Biodegradation (2007) 18:103–113
DOI 10.1007/s10532-006-9045-y

The contribution of water soluble and water insoluble organic fractions to oxygen uptake rate during high rate composting

D'Imporzano Giuliana & Adani Fabrizio*
*Dipartimento di Produzione Vegetale, Università degli Studi di Milano, Via Celoria 2, 20133 Milano, Italy (*author for correspondence: e-mail: fabrizio.adani@unimi.it)*

Accepted 12 January 2006

Key words: biodegradability test, composting, dissolved organic matter, DRIFT spectroscopy, oxygen uptake rate

Abstract

This study aims to establish the contribution of the water soluble and water insoluble organic fractions to total oxygen uptake rate during high rate composting process of a mixture of organic fraction of municipal solid waste and lignocellulosic material. This mixture was composted using a 20 l self-heating pilot scale composter for 250 h. The composter was fully equipped to record both the biomass-temperature and oxygen uptake rate. Representative compost samples were taken at 0, 70, 100, 110, 160, and 250 h from starting time. Compost samples were fractionated in water soluble and water insoluble fractions. The water soluble fraction was then fractionated in hydrophilic, hydrophobic, and neutral hydrophobic fractions. Each fraction was then studied using quantitative (total organic carbon) and qualitative analysis (diffuse reflectance infrared spectroscopy and biodegradability test). Oxygen uptake rates were high during the initial stages of the process due to rapid degradation of the soluble degradable organic fraction (hydrophilic plus hydrophobic fractions). Once this fraction was depleted, polymer hydrolysis accounted for most of the oxygen uptake rate. Finally, oxygen uptake rate could be modeled using a two term kinetic. The first term provides the oxygen uptake rate resulting from the microbial growth kinetic type on easily available, no-limiting substrate (soluble fraction), while the second term considers the oxygen uptake rate caused by the degradation of substrate produced by polymer hydrolysis.

Introduction

Composting is used in waste management to convert organic waste into agriculturally useful products (Chen & Inbar 1993). Composting organic fractions of municipal solid waste (MSW) combines low cost and environmentally safe waste discharge combined with the restoration of an adequate organic level in agricultural fields. This is particularly remarkable since industrialized agricultural systems do not input organic matter. Composting process is an aerobic solid state biological process typically divided into two phases: high rate and curing. The first phase is characterized by intense microbial activity decomposing most of the biodegradable material and leading to biological stability. The second phase is characterized by slow degradation processes and by part of the remaining organic matter being converted into humic substances (Adani et al. 1997).

Intense microbial activity occurs in the high rate phase. Therefore, control of this phase during the composting process is more important than during the low rate phase. This requires more accurate plant design in order for air (O_2 supplier), which is a fundamental factor in the rapid degradation of the more easily degradable organic matter, to be managed correctly so that biological stability is obtained and undesirable environmental impacts are prevented (e.g. odors, anaerobic condition, etc.).

Composting is a complex process involving many coupled physical–biological mechanisms (Bizukojc et al. 2002; Chad and Walker 2001; Hamoda et al. 1998; Kaiser 1996; Keener et al. 1993). Hamelers (2001 and 2002) recently proposed an interpretation of the composting process stressing the importance of the oxygen uptake rate (OUR) as a descriptor of the whole process. He found a relationship between OUR and the degradation of the soluble and insoluble fractions of organic matter in water, suggesting that the soluble fraction is responsible for high OUR during high rate composting as a result of it being rapidly degraded by a microbial growth kinetic type reaction. On the other hand, water insoluble fraction is responsible for low OUR as a result of substrate degradation produced by polymer hydrolysis. As hydrolysis kinetic is much slower than bio-oxidation kinetic, OUR in the degraded insoluble fraction is lower than that measured in the degradation of the readily soluble organic molecules.

The sum of the two terms represents the total OUR.

The purpose of this study is to increase knowledge of composting science by studying the contribution of water soluble and water insoluble fractions to the total OUR during high rate phase composting. Consequently, research was organized to provide experimental evidence and support the more complex research carried out by Hamelers (2001 and 2002), who uses a deductive mathematical model to describe the composting process. This model contains the basic parameters representing the theoretical basis of the composting process.

Materials and methods

Composting process

Thirty kilograms of a mixture of separated collected organic fraction of MSW and lignocellulosic waste were collected from a full scale composting plant in northern Italy (1:1 ratio v/v) (moisture content of 710 g kg^{-1} wet weight, volatile solids (VS) of 669 g kg^{-1} total solids (TS), pH 6.3, total organic carbon (TOC) 367 g kg^{-1} TS, nitrogen (N) 14.1 g kg^{-1} TS, C/N ratio of 26, bulk density (0.55 Mg m^{-3})). The U.S. Composting Council guidelines for compost sampling were used to obtain the samples (The U.S. Composting Council, 1997). Sample obtained was immediately transported to the DiProVe (Dipartimento Produzione Vegetale) – Università degli Studi di Milano (Italy), for successive preparation, chemical characterization, and laboratory scale experiment. Approximately 4 kg of the sample was dried at 105 °C so that moisture content could be determined and then reduced in size to 0.5 mm and stored for successive analyses. Following this, volatile solids, ash, TOC, N, and pH tests were performed on a dried sample using normal analytical procedures (The U.S. Composting Council, 1997). The remaining sample was stored untransformed at 4 °C and then used for biostabilization experiment within 2 days of sampling.

Composting experiment was performed on 10 kg of sample using laboratory scale composter apparatus (Costech, Cernusco S.N., Milano, Italy) (Adani et al. 2001).

The composter was composed of a 20 l insulated container (reactor), a control cabinet, an air supply system, a PC unit, and a biofilter. The apparatus was set up so that it worked under adiabatic conditions (self-heating). Process parameters, such as biomass temperature (T) (°C), oxygen concentration in the inlet and outlet airflows (ml l^{-1}), airflow rate (Q) (l min^{-1}), and the Oxygen Uptake Rate (OUR) (mg O_2 kg C^{-1} h^{-1}) were measured and recorded hourly (Adani et al. 2004).

Since the aim of this paper was to study the high rate phase (biostabilization phase) of a composting process, the experiment lasted until biological stability was reached. The latter was ascertained by measuring the OUR. OUR indicates biological stability when it is below 1000 mg O_2 kg VS^{-1} h^{-1} (Adani et al. 2004), which was obtained after 250 h.

Organic matter fractionation

Six representative samples of 300 g each were collected from biomass during high rate composting (The U.S. Composting Council 1997) at 0, 70, 100, 110, 160, and 250 h from starting time. Each sample was dried at 60 °C under vacuum, ground to 0.5 mm by using a blade-mill, and stored for subsequent analysis. Each sample was characterized for pH, VS, and TOC content (The U.S. Composting Council 1997). Following this,

dissolved organic matter (DOM) was determined using the method reported by Adani et al. (2003) but with substantial modifications. In particular, 5 g of dried material was extracted by water (1:20 solid:liquid ratio, w/w) using a Dubnoff bath at 60 rpm for 30 minutes at 40 °C. To obtain highest DOM yield and to avoid hydrolysis, extraction parameters were those used in a previous set up (D'Imporzano, 2003, data not published). Following this, the suspension obtained was centrifuged for 15 minutes at 6500 rpm and then filtered twice: firstly, by using fast cellulose filter (Whatman paper filter N.4), and then 0.45 μm millipore membrane (Advantec MFS, Pleasanton, CA). Solution obtained represented the dissolved organic matter (DOM). DOM was then separated into hydrophilic (Hi), hydrophobic (Ho), and neutral hydrophobic (NHo) fractions according to the procedure proposed by Leenheer (1981), which was partially modified by the authors. In particular, Amberlite XAD-7 (Sigma-Aldrich Steinheim, Germany) was prepared in 40 cm high glass column, 2.5 cm in diameter, activated with 0.5 mol l^{-1} of H_2SO_4 and then washed until pH neutral. Two hundred ml of DOM previously acidified (pH < 2) with 0.5 mol l^{-1} of H_2SO_4 was loaded onto the column and eluted at the velocity of 2 ml min^{-1}. After this, column was washed with distilled water (2 bed volume). Fraction eluted represented the Hi fraction. Then, Ho fraction was eluted by using 0.05 mol l^{-1} of NaOH (1.25 bed volume) and distilled water (2 bed volume). Following this, XAD-7 resin was dried at 40 °C for 15 h, and then extracted using Shoxlet apparatus and anhydrous MeOH to obtain NHo fraction. Meanwhile, Ho fraction was loaded onto a column filled with a cation exchange resin (Amberlite IR 120, Merck, Darmstad, Germany) to eliminate Na. DOM fractionation was repeated three times.

The insoluble fraction (water insoluble fraction plus particulates recovered from filtration of the soluble fraction) (IF) resulting from DOM extraction was dried at 60 °C under vacuum and stored. Part of the fractions obtained was immediately used for biodegradability test (see later) and part dried at 60 °C under vacuum for successive analysis. All fractions, i.e., compost, IF, DOM, Hi, Ho, and NHo were quantified using total organic carbon determination, from which compost-C, IF–C, DOM–C, Hi–C, Ho–C, and NHo–C were obtained.

Degradability tests

Composts and DOM, IF, Hi, Ho, and NHo fractions obtained at different composting times underwent biodegradability test, which measured the oxygen uptake rate under liquid condition (OURL) for organic carbon degradation. Test was performed using the method reported by Lasaridi & Stentiford (1998). In brief, oxygen uptake rate was measured for 20 h under liquid condition using a solid:liquid ratio of 1:100 (w/w). During the test, standard conditions were maintained so that optimal microbial activity and reaction rates were obtained. In particular, so as to avoid any pH and element nutrition limiting growing condition occurring (Lasaridi & Stentiford 1998), 5 g of dry matter (or aqueous extracts obtained from 5 g of compost dry matter) were set in a flask and the following were added: 500 ml of deionized water, 12 ml of phosphate buffer solution (KH_2PO_4 0.062 mol l^{-1}, K_2HPO_4 0.125 mol l^{-1}, $Na_2HPO_4{\cdot}7H_2O$ 0.125 mol l^{-1}; pH 7.2), and 5 ml of nutritive solution ($CaCl_2$ 0.25 mol l^{-1}, $FeCl_3$ 0.9 mmol l^{-1} and $MgSO_4$ 0.09 mol l^{-1}) made up according to the standard BOD test method procedures (APHA 1992). No nitrogen was added to the solution, except for Ho and NHo fractions as previous tests revealed that N limits microbial activity in these two fractions. Nitrogen was supplied in the form of $(NH_4)_2NO_3$ until a C/N ratio of 20 was reached. In order for oxygen diffusion to occur, the slurry was agitated every 15 min using a magnetic stirrer, causing intermittent aeration. OURL was detected by measuring the slope of the decrease of the oxygen concentration in the slurry during the absence of aeration (Lasaridi & Stentiford 1998). The cumulative oxygen consumption during the 20 h test-length (mg O_2 g^{-1} C 20 h^{-1}) represented the degree of biodegradability reported. The OURL values refer to both the total Compost-C and to the contents of each carbon-fraction.

Spectroscopic analysis

Compost fractions were analyzed by Diffuse Reflactance Infrared Fourier Transformed (DRIFT) spectroscopy using an Avatar 370 FT-IR from ThermoNicolet Instruments (Madison, WI, USA). Samples (7 mg), previously dried at 65 °C for 48 h, and KBr (700 mg; FT grade, Aldrich

Chemical Co, ST Louis, Missouri) were finely ground for 10 minutes using an agate ball mill (Specamill-Greseby-Specac, Kent, UK). Instrument parameters used were: scanning 128, resolution 4 cm^{-1}, and frequency 400–4000 cm^{-1} gain 16.

Composting kinetic model

The deductive model for composting process proposed by Hamelers (2001) was used to describe composting process. The model stresses the value of oxygen uptake as a result of the whole biological process, and described the OUR parameter by examining base principles of multi-particle system. Model as indicated by Hamelers (2001) was modified and simplified by Adani et al. (2004). In particular, OUR behavior was determined by:

$$\mathrm{OUR}(t) = \sqrt{\frac{\beta_{\mathrm{eff}}}{\beta_{\mathrm{eff}} + e^{-\mu t}}}\mathrm{OUR}_{i\max} e^{-\zeta(t)} + A_h$$

In which β_{eff} is the effective dimensionless biomass concentration, μ is the effective growth rate constant (h^{-1}), ζ is the scaled particle size (dimensionless), t is the composting time (h), $\mathrm{OUR}_{i\max}$ is the maximum OUR measured during the process (mg O_2 kg C^{-1} h^{-1}), and A_h is the OUR caused by the degradation of hydrolyzed biomass (mg O_2 kg C^{-1} h^{-1}).

Model assumed that hydrolysis proceeded as a zero order kinetics ($A_h = -k$) for a limited time instead of proceeding as first order kinetics (Hamelers 2002). Parameters in the above reported equation were determined using the method previously reported by Adani et al. (2004).

Statistical analysis

Results were analyzed using ANOVA, and statistical difference between means was assessed using Tukey's test. Chemical analyses were performed on three analytical samples taken from the 300 g composite bulk sample, and since standard deviation values were calculated using the data obtained from these three replicates, they represent estimates of the variability caused by both the waste bed homogeneity and the analytical method.

Fitting indices were used to compare the simulated OUR data obtained by mathematical model and the experimental data (Greenwood et al. 1985; Loague & Green 1991). The fitting indices used were: (i) the Relative Root Mean Square Error (RRMSE: range $0 \div +\infty$, optimum = 0%), which describes the differences between the measured and the simulated values. (ii) the Modelling Efficiency (EF: range $-\infty \div +1$, optimum = 1), which, if positive, indicates that the model is a better predictor than the average of the measured values, and lastly, (iii) the Coefficient of Residual Mass (CRM, $-\infty \div +\infty$, optimum = 0) which assumes a positive sign in cases of model underestimation. Moreover, observed and predicted values were used to calculate the parameters of the regression equation (slope and intercept).

Results

Composting process

The usual high rate composting resulted from the composting processes (Adani et al. 1997) (Figure 1). In particular, after a lag-phase of 62 h, OUR increased exponentially due to microbial growth (phase A), subsequently becoming stable for a short period (phase B). Then OUR decreased rapidly (phase C) until entering a stable phase (phase D) (Figure 1). Temperature trend was similar, correlating well with OUR trend ($r = 0.96$; $P < 0.01$).

During the process, the chemical parameters changed in response to the biological activity (Table 1). Compost-C decreased from 367 g kg^{-1}d.m. to 346 g kg^{-1}d.m. Relative nitrogen content remained constant and so C/N ratio dropped from 26.2 at the beginning of the process to a final value of 22. Total carbon fractions also changed. The relative contents of DOM–C, Hi–C, and Ho–C decreased by 470, 800, and 710 g kg^{-1} compared to their respective initial contents. In contrast, NHo-C content increased by 3,700 g kg^{-1} compared to its initial content.

During the course of the process a change occurred in the contribution each soluble fraction made to the total dissolved organic carbon. At the beginning (sample 0 h) Hi–C, Ho–C, and NHo–C contents represented 620, 300, and 70 g kg^{-1} of the DOM–C respectively. In contrast, at the end of the process (sample 250 h) the same fractions respectively contributed 230, 160, and 590 g kg^{-1} to DOM–C. Trends in absolute carbon content (g) in

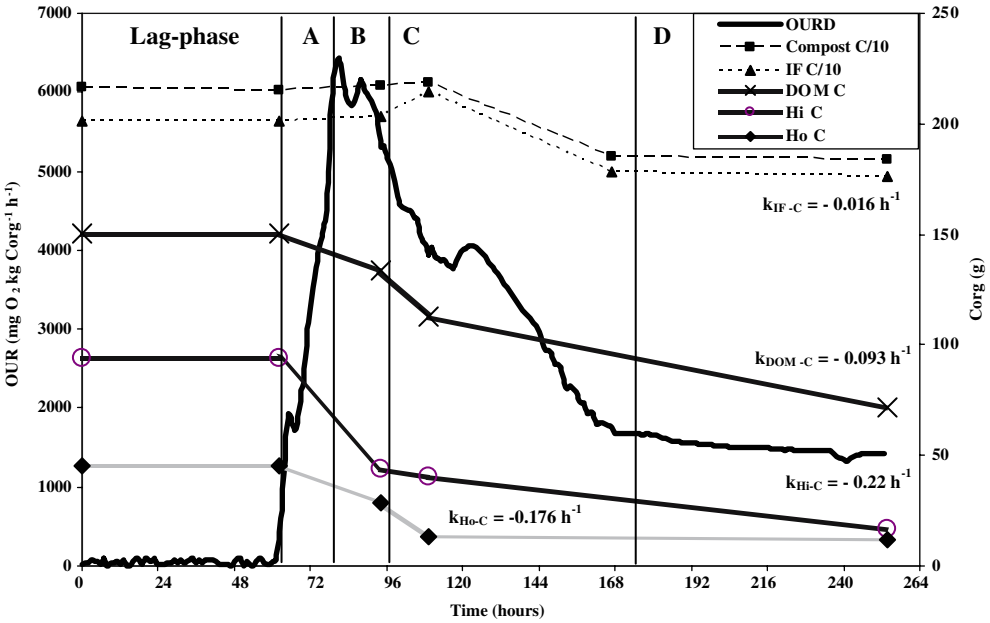


Figure 1. OUR and compost carbons fraction trend, during composting experiment.

Table 1. Total carbon, total nitrogen and volatile solids content on compost, organic carbon value in DOM, Hi and Ho fractions

Sample (h)	Compost-C	N	IF–C	DOM–C (g kg dm^{-1})	Hi–C	Ho–C	NHo–C
0	367 ± 7b[a]	14.1 ± 0.7a	341 ± 1b	25.5 ± 0.4d	15.9 ± 0.4d	7.7 ± 0.4c	1.7 ± 0.2a
70	365 ± 2b	15.1 ± 0.4a	n.d.	n.d.	n.d.	n.d.	n.d.
100	369 ± 5b	14.7 ± 0.6a	345 ± 0c	22.7 ± 0.4c	7.4 ± 0.3c	4.9 ± 0.2b	n.d.
110	372 ± 7b	15.4 ± 0.9a	364 ± 0d	19.2 ± 0.7b	6.9 ± 0.2b	2.3 ± 0.5a	n.d.
160	348 ± 3a	14.9 ± 0.8a	n.d.	n.d.	n.d.	n.d.	n.d.
250	346 ± 4a	15.6 ± 0.5a	333 ± 1a	13.5 ± 0.3a	3.1 ± 0.1a	2.2 ± 0.4a	8.0 ± 0.5a

[a]means in the same column followed by different letter are statistically different for $P < 0.05$.
n.d.: not determined.

each C fraction proved to be more interesting (Figure 1). The content of compost-C did not change significantly during the first two phases of composting (phases A and B), but decreased by 350 g during phase C, and then remained constant during phase D. So degradation of compost-C does not follow the OUR trend, i.e. compost-C started to be degraded after maximum oxygen uptake was detected. Insoluble carbon (IF–C) initially increased by 22.4 g (phases B and C) but then decreased by 272 g (phase C). On the other hand, through the whole duration of the process, soluble carbon (DOM–C) decreased by 79 g.

The fact that during phase A IF–C increased and compost-C was not degraded suggests insolubilization of part of the DOM–C as microbial body (Hamelers 2001).

The decrease of DOM–C during the process was due to degradation of both Hi–C and Ho–C (Figure 1) (Chefetz et al. 1998). Hi–C content was 93 g at the beginning of the process, and fell to 16 g by the end. Ho–C losses where 34 g, decreasing from 45 to 12 g. On the other hand, NHo–C increased during composting by approximately 20 g, increasing from 6 to 26 g (not shown in Figure 1) (Chefetz et al. 1998). HiC degradation precedes HoC degradation although Ho degradability is higher than that of HiC. This fact was also observed during SOUR test (see biodegradability section), where maximum oxygen uptake in HiC

fractions occurred within 6–8 h from the test beginning, in contrast to HoC fractions, which took 14–18 h. This is probably due to the different chemical structures of these fractions (see DRIFT section) influencing microbial population and/or molecule solubility and therefore their degradability.

Biodegradability test

Biodegradability test performed on both compost samples and its fractions provided both information concerning their degradability over time (Table 2), and information concerning the contribution of each fraction to total compost degradability (Table 3). Compost showed a higher degradability coefficient (higher OURL) at the beginning of the process (sample 0 h) (Table 2) than at the end. Insoluble fraction (IF) changed in degradability during the process, increasing in the final sample. This could be caused by the greater presence of polymer-hydrolyzing microorganisms (e.g. actinomyces) after the thermophilic phase of composting (Klamer and Bååth 1998).

Biodegradation of water soluble fractions, i.e. Hi, Ho, and NHo, differed. Hi and Ho fractions were biodegradable throughout the whole experiment. In particular, Hi showed similar OURL for both starting (sample 0 h) and end samples (sample 250 h). In contrast, OURL final sample Ho increased by approximately 138%. Regarding the NHo fraction, no oxygen uptake was registered during tests on both starting (sample 0 h) and final samples (sample 250 h), so NHo fraction was not degradable. Each fraction contributed to the total

Table 2. Biodegradability degree of compost and derived fractions

	OURL (mg O_2 g C^{-1})[a] sample 0 h	OURL (mg O_2 g C^{-1}) sample 250 h
Compost	97.6 ± 12b[b]	46.0 ± 5a
IF	19.9 ± 10a	31.7 ± 2b
DOM	813.2 ± 60b	516.5 ± 20a
Hi	701.9 ± 14a	703.5 ± 100a
Ho	945 ± 92a	2249 ± 329b
Nho	0a	0a

[a]OURL expressed on own carbon content.
[b]means in the same row followed by different letter are statistically different for $P < 0.05$.

Table 3. The contribution of compost fractions to the total compost oxygen uptake rate (OURL)

	OURL Sample 0 h (mg O_2 g compost-C^{-1})	OURL Sample 250 h (mg O_2 g compost-C^{-1})
Compost	97.6 ± 12.2	46.0 ± 5.2
Compost*	74.9[a]	51.5 [a]
IF	18.4 ± 4.2	30.6 ± 2.1
DOM	56.5 ± 4.4	20.9 ± 0.8
DOM**	50.6 [b]	19.1 [b]
Hi	30.0 ± 0.6	6.1 ± 0.9
Ho	20.6 ± 2.0	13.0 ± 1.9
NHo	0	0

[a]obtained as the sum of OURL of IF and DOM.
[b]obtained as the sum of (Hi + Ho + NHo).
*,** $P < 0.05$.

OURL (compost-OURL) in different proportions, and the composting process also modified these contributions. Hi, Ho, and IF fractions contributed 50, 30, and 20% respectively to compost-OURL at the beginning of the process (Table 3). These percentages had changed in the final sample (sample 250 h) being 13, 28, and 66% for Hi, Ho, and IF respectively (Table 3). Therefore, at the end of the process, the main contributor to the total oxygen uptake was insoluble carbon.

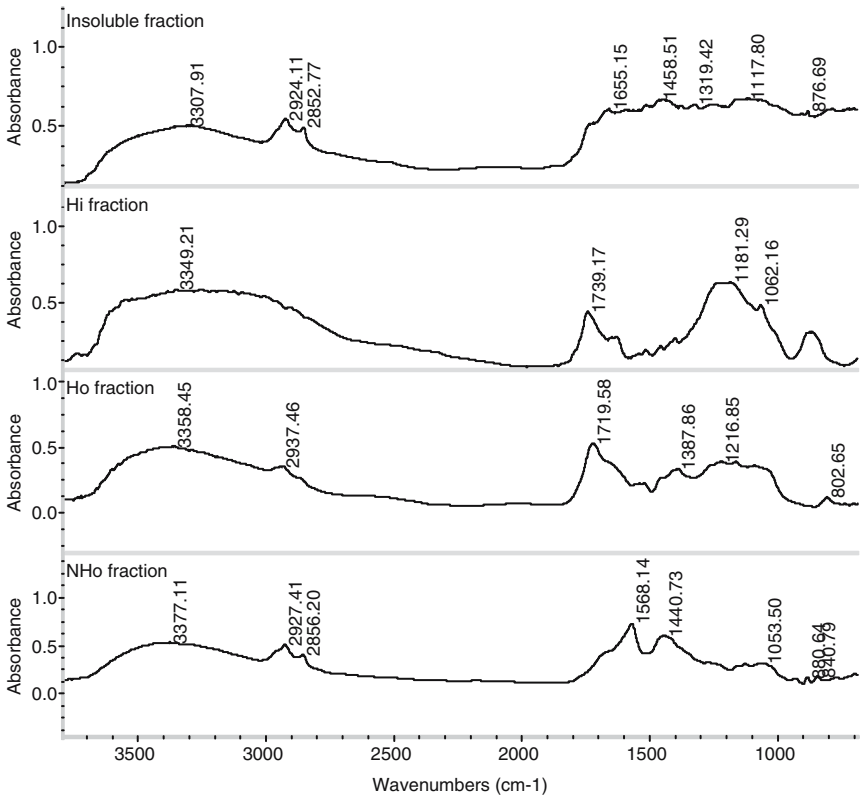
DRIFT spectroscopy

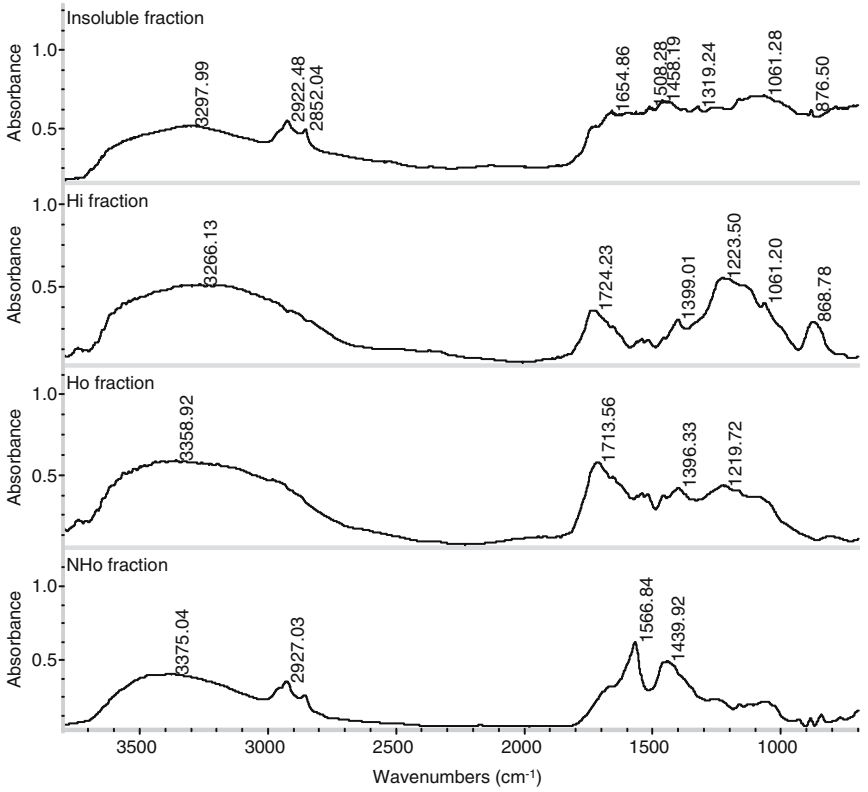
DRIFT spectroscopy was used as a qualitative means to identify main functional group in both compost and in its fractions, i.e. IF, DOM, Hi, Ho, and NHo. Spectra assignments were based on Smith (1999) and Socrates (1980) (Figure 2).

The spectra obtained for Hi, Ho, and NHo were well resolved and allowed the various functional groups to be differentiated.

Hi fractions were essentially composed of carbohydrates and carboxylic acids, as suggested by the large band between 3000 and 3400 cm^{-1} (–OH stretching), though water could also contribute to this large band, the peak at 1739 cm^{-1} (saturated C = O stretch of aldehyde, ketone, and carboxylic acids), the band between 1222 and 1181 cm^{-1} (C–C–C stretch of ketone functional

Figure 2. DRIFT spectra for compost water-soluble and water-insoluble fractions: Sample 0 h (top panels) and Sample 250 h (bottom panels).


Insoluble fraction
Absorbance
1.0
0.5
3307.91
2924.11
2852.77
1655.15
1458.51
1319.42
1117.80
876.69
Hi fraction
Absorbance
1.0
0.5
3349.21
1739.17
1181.29
1062.16
Ho fraction
Absorbance
1.0
0.5
0.0
3358.45
2937.46
1719.58
1387.86
1216.85
802.65
NHo fraction
Absorbance
1.0
0.5
0.0
3377.11
2927.41
2856.20
1568.14
1440.73
1053.50
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)


Insoluble fraction
Absorbance
1.0
0.5
3297.99
2922.48
2852.04
1654.86
1508.28
1458.19
1319.24
1061.28
876.50
Hi fraction
Absorbance
1.0
0.5
3266.13
1724.23
1399.01
1223.50
1061.20
868.78
Ho fraction
Absorbance
1.0
0.5
3358.92
1713.56
1396.33
1219.72
NHo fraction
Absorbance
1.0
0.5
3375.04
2927.03
1566.84
1439.92
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

group, –C–OH), and the peak at 1062 cm^{-1} (C–O stretch of carbohydrates and/or organic acids). The small peak at 1626 cm^{-1} also suggests the presence of proteinaceous material (amide scissor), but it could also indicate carboxylate groups. Composting process did not cause appreciable modification of DRIFT spectra, which suggests that chemically Hi fraction remained substantially unmodified during composting.

Hydrophobic (Ho) fraction is mainly composed of short chain and/or branched fatty acids and aliphatic ketones and/or carbohydrates. The short chain and/or branched fatty acids peak at 2937 cm^{-1} (asymmetric CH stretch of CH_2), the small shoulder at 2855 cm^{-1} (symmetric stretch of CH_2), the peak at 1719 cm^{-1} (C = O stretching of carboxylic carbon), and peak at 1387 cm^{-1} (symmetric C–H bending vibration of CH_3 group). Aliphatic ketones and/or carbohydrates are suggested by the band between 1300 and 1050 cm^{-1} (C–C–C stretch of ketone functional group, C–OH and C–O stretch of carbohydrates and/or organic acid). Composting process, which probably caused the degradation of fatty acid at peaks 2937 and 2855 cm^{-1}, disappeared (Figure 2).

The presence of the typical IR spectra of this molecule suggests NHo fraction was essentially formed of lignin-like material (Nada et al. 1998). In particular, the large band between 3000 and 3600 cm^{-1} could be attributed to C–H stretch of aromatic rings. Peaks at 2937, 2860, and 1440 cm^{-1} were due to O–CH_3 bonds, and peak at 1568 cm^{-1} to C–H vibration of aromatic rings. This interpretation agrees with both NHo solubility in CH_3–OH and its recalcitrant properties (see Biodegradability test).

DOM fraction (spectra not reported) was obviously a miscellanea of the three fractions.

As expected, IF fraction was composed of polymers such as lignin (band between 3000–3600 cm^{-1} with peaks at 2922, 2857, 1560, and 1458 cm^{-1}), proteins (peaks at 1655 cm^{-1}, 1319 cm^{-1}), and polysaccharides (band between 1200 and 1000 cm^{-1}) though overlapped bands make any interpretation difficult.

Discussion

As suggested by Hamelers (2001), high-rate composting can be described by the oxygen uptake rate (OUR) and divided into four phases (A, B, C, and D) (Figure 1). Analogous schemes for interpreting composting are proposed in the literature (Kaiser 1996; Liwarska-Bizukojc et al. 2002). All the same, Hameler's model is used in this discussion. Phase A corresponded to the exponential increase of OUR which was caused by microbial growth on available non-limiting substrate (DOM-C) (Hamelers 2001; Stenstrom et al. 2001). During this phase soluble carbon (DOM–C) provided the main source of carbon available to microorganism, becoming partially degraded to CO_2 and H_2O, and partially used to build up microbial body (Chefetz et al. 1998; Guardia et al. 2002). Although decreasing during the second phase (Phase B), DOM–C still continued to support high microbial activity (high OUR). Phase C was characterized by a rapid decrease of OUR. This fact suggests a limitation of the available substrate because of rapid degradation of the DOM (Hamelers 2001). Effectively, the DOM decreased during Phase B and C, but not as rapidly as to explain the drastic reduction in OUR (Figure 1). On the other hand, Hamelers (2001) reported that a rapid decrease of OUR coincided with the complete depletion of the soluble carbon, but this did not happen in this study. The soluble fraction (DOM) at the end of the process (Phase D) is about 500 g kg^{-1} of its initial value, and consequently much greater than zero (Figure 1).

To understand this question, it is important to understand that soluble fraction (DOM) does not necessarily mean degradable fraction (Chefetz et al. 1998). DOM fractionation and successive characterization of the soluble fractions (Hi, Ho, NHo) in degradability test and DRIFT in both starting and final samples suggested that NHo fraction, as formed by lignin residue-like materials, was not degradable. Moreover, both DRIFT data and biodegradability test suggest that no substantial modification of the nature of this fraction took place during high rate composting, supporting the idea of lignin catabolism as an origin.

This contrasts to Hi and Ho, which are mainly composed of carbohydrates, proteinaceous material, and fatty acids (Chefetz et al. 1998).

Biodegradability tests revealed that Hi and Ho fractions still contributed to the total OUR in the final stages of composting as they were as degradable as starting samples (Hi), or even more so in the case of Ho. In fact, these biodegradability

tests showed no modification of OURL uptake for start and end Hi samples, and unexpectedly showed higher degradability of Ho fraction in the final samples (Table 2). The higher Ho degradability for final sample is not easy to explain. In contrast to the increase in OURL, the loss of lipid-like material reported by DRIFT analysis suggests a decrease of OURL. All the same, the isolated fractions (final stage) may behave differently from the same materials in the original mixture. Moreover, water-soluble fractions represent a miscellany of different molecules only partially detected by DRIFT analysis, which is not quantitative. Therefore, biodegradability modification of Ho could be caused by both chemical modification and/or concentration of more degradable molecules in the Ho fraction. Another hypothesis involves the contribution of new fraction from insoluble-C. This observation is supported by the fact that starting from 110th h, Ho fraction remained quantitatively constant, although biodegradability test indicates high degradability. Therefore, Ho degradation and formation processes probably coexist during composting, a fact that should be considered in the discussion. The same may occurs for Hi fraction, but its degradation kinetics is probably faster than its production so that the net result is a sharp decrease of Hi.

The degradable soluble fraction, i.e. Hi + Ho, was degraded by 800 g kg^{-1} of its initial content by the end of the process (phase D), and it is this which causes the drastic total OUR reduction. On the other hand, NHo increased during composting by 3700 g kg^{-1} of its initial content because of the contribution of new NHo fraction originating from the insoluble carbon (Table 1) and its recalcitrant properties (Chefetz et al. 1998). Nevertheless, NHo did not contribute to total OUR because of its non-degradability.

The low presence of degradable soluble-C (Hi + Ho) agreed with the low OUR recorded (Hamelers 2001). Consequently, in the final stages of composting the OUR could largely be caused by the degradation of the substrate available after polymer hydrolysis (Hamelers 2002), the OUR thus representing an indirect measure of the kinetic rate of hydrolysis (Adani et al. 2004).

Such a description of the high rate composting finds mathematical expression in the equation reported in M & M section (Hamelers 2001) (Figure 3).

This trend was supported by the experimental results. In fact, taking a theoretical respiration quotient of 1 into consideration (mole CO_2:mole O_2) (Adani et al. 2001) and the absolute amounts of degraded carbons, a theoretical oxygen

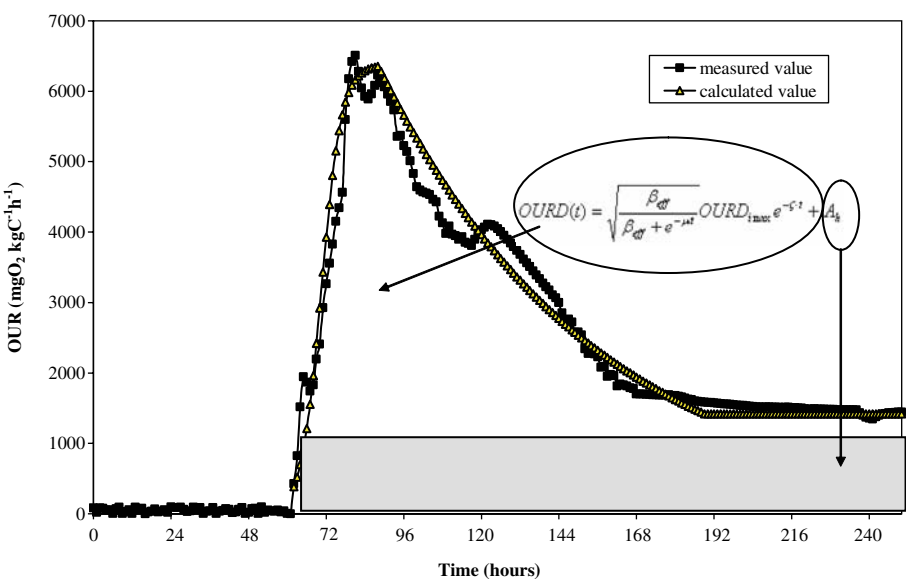


Figure 3. OUR trend: a representation of the two-type kinetic reaction and comparison between experimental and calculated values. Statistical parameters (see text): RMSE = 11.72; EF = 0.95; CRM = −0.02; slope = 0.90; intercept = 125.9; $R^2 = 0.97$; Significance < 0.001; Observed mean = 1502; Estimated mean = 1528.

consumption of 250,666 mg O_2 kg C^{-1} and of 245,333 mg O_2 kg C^{-1} were calculated for degraded (Hi + Ho)–C and IF–C. As the cumulated oxygen uptake rates calculated as the integrals of the experimental OUR curve (Figure 3) were 249,349 mg O_2 kg C^{-1} for (Hi + Ho)–C and 272,748 mg O_2 kg C^{-1} for IF–C, there is good agreement between this data and that of the model presented by Hamelers (Hamelers 2001) (see fitting indices reported in Figure 3 (Legend), which were very close to the optimum values reported in the M & M section).

This study contributes to knowledge of composting processes, and particularly to the contribution of water soluble fractions as these influence OUR significantly during composting and thus also influence composting plant design.

Moreover, the experiment suggested that the composting process not only causes a decrease in the water soluble fraction but also modifies its composition. Consequently, both quantitative and qualitative studies in the future could measure composting maturity (e.g. biological stability and/or maturity) (Chefetz et al. 1998).

Acknowledgement

Authors are in debt to Dr. Cesare Ubbiali and Dr. Roberto Confalonieri for their help in the performance of composting process performance and mathematical model set up. In addition, thanks go to the reviewer with the ability and patience to significantly improve the paper.

References

Adani F, Confalonieri R & Tambone F (2004) Dynamic respiration index as descriptor of the biological stability of organic wastes. J. Environ. Qual. 33: 1866–1876

Adani F, Gigliotti G, Valentini F & Laraia R (2003) Respiration index determination: a comparative study of different methods. Compost Sci. Utiliz. 11: 144–151

Adani F, Lozzi P & Genevini PL (2001) Determination of biological stability by oxygen uptake on municipal solid waste and derived products. Comp. Sci. Utiliz. 9: 163–178

Adani F, Genevini PL, Gasperi F & Zorzi G (1997) Organic matter evolution index (OMEI) as a measure of composting efficiency. Compost Sci. Utiliz. 5: 5–62

APHA (1992) Standard Methods for the Examination of Water and Wastewater. 18th ed., Water Pollution Control Federation, Washington, DC

Chad WH & Walker LP (2001) Validation of new model for aerobic organic solids decomposition: simulation with substrate specific kinetics. Process Biochem. 36: 875–884

Chefetz B, Hadar Y & Chen Y (1998) Dissolved organic carbon fractions formed during composting of municipal solid waste: properties and significance. Acta Hydrochim. Hydrobiol. 26: 172–179

Chen Y & Inbar Y (1993) Chemical and spectroscopical analyses of organic matter transformation during composting in relation to compost maturity. In: Hoitink HAJ & Keener HM (Eds) Science and Engeneering of Composting: Design, Environmental, Microbiology and Utilization Aspects (pp. 551–600). The Ohio State University, Wooster, OH

De Guardia A, Brunet S, Rogeau D & Matejka G (2002) Fractionation and characterisation of dissolved organic matter from composting green wastes. Bioresource Technol. 83: 181–187

Greenwood DJ, Neeteson JJ & Draycott A (1985) Response of potatoes to N fertilizer: dynamic model. Plant Soil 85: 185–203

Hamelers HVM (2001) A mathematical model for composting kinetics. Ph.D thesis, Wageningen University, Wageningen, The Netherlands

Hamelers HVM (2002) Modeling composting kinetics: a deductive approach. In: Michel FC, Rynk RF & Hoitink HAJ (Eds) Proceedings of 2002 International Symposium Composting and Compost Utilization Process kinetics and Modeling (on CD). The J.G Press. Inc. Emmaus, PA

Hamoda MF, Abu Qdais HA & Newham J (1998) Evaluation of municipal solid waste composting kinetics. Res. Conserv. Rec. 23: 209–223

Kaiser J (1996) Modelling composting as a microbial ecosystem: a simulation approach. Ecol. Modell. 91: 25–37

Keener HM, Merugg C, Hansen RC & Hoitink HAJ (1993) Optimizing the efficiency of the composting process. In: Hoitink HAJ & Keener HM (Eds) Science and Engineering of Composting: Design, Environmental, Microbiology and Utilization Aspects (pp. 59–94). The Ohio State University, Wooster, OH

Klamer M & Bååth E (1998) Microbial community during composting of straw material studied using phospholipid fatty acid analysis. Microbiol. Ecol. 27: 9–20

Lasaridi KE & Stentiford EI (1998) A simple respirometric technique for assessing compost stability. Wat. Res. 32: 3717–3723

Leenheer JA (1981) Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. Environ. Sci. Technol. 15: 578–587

Liwarsa-Bizukojc E, Bizukojc M & Ledakowicz S (2002) Kinetics of the aerobic biological degradation of shredded municipal solid waste in liquid phase. Wat. Res. 3: 2124–2132

Loague K & Green RE (1991) Statistical and graphical methods for evaluating solute transport models: overview and application. J. Contam. Hydrol. 7: 51–73

Nada AMA, Yousef MA, Shaffei KA & Salah AM (1998) Infrared spectroscopy of some treated lignis. Polymer Degrad. Stab. 62: 157–163

Smith BC (1999) Infrared Spectra Interpretation: A Systematic Approach. CRC Press, New York

Socrates C (1980) Infrared Characteristic Group Frequencies. John Wiley & Sons, Chichester UK

Stenstrom J, Svensson K & Johansson M (2001) Reversible transition between active and dormant microbial states in soil. Microbiol. Ecol. 36: 93–104

Sutherland JP, Bayliss AJ & Braxton DS (1995) Predictive modelling of growth of *Escherichia coli* O157:H7: The effects of temperature, pH and sodium chloride. Int. J. Food Microbiol. 25: 29–49

The U.S. Composting Council (1997) Test methods for the examination of composting and compost. In: Leege PB & Thompson WH (Eds) Test Methods for the Examination of Composting and Compost. The U.S. Composting Council, Bethesda, Maryland, USA