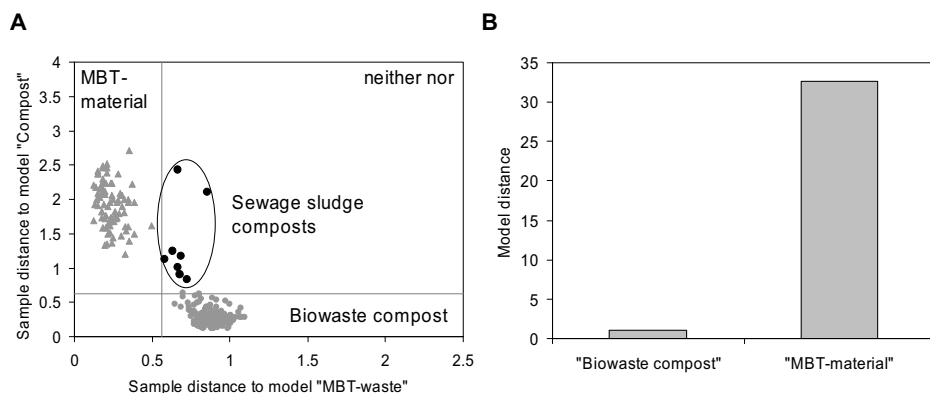


Fig. 18 (A) Coomans plots of the considered classes “Compost” and “MBT-waste” and classified sewage sludge composts; (B) Model distances from SIMCA classes (“Compost” and “MBT-waste”) to the class “Compost”.

ted waste (MBT-waste) can be clearly distinguished from separately collected biowaste by means of the spectral pattern and principal component analysis (PCA). The PCA was performed using wavenumber ranges from 3000 to 2800 cm^{-1} , 1800 to 1394 cm^{-1} and 1375 to 400 cm^{-1} of 283 samples including composts and MBT-wastes. The scores plots in **Fig. 17A** and **17C** display differences between the two materials. **Fig. 17B** and **17D** show the corresponding loading plots of three calculated principal components (PCs). Each PC explains the individual contribution to the total variance. PC 1 reveals the influence of organic (2920, 2850, 1640 and 1170–900 cm^{-1}) and inorganic compounds (1430 and 875 cm^{-1}). PC 2 and PC 3 indicate the influence of organic (1595 and 1170–900 cm^{-1}) components. Composts and MBT-waste can be clearly distinguished by means of these calculated PCs. The band at 1595 cm^{-1} reflects high HA con-

tents (Meissl *et al.* 2007). The polysaccharide region (cellulose) at 1140–900 cm^{-1} confirms MBT-waste.

A specific model was developed for each material. Model development and evaluation were described by Smidt *et al.* (2008). Biowaste composts differ considerably from MBT-waste (**Fig. 18A, 18B**). **Fig. 18B** displays the model distance between composts and MBT-wastes. Distances of more than 3 indicate a significant segregation between the defined classes (Esbensen 2002).

Sewage sludge composts were classified using the developed models mentioned above. Sewage sludge composts additionally contained bulk materials (e.g. yard waste). **Fig. 18A** illustrates the assignment of sewage sludge composts in the classification model for MBT- and biowaste and the location in the Coomans plot.

The role of the input material also becomes visible in the DSC curves (**Fig. 19**). In **Fig. 19** the DSC profiles of biowaste compost and sewage sludge compost are illustrated. The sewage sludge compost has a low HA content of 13.2% ODM which is reflected by the missing second exothermic peak. The prominent first exothermic peak at 322°C is caused by the special composition containing primarily proteins, lipids from sewage sludge and cellulose from paper sludge. The HA content of the biowaste compost is 43.5% ODM. Due to these characteristic features these compost types can be easily distinguished in a PCA.

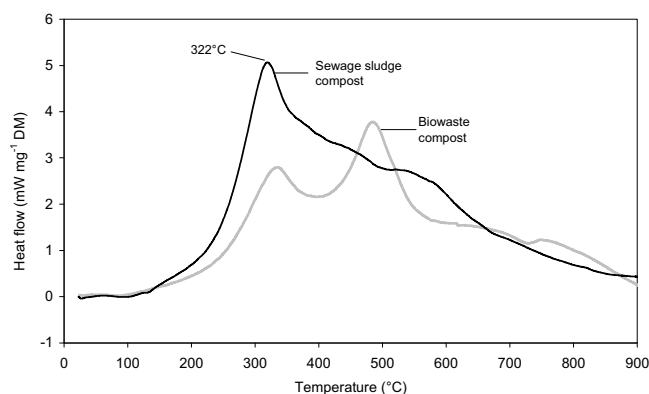


Fig. 19 DSC-profiles of sewage sludge compost and biowaste compost

CONCLUSIONS

Many biogenic materials from different sources are available for composting and valuable in the context of resource recovery and compost design for different purposes, provided that a standard quality regarding pollutants is reached. If humification is the aim, biowaste that contains a well-

balanced mixture of biogenic materials such as end-products from composting processes C, E and F were found to have the best qualification. The variety of chemical compounds includes a variety of degradability which is important to start and to maintain the metabolic process. Adequate aeration at the beginning and moderate aeration after the intensive rotting phase yield the best results in humification. All composting systems, boxes combined with open windrows or exclusively open windrows meet these claims.

Due to the individual spectral pattern biogenic materials differ more, or less from one another and can be classified by principal component analysis (PCA). Unbalanced mixtures of biogenic materials as in the case of process B do not achieve high HA contents. Therefore verification by FT-IR spectra and PCA might be helpful.

Further investigations will focus on optimization of material composition regarding humification and identification of appropriate mixtures by means of FT-IR spectroscopy and multivariate methods. Ecological and economical considerations in the context of carbon sequestration will be a main topic in future research. According to estimates in the IPCC Second Assessment Report 400-800 MtC/yr could be sequestered in agricultural soils reaching a finite capacity after 50 to 100 years (Smith *et al.* 2007). Soil organic carbon contributes about 89% to the global technical potential for mitigation in agriculture by 2030 (Smith *et al.* 2007). The increase of soil carbon by humified organic matter could improve these estimates. Therefore reliable analytical tools are necessary to verify the contribution of stable compost organic matter. Thermal analysis provides a good approach for this purpose.

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