

Dissolved Organic Carbon Fractions Formed during Composting of Municipal Solid Waste: Properties and Significance

Gelöster organisch gebundener Kohlenstoff bei der Kompostierung von Hausmüll: Eigenschaften und Anteil einzelner Fraktionen

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Keywords: Compost, Dissolved Organic Matter, Dissolved Organic Carbon, Humic Substances, NMR, FTIR, DRIFT

Summary: The properties and transformation of dissolved organic matter (DOM) extracted (10 L water per kilogram compost) from municipal solid waste (MSW) compost at five stages (days 47, 77, 105, 126, and 187) of composting were investigated. The DOM was fractionated into hydrophobic or hydrophilic neutrals, acids, and bases. The unfractionated DOM, the hydrophobic acids and neutrals (HoA and HoN, respectively), and the hydrophilic neutrals (HiN) fractions were studied using solid-state ^{13}C -NMR, FTIR, and DRIFT spectroscopy. The HoA fraction was found to be the dominant (percentage of total DOM) hydrophobic fraction, exhibiting a moderate increase during composting. The HoN fraction increased sharply from less than 1% to 18% of the total DOM during 187 days of composting, while the hydrophobic bases (HoB) exhibited the opposite trend. The HiN represented the major fraction of the hydrophiles up to 120 days of composting, decreasing thereafter by 38%. The relative concentration of the hydrophilic acids and bases (HiA and HiB, respectively) exhibited no consistent trend during composting. DRIFT spectra of the unfractionated DOM taken from the composting MSW revealed a decreasing level of polysaccharide structures with time. The ^{13}C -NMR and FTIR spectra of the HoA fraction exhibited a polyphenol-humic structure, whereas the HoN spectra exhibited strong aliphatic features. The spectra of the HiN fraction confirmed its polysaccharide nature. During the final stage of composting, the DOM concentration was steady, while a relative decrease of HiN concomitant with an increase of HoA and HoN fractions was observed. These indicate that the DOM contained a low concentration of biodegradable organic matter and a higher content of macromolecules related to humic substances. The biological significance and heavy metal binding of these fractions are being studied based on earlier observations showing enhanced plant growth in the presence of DOM extracted from mature as opposed to immature compost.

Schlagwörter: Kompost, gelöste organische Substanz, gelöster organisch gebundener Kohlenstoff, Huminstoffe, NMR, FTIR, DRIFT

Zusammenfassung: Untersucht wurden Eigenschaften und Umsetzung der gelösten organischen Substanz (dissolved organic matter – DOM) in Komposteluat. Zur Gewinnung der DOM wurde kompostierter Hausmüll in verschiedenen Stadien der Kompostierung (47., 77., 105., 126. und 187. Tag) mit Wasser extrahiert (10 L Wasser auf 1 kg Kompost). Nach einem operationellen Fraktionierungsschema wurde die DOM aufgeteilt in hydrophobe und hydrophile Komponenten, innerhalb dieser beiden Kategorien noch einmal nach sauer, neutral und basisch. Die unfractionierte DOM, die Fraktion hydrophob/sauer (HoA), die Fraktion hydrophob/neutral (HoN) und die Fraktion hydrophil/neutral (HiN) wurden mittels Festkörper- ^{13}C -NMR-, FTIR- und DRIFT-Spektroskopie untersucht. Innerhalb der hydrophoben Fraktionen dominierte die saure Fraktion, HoA, ihr Anteil an der Gesamt-DOM nahm im Laufe des Kompostierungsprozesses noch zu. Der Anteil der HoN-Fraktion stieg im Laufe der 187 Tage während der Kompostierung stark an – von weniger als 1% auf 18% der gesamten DOM –, während die Fraktion hydrophob/basisch (HoB) die gegenläufige Tendenz entwickelte. Bei den hydrophilen Fraktionen stellte die neutrale Fraktion, HiN, bis zum 120. Tag der Kompostierung die Hauptfraktion dar; dann verringerte sich ihr Anteil um 38%. Für die Fraktionen hydrophil/sauer und hydrophil/basisch war keine eindeutige Tendenz im Verlauf der Kompostierung zu beobachten.

Den DRIFT-Spektren der unfractionierten DOM des Komposteluates ist zu entnehmen, daß im Verlauf der Kompostierung der Anteil an Polysaccharidstrukturen in der DOM zurückgeht. ^{13}C -NMR- und FTIR-Spektren der HoA-Fraktion deuten auf Polyphenole und huminstoffähnliche Strukturen hin, während die Spektren der HoN-Fraktion von den charakteristischen Merkmalen aliphatischer Strukturen geprägt sind. Die Spektren der HiN-Fraktion bestätigen den Polysaccharidcharakter dieser Fraktion. In der letzten Phase der Kompostierung – nach etwa 100 Tagen – stellte sich eine stationäre DOM-Konzentration ein, dabei wird die relative Abnahme des Anteils der HiN-Fraktion an der DOM durch die gleichzeitige Zunahme des Anteils der Summe aus HoA- und HoN-Fraktion kompensiert. Das deutet darauf hin, daß in der DOM wenig bioabbaubare organische Stoffe und ein größerer Anteil an huminstoffartigen Makromolekülen enthalten waren. Auf dem Hintergrund einer früheren Beobachtung – verstärktes Pflanzenwachstum in Gegenwart von DOM aus Komposteluat von gereiftem Kompost, der gegenteilige Effekt durch DOM aus Komposteluat von jungem Kompost – sollen die biologische Bedeutung dieser Fraktionen und ihr Bindungsvermögen für Schwermetalle Gegenstand weiterer Forschung sein.

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1 Introduction

Composting is a traditional, yet not fully understood approach to integrated waste management. The raw materials used for composting represent a wide spectrum of organic wastes such as municipal solid wastes (MSW), sewage sludge, yard and green wastes, animal manures, grape marc and many others. Composting is defined as a biological treatment in which aerobic microorganisms utilize organic matter (OM) as a substrate [1]. The final product (compost) consists of stable OM, water, minerals, and ash. As microorganisms are only active at the solid-liquid interphase, a study of the liquid fraction is essential to achieve better understanding of the C and N cycles during composting [2]. Moreover, characterization of the composition of the dissolved organic matter (DOM), the active OM fraction, has the potential of being a better indicator of the overall transformation of the OM than tests of the solid phase. Compost used as soil amendment is transformed into soil humus after a short decomposition period. DOM in compost is known to enhance plant growth due to its maintenance of Fe, Mn, Cu, and Zn in solution at sufficient levels [3]. In soils, DOM is related to C and N availability [4–6], metal complexation, and enhanced plant growth [7]. Although the transformation of OM during composting has been widely studied [8–14], most of the reports have focused on water-insoluble humic substances (HS).

The determination of DOM composition is difficult since it contains a mixture of low-molecular weight compounds (free amino acids and sugars) and chemically heterogeneous macromolecules (enzymes, amino-sugar complexes, polyphenols, and HS). Thus, preliminary fractionation was an essential step for better understanding of the variety of different physico-chemical and biological active compounds [15]. The objectives of this study were to investigate the transformation of DOM during MSW composting, employing a physicochemical fractionation scheme, and testing the various fractions using spectroscopic methods such as ^{13}C -NMR, FTIR, and DRIFT.

2 Materials and Methods

2.1 DOM Extraction

Aqueous compost extracts were prepared by placing 1 kg compost (wet weight) in 10 L of distilled water and shaking (125 rpm) for 2 h at room temperature. The suspension was then centrifuged (10 000 g for 30 min) and the supernatant filtered through a 0.45- μm membrane filter (Supor-450, Gelman Sciences). The concentration of the dissolved organic carbon (DOC) was measured immediately after extraction or fractionation using a total carbon monitor (TCM 480, Carlo Erba Instruments, Milan, Italy). The DOM concentration was calculated as C concentration.

2.2 Preparative Fractionation

Preparative DOM fractionation was performed using a procedure developed by Leenheer [15] with some modifications [16]. The following are simplified operational definitions of the isolated fractions (Fig. 1):

- Hydrophobic fraction – sorbed to XAD-8 (Ho):
 - Ho Base (HoB) – desorbed with 0.1 M HCl
 - Ho Acid (HoA) – desorbed with 0.1 M NaOH
 - Ho Neutrals (HoN) – desorbed with MeOH

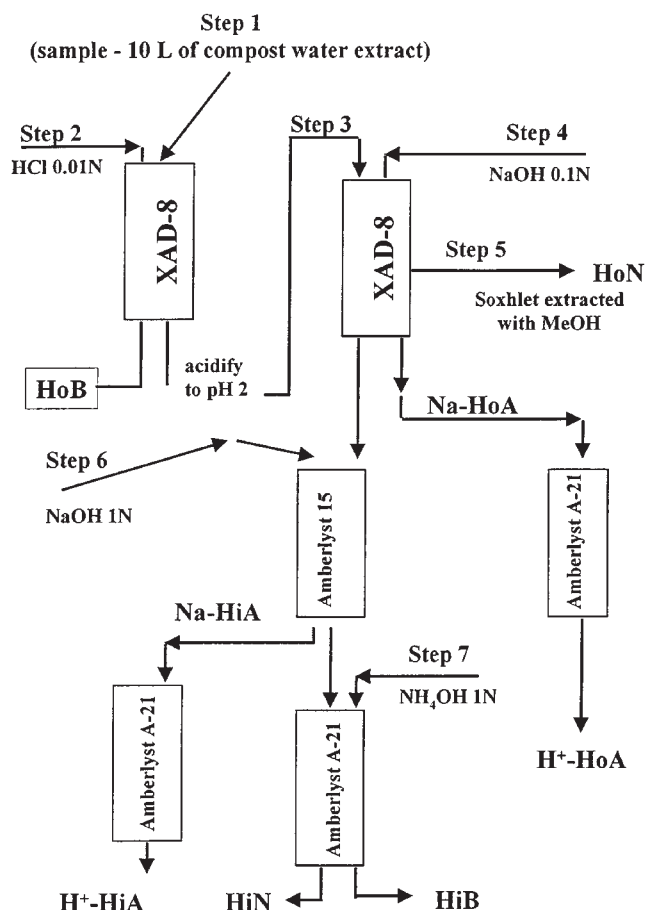


Fig. 1: Dissolved organic matter (DOM) fractionation scheme. Abbreviations used: hydrophobic base (HoB), hydrophobic acid (HoA), hydrophobic neutrals (HoN), hydrophilic base (HiB), hydrophilic acid (HiA), and hydrophilic neutrals (HiN).

Fraktionierungsschema für die gelöste organische Substanz. Bezeichnung der Fraktionen: hydrophob/basisch (HoB), hydrophob/sauer (HoA), hydrophob/neutral (HoN), hydrophil/basisch (HiB), hydrophil/sauer (HiA), hydrophil/neutral (HiN).

Hydrophilic fraction – not sorbed to XAD-8 (Hi) (obtained after sample elution through a XAD-8 column):

- Hi Base (HiB) – sorbed to H^+ cation exchange resin, desorbed with 0.1 M NH_4OH
- Hi Acid (HiA) – sorbed to anion exchange resin, desorbed with 1.0 M NaOH
- Hi Neutrals (HiN) – remaining in deionized-water solution after all column separation

Various fractions concentrations were calculated as C concentration.

2.3 Solid-state ^{13}C -NMR Spectroscopy

Solid-state ^{13}C -NMR spectra with CPMAS (Cross Polarization Magic Angle Spinning) were obtained using a Chemagnetics M-100 NMR spectrometer. The spectrometer was operated at a ^1H frequency of 100 MHz and a ^{13}C frequency of 25 MHz. Pertinent experimental parameters were as follows: a contact time of 1 ms, a recycle delay time of 0.8 s, a sweep width of 14 kHz (562.5 ppm), and a line broadening of 30 Hz. Dried samples (48 h at 65°C) were placed into a rotor and spun at a frequency of 3.5 kHz at the magic angle (54.7° to the magnetic field).

The ^{13}C -NMR spectra were divided into five regions [17]. Region I (0...50 ppm) is assigned to paraffinic carbon or carbons that are bonded only to other carbons. Region II (50...112 ppm) is assigned to C-O, C-N bonds as in carbohydrates, alcohols, esters, and amines. Region III (112...163 ppm) is assigned to aromatic and phenolic carbons. Region IV (163...190 ppm) represents carboxyl, ester, and amide carbon groups. Region V (190...215 ppm) represents the carbonyl carbons. The region 0...112 ppm was calculated as aliphatic carbon, 60...112 ppm as polysaccharide carbon, and 112...163 ppm as aromatic carbon. Total aromaticity was calculated by expressing aromatic C (112...163 ppm) as a percentage of the aliphatic C (0...112 ppm) plus aromatic C [18].

2.4 DRIFT and FTIR Spectroscopies

The Diffuse Reflectance Infrared Fourier-Transform (DRIFT) spectra of the unfractionated DOM were obtained for a wavenumber range of 4000 to 400 cm^{-1} using a Nicolet 550 Magna-IRTM spectrometer (Nicolet Instruments Corporation, Madison, WI, USA). Samples were prepared for analysis according to the methods of Niemeyer et al. [19], using 15 mg of dried sample mixed with KBr for a total sample weight of 310 mg. The samples were transferred to a macro-sample holder and smoothed with a glass slide. To obtain DRIFT spectra, 400 scans were collected. Spectra of the residual ash obtained after ignition at 550°C for 8 h and loss of the OM were recorded using the same methodology. To compare one spectrum to another, a linear baseline correction was applied using 4000 cm^{-1} , 2000 cm^{-1} , and 860 cm^{-1} as zero absorbance points. The spectra of the ash free OM were calculated by subtracting the spectrum of the ash from that of the bulk materials, using the OMNIC software (Nicolet Instruments Corporation).

The Fourier-transform Infrared (FTIR) spectra of the HoA, HoN, and HiN fractions were obtained for a wavenumber range of 4000 to 400 cm^{-1} on a Nicolet 550 Magna-IRTM spectrometer. Samples were oven-dried at 65°C for 48 h and finely ground prior to analysis. Samples were prepared for the analyses by mixing 98 mg of KBr with 2 mg of the detected material and then compressing the mixture into pellets. To obtain FTIR spectra, 40 scans were collected.

3 Results

3.1 DOM Concentration and Fractionation

The measurement of DOM concentration (as determined in 1:10 w:v compost:water extract) during composting revealed changes in three phases: (i) a rapid decrease from the initial concentration of 4727 to 731 mg L^{-1} over the first month; (ii) DOM concentration continued to decrease at a moderate rate to 375 mg L^{-1} up to three months; (iii) DOM concentration reached a plateau (375 to 367 mg L^{-1}) during the three to six month period. The question to be asked regarding the steady C concentration during the last stage of composting (curing stage) is whether it reflects a steady composition or a steady-state situation.

The C level of each fraction during the process (Table 1) indicated that the HoN fraction was the only fraction which exhibited an increase during composting (from 0.1 to

Table 1: Distribution of the DOM fractions extracted from MSW compost at six stages of composting (average C concentration given in mg L^{-1} , measured in 1:10 w:v compost:water extract).

Verteilung der DOM-Fractionen wäßriger Extrakte aus kompostiertem Hausmüll in 6 verschiedenen Stadien der Kompostierung (Extraktion: 10 L Wasser auf 1 kg Kompost; DOM angegeben als C, in mg L^{-1}).

Composting time (day)	Unfractionated DOM	HoA	HoB	HoN	HiA	HiB	HiN
47	732	121	100	0	143	120	248
77	600	112	12	37	180	68	191
105	374	80	2	26	95	49	122
126	366	71	1	43	67	58	126
161	371	78	4	67	94	29	99
187	309	69	2	52	80	40	66

52.5 mg L^{-1}), whereas all the other fractions decreased. The significant changes of the various fraction levels were recorded during the stabilization stage of composting (days 47 to 105). During the curing stage (days 105 to 187) the hydrophilic fractions exhibited higher degradation than the hydrophobic ones. At this stage the hydrophilic fraction levels decreased by 15, 18, and 46 % for the HiA, HiB, and HiN fractions, respectively. While the HoA and the HoB fraction levels decreased by 13 and 5 %, respectively, the HoN fraction level doubled from 25.9 to 52.5 mg L^{-1} .

The data presented in Table 1 were normalized to a percentage of the total DOM in each sample and the following changes were noted: (i) the hydrophobic fractions increased from 30 % of the total DOM at 47 days of composting, to 40 % at 161 days of composting; (ii) the HoA fraction remained the dominant hydrophobic fraction throughout the process exhibiting a moderate increase rate; (iii) the HoB fraction decreased sharply from 14 % to less than 1 % of the total DOM after 105 days of composting, whereas the opposite trend was exhibited by the HoN fraction, which increased to a maximum level after 161 days of composting; (iv) the HiN fraction was the major fraction of the total DOM up to 126 days of composting; thereafter it decreased by 38 %, while the HiA fraction became the dominant hydrophilic fraction; and (v) the HiA and HiB fractions showed no consistent trends of change during composting.

3.2 DRIFT Spectra of Unfractionated DOM

The main absorbance bands of the DRIFT and FTIR spectra of the unfractionated DOM and those of the various fractions were: a broad band at 3300...3400 cm^{-1} (H-bonds, OH groups), two peaks at 2930 and 2850 cm^{-1} (C-H asymmetric, C-H stretch of -CH), a peak or a shoulder around 1716 cm^{-1} (C=O of COOH), a wide peak at 1620...1650 cm^{-1} (C=C in aromatic structure, COO⁻, H-bonded C=O), a peak at 1540...1580 cm^{-1} (amide II bonds), a very small peak at 1518 cm^{-1} (C=C of aromatic rings), a peak at 1400...1450 cm^{-1} (C-H deformation of CH₂ or CH₃ groups), a small peak at 1407 cm^{-1} (CH₂, COO⁻), a peak at 1375...1380 cm^{-1} (CH₃, COO⁻), a peak at 1222 cm^{-1} (aromatic C, C-O stretch), a peak at 1152 cm^{-1} (C-O stretch of aliphatic OH), and two peaks at 1126 and 1031 cm^{-1} (C-O stretch of polysaccharide) [5, 9, 19-21].

All the DRIFT spectra of unfractionated DOM extracted from the compost at the five stages of composting exhibited similar peaks (Fig. 2). The spectra of unfractionated DOM extracted from 47- and 77-day compost samples exhibited high levels of aliphatic and polysaccharide structures (sharp peaks at 2850...2930 cm^{-1} and two distinct peaks in the 1000...1100 cm^{-1} region). The main change in the unfractionated DOM spectra was a reduction of the 1050 cm^{-1} peak (polysaccharide) to a small shoulder in the DOM obtained from mature compost.

3.3 Hydrophobic Acid (HoA) Fraction

The CPMAS ^{13}C -NMR spectra of the various fractions exhibited major peaks at: 25 ppm (microbial deoxy sugars or methyl C), 30 ppm (methylene C, protein), 40 ppm (methyl C), 56 ppm (methoxyl C), 75 ppm (carbohydrates or aliphatic alcohols), 105 ppm (anomeric C of polysaccharides), 115 ppm (protonated aromatic C), 130 ppm (C-substituted aromatic C), 145 ppm (C3 and C5 in etherified phenolic syringyl units), 145...150 ppm (O-substituted aromatic C), and 175 ppm (carboxyl C) [22–24].

The spectra of the HoA fraction extracted during the 5 stages of composting (Fig. 3) exhibited a relatively high aliphatic C-containing group (59% of the total C), and the following changes were exhibited during composting: a decrease in the 25- and 56-ppm peaks and a relative increase in the aromatic C-containing group region (10.4%) in the 187-day spectrum.

The FTIR spectra of the HoA fraction exhibited a decrease in the 1650 cm^{-1} and 1044 cm^{-1} peaks during composting (Fig. 4). Following Inbar et al. [21] we monitored the changes in the FTIR spectra by calculating the ratio between the intensities of the peaks at 2930 cm^{-1} , 1720 cm^{-1} , and 1040 cm^{-1} . The ratio 1720/1040 (carboxyl C/polysaccharide C) increased in the HoA spectra from 1.1 to 2.6, and the ratio 1720/2930 (carboxyl C/aliphatic C) increased from 0.66 to 1.92.

HYDROPHOBIC ACIDS (HoA)

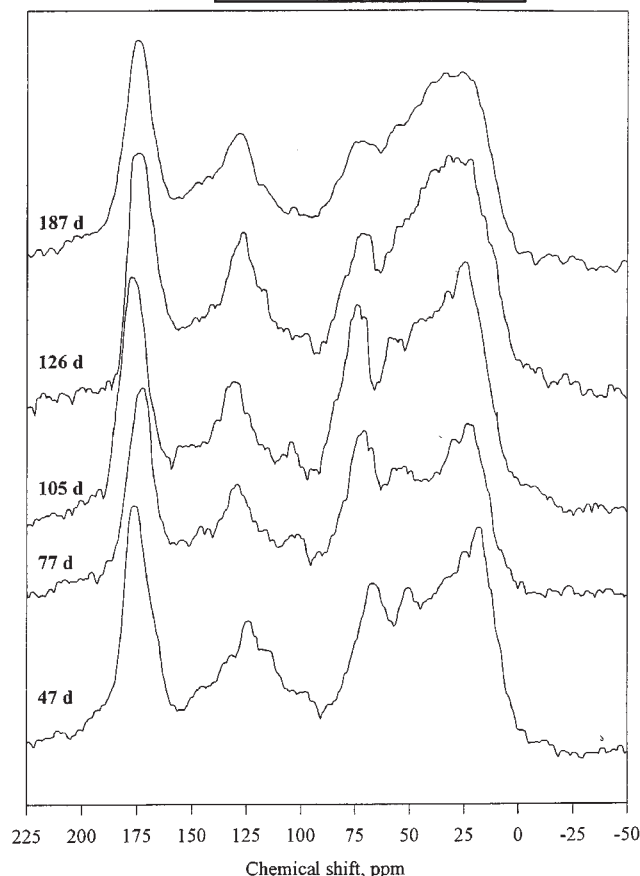


Fig. 3: CPMAS ^{13}C -NMR spectra of the hydrophobic acid (HoA) fraction extracted from MSW compost samples at five stages of composting (47, 77, 105, 126, and 187 days).

CPMAS- ^{13}C -Spektren der hydrophob/sauren Fraktion (HoA) der DOM aus Komposteluat. Die DOM wurde aus kompostiertem Hausmüll in fünf verschiedenen Stadien der Kompostierung (47, 77, 105, 126 und 187 Tage) durch wässrige Extraktion gewonnen.

UNFRACTIONATED DOM

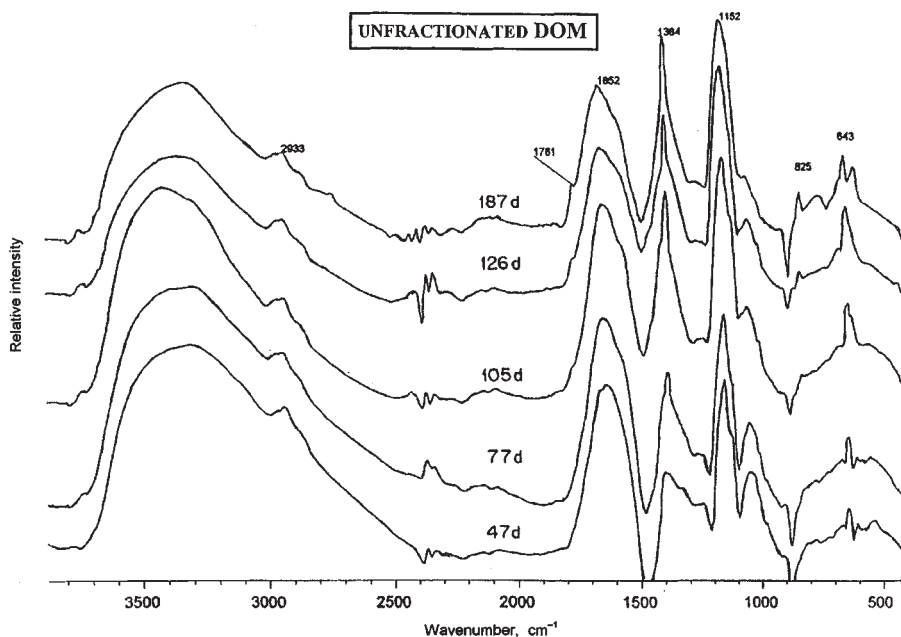


Fig. 2: DRIFT spectra of ash free unfractionated DOM extracted from MSW compost samples at five stages of composting (47, 77, 105, 126, and 187 days).

DRIFT-Spektren von aschefreier unfraktionierter DOM aus Komposteluat. Die DOM wurde aus kompostiertem Hausmüll in fünf verschiedenen Stadien der Kompostierung (47, 77, 105, 126 und 187 Tage) durch wässrige Extraktion gewonnen.

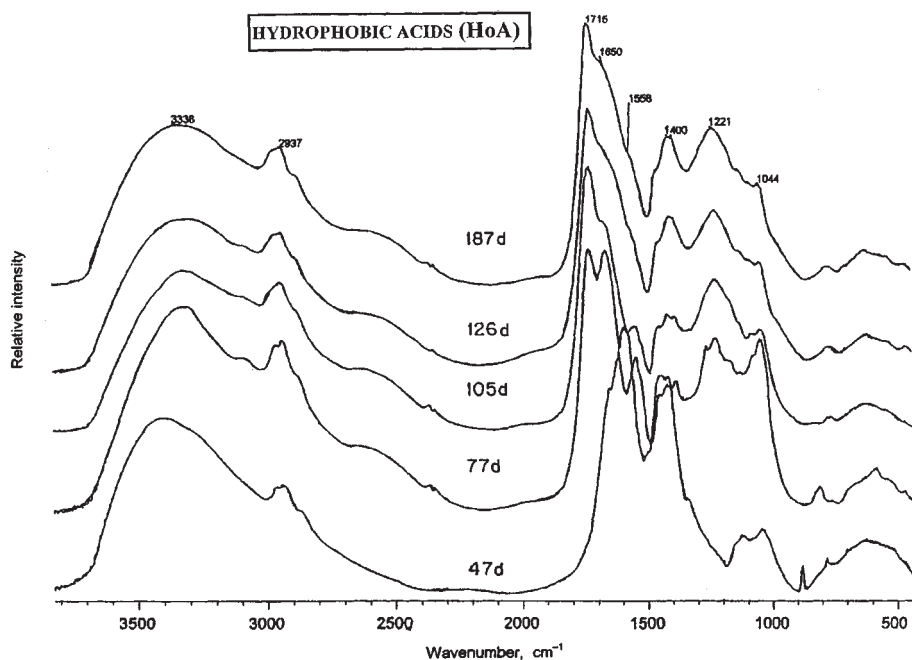


Fig. 4: FTIR spectra of the hydrophobic acid (HoA) fraction extracted from MSW compost samples at five stages of composting (47, 77, 105, 126, and 187 days).

FTIR-Spektren der hydrophob/sauren Fraktion (HoA) der DOM aus Komposteluat. Die DOM wurde aus kompostiertem Hausmüll in fünf verschiedenen Stadien der Kompostierung (47, 77, 105, 126 und 187 Tage) durch wäßrige Extraktion gewonnen.

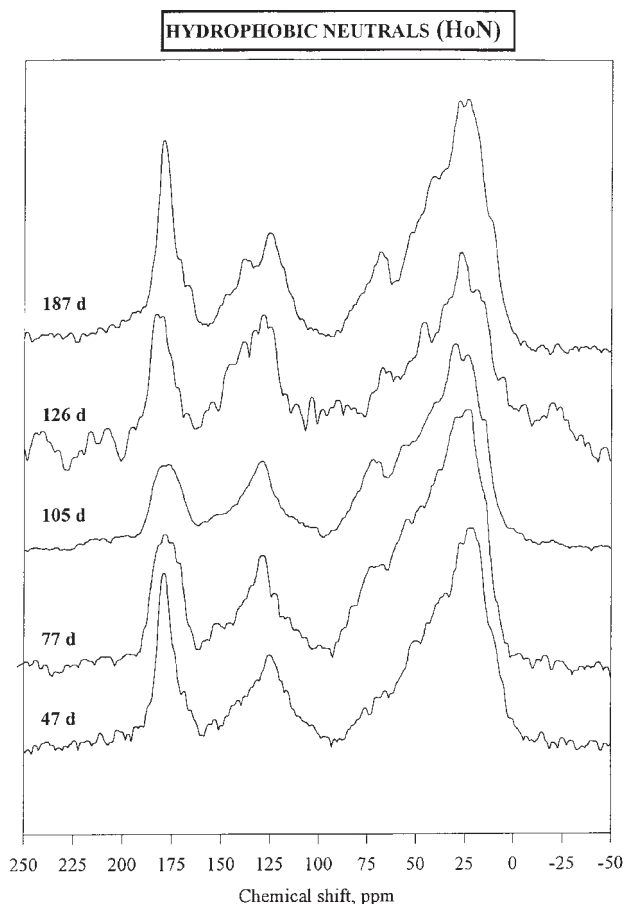


Fig. 5: CPMAS ^{13}C -NMR spectra of the hydrophobic neutrals (HoN) fraction extracted from MSW compost samples at five stages of composting (47, 77, 105, 126, and 187 days).

CPMAS- ^{13}C -Spektren der hydrophob/neutralen Fraktion (HoN) der DOM aus Komposteluat. Die DOM wurde aus kompostiertem Hausmüll in fünf verschiedenen Stadien der Kompostierung (47, 77, 105, 126 und 187 Tage) durch wäßrige Extraktion gewonnen.

3.4 Hydrophobic Neutrals (HoN) Fraction

The ^{13}C -NMR spectra of the HoN fraction extracted from the 5 stages of composting (Fig. 5) exhibited a higher percentage of aliphatic and aromatic structures than the HoA fraction. The HoN fraction exhibited four well-resolved peaks at 25...30 ppm, 75 ppm, 130 ppm and 178 ppm, and a shoulder at 145 ppm. The alkyl C-containing group is the dominant structure in the spectra (48...44%). The main changes in the HoN spectra during composting were: the appearance of the 75-ppm and 145-ppm peaks, a 33% increase of the 60...98 ppm region (alcohols and aliphatic alcohols), a 49% increase of the C-O, C-N C-containing groups, and a 12% increase of the aromaticity in the 187-day spectrum.

The FTIR spectra of the HoN fraction (Fig. 6) exhibited seven well-resolved peaks at 2930, 2870, 1650, 1580, 1440, 1338 and 880 cm^{-1} , and the dominant peak was at 1400 cm^{-1} . The main changes exhibited during composting were a sharp decrease of the aromatic peak at 1650 cm^{-1} and a relative increase of the aliphatic peak at 1400 cm^{-1} . Thus, the ratio 1400/1650 (aliphatic C/aromatic C) increased from 1.86 in the 47-day compost to 3.91 in the 187-day compost.

3.5 Hydrophilic Neutrals (HiN) Fraction

The ^{13}C -NMR spectra of the HiN fractions exhibited four well-resolved peaks at 25, 75, 112, and 178 ppm (Fig. 7). The configuration of the spectra indicated that this fraction contains mainly polysaccharides. The only differences between the 47- and 187-day spectra were a 23% decrease of the 60...120 ppm region (from 55% to 42%) and a 180% increase of the aromatic C region from 3% to 7% of the total C. The presence of a carbonyl peak (175 ppm) indicates that the polysaccharides are probably polyuronides.

The FTIR spectra of the HiN fraction during composting exhibited a dominant polysaccharide peak at 1051 cm^{-1} (Fig. 8). The major change exhibited during composting was the decrease of the amide II bond peak at 1558 cm^{-1} .

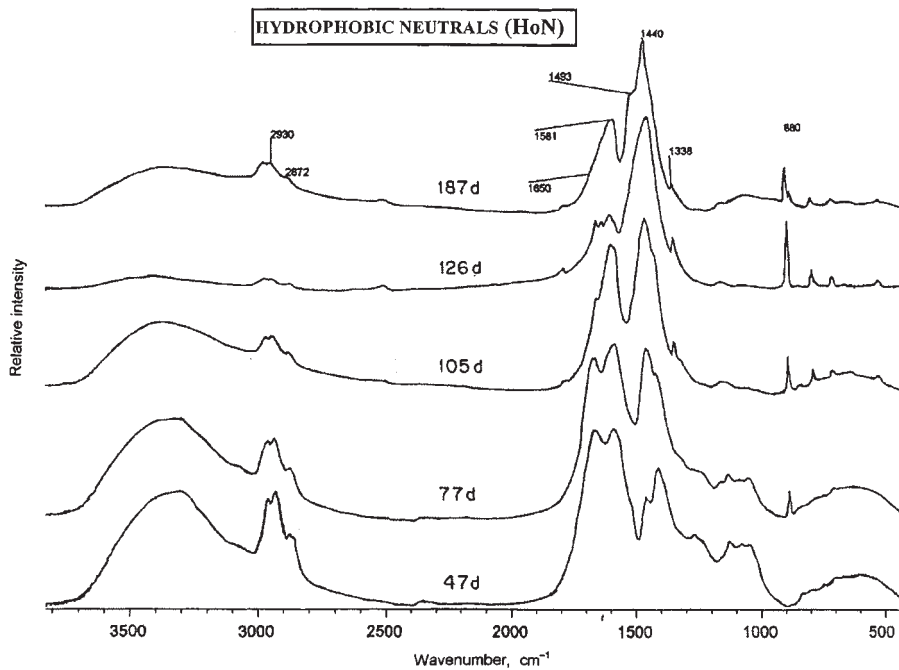


Fig. 6: FTIR spectra of the hydrophobic neutrals (HoN) fraction extracted from MSW compost samples at five stages of composting (47, 77, 105, 126, and 187 days).

FTIR-Spektren der hydrophob/neutralen Fraktion (HoN) der DOM aus Komposteluat. Die DOM wurde aus kompostiertem Hausmüll in fünf verschiedenen Stadien der Kompostierung (47, 77, 105, 126 und 187 Tage) durch wässrige Extraktion gewonnen.

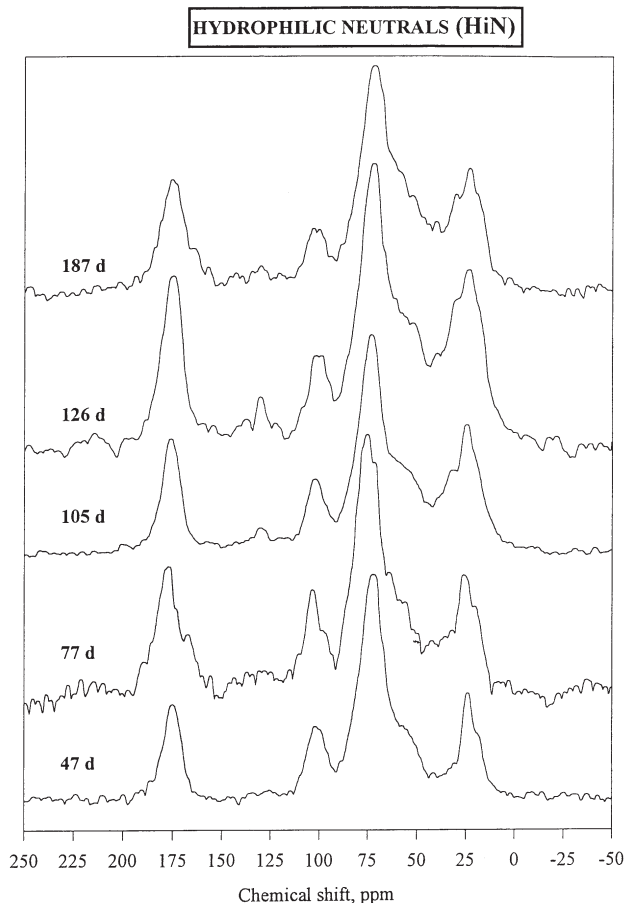


Fig. 7: CPMAS ^{13}C -NMR spectra of the hydrophilic neutrals (HiN) fraction extracted from MSW compost samples at five stages of composting (47, 77, 105, 126, and 187 days).

CPMAS- ^{13}C -Spektren der hydrophil/neutralen Fraktion (HiN) der DOM aus Komposteluat. Die DOM wurde aus kompostiertem Hausmüll in fünf verschiedenen Stadien der Kompostierung (47, 77, 105, 126 und 187 Tage) durch wässrige Extraktion gewonnen.

4 Discussion

The decomposition of the OM process is reflected in the DOM composition in compost at various stages. In this research we monitored the composition and properties of DOM during the composting of MSW in an attempt to understand DOM transformations. The quantitative results of the DOM fractionation demonstrate the importance of HoA and HoN as the main organic fractions remaining in the liquid phase of the mature compost. The C level of all the fractions (excluding HoN) decreased during composting. The HoA, HiA, and the HiB C levels decreased in a parallel trend to that of the total DOM decrease during the curing stage of composting (105 d and on). In contrast, the C level of the HiN fraction decreased more sharply than the total DOM. Thus, it can be concluded that the HoA, HiA and the HiB fractions represent a steady state composition of the DOM, whereas the HoN is formed during composting while the HiN is degraded.

According to Chefetz et al. [16] the distinct changes in the unfractionated DOM, as recorded from ^{13}C -NMR spectra during composting, were: (i) the polysaccharides C containing group decreased by 16%, and the C–O and C–N groups decreased by 20%; and (ii) the aromatic components, including aromatic and phenolic carbons increased by 51%. A similar qualitative trend was observed for the DRIFT spectra.

The HoA fraction represents the dominant fraction of DOM extracted from forest floor soils, arable soils and lakes [6, 25–28]. The relative percentage of the HoA in the compost was much lower than the one reported for soils. The chemical structures as obtained from the NMR and FTIR spectra indicated a fulvic acid structure for the HoA fraction [16], as suggested by Qualls and Haines [25]. The NMR data suggested an increase of the aromatic C-containing groups during composting, and the FTIR spectra showed an increase of the carboxylic C peak. Both NMR and FTIR spectra indicated a slight decrease of the aliphatic C structures. The suggested polyphenolic structure of the HoA fraction explains its higher propor-

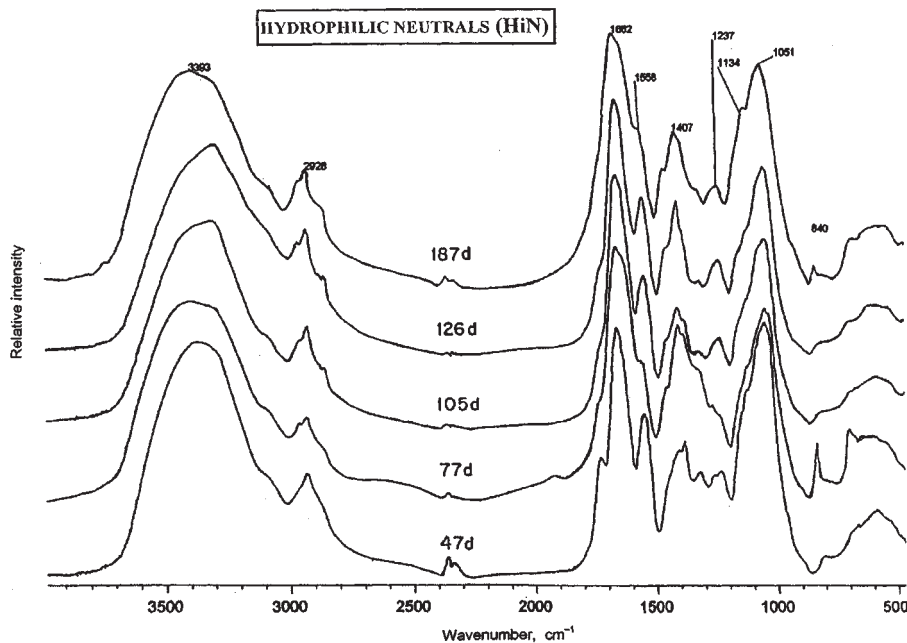


Fig. 8: FTIR spectra of the hydrophilic neutrals (HiN) fraction extracted from MSW compost samples at five stages of composting (47, 77, 105, 126, and 187 days).

FTIR-Spektren der hydrophil/neutralen Fraktion (HiN) der DOM aus Komposteluat. Die DOM wurde aus kompostiertem Hausmüll in fünf verschiedenen Stadien der Kompostierung (47, 77, 105, 126 und 187 Tage) durch wäßrige Extraktion gewonnen.

tion in soils exhibiting higher humification indexes than those of compost [29]. In general it seems that the HoA fraction did not change qualitatively during composting but quantitatively it increased to become the major DOM component.

The amount of the HoN fraction increased sharply throughout the composting process. Based on the fractionation procedure and the NMR and FTIR data, it can be concluded that the HoN fraction consists of highly apolar compounds with 44...48 % aliphatic structures and that it contains the least-soluble organic molecules of the DOM. The relatively high aromaticity and high apolarity suggest that this fraction may represent an intermediate stage in the transformation of DOM compounds to HS.

The HiN fraction of the compost represented 21...34 % of the total DOM, whereas in the aqueous soil solution this fraction usually represents only 0...10 % [6, 25, 30]. The spectroscopic spectra show that the HiN fraction contained mainly poly- and oligosaccharides resulting from plants and microbial polysaccharides [5, 6, 15, 16, 31]. The sharp decrease of this fraction during composting as well as the spectroscopic data indicate that this fraction is of importance to OM degradation, whereas in ecosystems showing slow degradation rates (soils and lakes) HiN represents a lower percentage of the DOM.

The data presented here may explain some of the mechanisms involved in compost utilization and the benefits which can be derived from it. The higher HoN and HoA concentrations result in an increase in the concentration of functional groups which are able to chelate metals and thus may improve their uptake by plants. An additional, different hypothesis is that the reduced concentration of HiN results in the removal of compounds toxic to plants. Monitoring the chemical and biological changes in DOM during the composting process, in particular during the maturation stage, can improve our understanding of the transformations of OM during the process of rapid humification.

Acknowledgement

The authors wish to thank the German Israel Fund (GIF) and the Deutsche Forschungsgemeinschaft (DFG) for their financial support of this project.

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received 8 October 1997
accepted 10 December 1997