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Determining C/N ratios for typical organic wastes using biodegradable fractions

*Belén Puyuelo, Sergio Ponsá, Teresa Gea, Antoni Sánchez**

Composting Research Group. Department of Chemical Engineering, Escola d'Enginyeria,
Universitat Autònoma de Barcelona, 08913-Bellaterra (Barcelona), Spain.

Corresponding author: Antoni Sánchez

Phone: 34-93-5811019, Fax: 34-93-5812013

E-mail address: antoni.sanchez@uab.cat

Abstract

It is well established that an optimal aerobic and anaerobic microbial metabolism is achieved with a C/N ratio between 20 and 30. Most studies are currently based on chemically-measured carbon and nitrogen contents. However, some organic wastes can be composed of recalcitrant carbon fractions that are not bioavailable. To know the biodegradable C/N ratio, two different methods to determine the aerobic and anaerobic biodegradable organic carbon (BOC_{AE} and BOC_{AN}) are proposed and used to analyze a wide variety of different organic samples. In general, raw wastes and digested products have more amount of BOC_{AE}. On the contrast, the samples collected after an aerobic treatment have higher content of BOC_{AN}. In any case, all the BOC fractions are lower than the total organic carbon (TOC). Therefore, the C/N ratios based on BOC are always lower than the total C/N ratio based on the TOC measure. The knowledge of the real bioavailable C/N ratio is crucial for the biological treatments of organic materials. To reduce the test time necessary for BOC determination, the values of BOC for all the samples obtained at different times were compared and correlated with the final BOC. A method that allows for the determination of BOC_{AE} in 4 d is proposed. In relation to the anaerobic assay, the biogas potential calculated after 21 and 50 d was positively correlated with the final potential defined after 100 d of assay.

Keywords: Biodegradable Organic Carbon (BOC); Total Organic Carbon (TOC); Bioavailability; Respiration Index; Biogas potential; C/N ratio.

1. Introduction

Biological treatment processes, such as composting and anaerobic digestion, have been widely studied and they are the main biological treatments used to stabilize the biodegradable organic matter of solid wastes. Often the application of these biological treatments to some organic materials does not result as expected. This is mainly because these materials do not meet the biological requirements such as a suitable C/N ratio or pH to be successfully composted (Barrena et al., 2006) or anaerobically digested (Sung and Liu, 2003). The initial C/N ratio is one of the most important factors affecting the composting process and the compost quality (Gao et al., 2010) as well as in industrial wastewater treatment. It is generally used in the composting industry as a feedstock recipe and final product quality guideline (Haug, 1993; Larsen and McCartney, 2000). C/N ratio is also a key parameter in the anaerobic digestion process (Puñal et al., 2000; Miqueleto et al., 2010).

Haug (1993) proposes an optimum C/N ratio value within 15 to 30. Other works reduce this range to 25 to 30 (Huang et al., 2004; Zhu, 2007). Similar ranges, from 20 to 30, have been suggested for anaerobic digestion (Zhang et al., 2008). Traditionally, the assessment of the C/N ratio in solid samples has been determined on total organic fractions through the determination of total organic carbon (TOC) and total nitrogen (TN), assuming that both nutrient sources are fully biodegradable (Eiland et al., 2001; Zhu, 2007).

In numerous works, to adjust the initial C/N ratio of several raw materials, the co-digestion (Zhang et al., 2008) and the co-composting processes (Gea et al., 2007) have been presented as alternative options. The co-utilization of waste-derived materials in the composting process has the potential to increase the range of uses for recycled products, and to reduce odorous emissions related to pH or C/N ratio (Huang et al., 2004; Sánchez-Arias et al., 2008). However, the knowledge or the adjustment of a C/N ratio to start-up the process is not a guarantee of the most favorable performance of the process, since this C/N ratio does not usually correspond to the bioavailable or biodegradable C/N ratio. In previous studies, the discussion on the relevance of the C/N ratio has already been focused on the biodegradable fractions of nutrients (Kayhanian and Tchobanoglous, 1992; Haug, 1993; Larsen and McCartney, 2000). The BOC/N ratio should be based on the biodegradable organic carbon (BOC) content, since most of the nitrogen content in organic samples is present in the form of protein molecules, which are relatively biodegradable (Haug, 1993), but a large part of non-biodegradable carbon source can be present. Nevertheless, it should be kept in mind that a small amount of nitrogen can eventually become a part of humic substances. However, it is well referred that this nitrogen is slowly biodegradable and its content is negligible when compared to the waste initial nitrogen content (de Guardia et al., 2010). Actually, BOC measurements of a given sample should be specifically calculated from aerobic (BOC_{AE}) or anaerobic (BOC_{AN}) metabolism depending on its future treatment. These biological measurements usually take longer times than short chemical determinations but the latest cannot provide an accurate measure of biodegradable organic matter. Also, it is important to mention that the BOC can be even divided in two different fractions i.e., readily and slowly biodegradable (Fernández et al., 2008; Ponsá et al., 2011c). Consequently, when considering wastes with a high percentage of slowly biodegradable carbon, such as lignin, the BOC/N ratio can have a critical influence on the process and therefore the BOC degradation kinetics should be also considered for reliable BOC/N ratio measurements.

Haug (1993) presented a methodology to estimate the BOC value based on the use of a correction factor from the total lignin content and he compared biodegradable and chemical C/N ratios in four different wastes. He observed that, except for the organic fraction of municipal solid waste (OFMSW), the difference among both ratios was important. With the exception of Haug's methodology, no previous studies about the measure of BOC in solid wastes have been found, whereas several methodologies have been reported for the biodegradable dissolved organic carbon in water studies (Søndergaard and Worm, 2001; Tusseau-Vuillemin et al., 2003).

Regarding this, the use of the C/N ratio extractable in aqueous phase for the organic solid samples has been suggested, since the biological decomposition of the organic matter occurs in the aqueous phase (Chanyasak and Kubota, 1981). However, it must be considered that non-biodegradable compounds can be leached. Huang et al. (2004) studied the evolution of total C/N and aqueous C/N ratio and, as expected, the latter was always lower than the former. This measure presents the closest approximation to the real BOC content although it has the following disadvantages: (1) the solubilization of the organic matter is favored during the aqueous material extraction; and (2) as mentioned, all the quantified nutrients in the aqueous phase are not necessarily biodegradable.

A first reference to the approach of a direct determination of the BOC in solid wastes was proposed by Sánchez (2007) in his discussion about the cumulative CO_2 production data during composting presented by Komilis (2006). However, no systematic study has been conducted in this crucial issue for modern organic waste biological treatment.

The objectives of this paper are: (i) to establish a suitable and reliable methodology to determine the BOC_{AE} and the BOC_{AN} contents using aerobic and anaerobic assays, respectively, in several typical organic solid wastes, (ii) to investigate an alternative to reduce the time of both assays and (iii) to compare BOC_{AE} or BOC_{AN} with TOC and chemical or bioavailable C/N ratios.

2. Materials and Methods

2.1. Sampling

Several organic samples from different origins were analyzed in order to determine and to compare the biodegradable and total C/N ratios of the typical organic wastes generated in Catalonia, Spain. Specifically, the raw wastes collected were mixed municipal solid waste (MSW), pruning waste (PW), solid fraction of pig slurry, i.e. pig manure (PM) and two different samples of OFMSW, raw sewage sludge (RS) from wastewater treatment and cow manure (CM). Simultaneously, a single sample of digested and composted OFMSW (C-OFMSW) and two samples of mature and refined C-OFMSW (F-OFMSW), anaerobically digested sludge (DS) and composted sludge (CS) were the treated wastes obtained after biological treatment. When two samples were analyzed, these were collected at the same source but on different sampling dates.

All the municipal organic samples i.e., MSW, OFMSW, C-OFMSW and F-OFMSW were collected from a mechanical-biological treatment plant (Montcada i Reixac, Barcelona). The detailed operation of this facility has been previously described by Ponsá et al. (2008b). RS and DS came from Besòs (Barcelona) and Sabadell (Barcelona) wastewater treatment plants, respectively. CS came from the Olot (Girona) composting plant. PM and CM samples were selected as typical farm wastes around the Barcelona area and they were collected in a Vic (Barcelona) farm. Finally, a sample of PW from La Selva (Girona) composting plant was also studied since this is a typical waste used as bulking agent for providing porosity to other compostable wastes (Ruggieri et al., 2009).

Analytical methods were carried out on a representative sample (approximately 40 kg) obtained by mixing sub-samples of about 10 kg each, taken from at least four different points of the bulk material. This bulk material corresponds to an amount of 250 kg coming from an initial sample of 2 Mg that was quartered to reach this final mass. After collection, MSW and OFMSW samples were ground to 15-20 mm size of particle to reduce the dimension of the original materials and to obtain more representative samples. In the laboratory each sample was vigorously mixed and representative samples of about 1 kg were frozen and conserved at -18 ºC. Before analysis, the samples were thawed at room temperature for 24 h.

2.2. Analytical methods

Water content, Dry Matter (DM), Organic Matter (OM), TOC, Kjeldahl nitrogen and ammonium were determined according to the standard procedures (The US Department of Agriculture and The US Composting Council, 2001). Total Nitrogen (TN) content was determined adding organic nitrogen and NH_4^+-N. In this work it is assumed that TN content corresponds to the biodegradable nitrogen during the typical durations found in real biological treatment processes (de Guardia et al., 2010).

2.3. Respirometric tests

Microbial respiration was measured as O_2 consumption and CO_2 production in a dynamic respirometer built and started-up by Ponsá et al. (2010), which was based on the methodology described by Adani et al. (2006). Briefly, 150 g of organic sample were placed in a 500 mL Erlenmeyer flask that was introduced in a water bath at 37 ºC. A constant airflow was supplied to the sample and the on-line O_2 and CO_2 contents in the exhaust gases were measured. Low porosity samples (RS, DS, CM and PM) were mixed with an inert bulking agent. This bulking agents consists of small pieces (20 x 10 mm) of dishcloths (Spontex, Iberica) in 1:10 wet weight ratio (Spontex:Sample) that were chosen to improve the sample porosity. From the curve of oxygen concentration vs. time the Dynamic Respirometric Index (DRI) related to the O_2 consumption was obtained from each sample. All measurements were undertaken in duplicate. The addition of inoculums is not required in this aerobic test since waste samples are already colonized with sufficient microbial communities to start and complete the biodegradation process.

The DRI represents the average oxygen uptake rate (OUR) during the 24 h of maximum biological activity observed during the respirometric assay (normally, it is achieved between 24 or 48 h after starting) and it reports the stability degree (Adani et al., 2004; Ponsá et al., 2010). It is expressed in mg of O_2 g^{-1} OM (or DM) h^{-1}. However, as explained in the following section, the analysis was continued for BOC determination.

2.4. BOC

2.4.1. Aerobic assessment

The cumulative CO_2 production was calculated to know the total BOC_{AE} content for each sample modifying the previously described respirometric test. A time increase of the respirometric test allowed determining the total cumulative CO_2 production. The time required depended on the biostability of each sample i.e., the determination was concluded when the CO_2 production rate was considered negligible, that is when the measure of OUR was below the 5% of the maximum OUR achieved. At that moment, it can be considered that practically all the readily and almost all the slowly biodegradable carbon is consumed.

The aim of this methodology is to determine the BOC under composting (aerobic) conditions. Consequently, neither inoculum nor additional nutrient was added. However, in some samples the respirometric test can be limited by a deficit of a nitrogen source. To avoid this problem and assuming that at least the 60% of the TOC is really biodegradable, the initial C/N ratio based on chemical terms should not be higher than 50. In this case, an additional nitrogen source should be added. In this study, all the materials presented a C/N ratio below 50 and therefore an additional nitrogen source was not necessary.

As it is known, during the aerobic degradation of OM, the BOC is transformed by oxidation to CO_2. Thus, the total CO_2 production measured by the respirometric test is a direct BOC_{AE} measure of the sample, since this is all the carbon produced by the biological activity. From these data, and knowing that 1 mol of CO_2 corresponds to 1 mol of C, the BOC_{AE} can be calculated as a dry weight percentage from the final cumulative CO_2 production and the molecular weight ratios between carbon and carbon dioxide (12/44), as shown in Eq. 1:

$$BOC_{AE}(\%) = final\ cumulative\ CO_2\ \ production\ \left[\frac{mg\ \ CO_2}{g\ \ DM}\right]\frac{12\ \ mg\ \ C}{44\ \ mg\ \ CO_2}\frac{100}{1000}\ (1)$$

where: BOC_{AE} is the BOC under aerobic conditions and the cumulative CO_2 production is in mg CO_2 g^{-1} DM.

2.4.2. Anaerobic assessment

BOC_{AN} was calculated according to the methodology described by Ponsá et al. (2011a) and Ponsá et al. (2011b). Summarizing, a mixture of each sample with a specific inoculum (in dry basis ratio inoculum:substrate 1:2) was placed in a sealed aluminum bottle with a working volume of 1 L and incubated in a temperature controlled room at 37 ºC. Before each experiment, the bottles were purged with nitrogen gas to ensure anaerobic conditions. The bottles have a ball valve connected to a pressure digital manometer (SMC model ZSE30, Japan), which allowed the determination of the biogas pressure. The mixture bulk density was previously determined (in triplicate) to calculate the headspace volume of the bottles. The results on biogas production were calculated from the pressure determined in the bottle and the headspace volume. Excessive pressure (more than 200 kPa) in the bottle was released by purging periodically the biogas produced (typically 25-30 times during the experiment). The test was finished when no significant biogas production was detected (after 100 d). All tests were carried out in triplicate. A biogas production test containing only inoculum was also analyzed in triplicate to be used as a blank. The inoculum for anaerobic digestion tests was collected from the anaerobic digester of a plant treating the OFMSW (4500 m^3 of capacity, working temperature of 37 ºC and hydraulic retention time of 21 d) and it was kept at 37 ºC for 2 wk to remove any remaining easily biodegradable fraction of OM.

The assay permits to determine the cumulative biogas potential (GB), which is expressed as L of biogas produced kg^{-1} total solids (DM) during a specific time. From the biogas potential, and assuming that 1 mol of biogas is 1 mol of C both in form of CO_2 or CH_4, the BOC_{AN} is calculated as Eq. 2:

$$BOC_{AN}(\%) = \text{final cumulative biogas production}\left[\frac{\text{L biogas}}{\text{g DM}}\right]\frac{1\ \text{mol}}{25.4\ \text{L}}\frac{12\ \text{g C}}{1\ \text{mol biogas}}100 \quad (2)$$

3. Results and discussion

3.1. Physico-chemical characteristics

The main properties of the samples studied are reported in Table 1 and the TOC results are shown in Fig. 2. In general, DM content was higher and OM was lower in treated wastes than in raw materials. Most raw wastes presented a TOC content around 45%, which was higher than those of final products. F-OFMSW presented higher OM and TOC contents than C-OFMSW since inert materials and bulking agents were removed after final product post-treatment (Ruggieri et al., 2009). As expected, the highest TN content was found in RS.

3.2. DRI

Table 2 shows the DRI based on O_2 consumption in order to know the activity and stability degree. It is assumed that 1 mg O_2 g^{-1} OM h^{-1} is the maximum DRI threshold for biological stability (Adani et al., 2004, Baffi et al., 2007). Only C-OFMSW, CS and PW were below this limit and therefore, they were considered stabilized samples with low biodegradable OM content. On the contrary, higher indices were found for RS, CM, PM, OFMSW, MSW and DS. Recently, Ponsá et al. (2010) have presented a qualitative classification of wastes in three categories based on the material typology and its stability indices. According to this classification, RS and PM are highly biodegradable wastes because both present an stability index higher than 5 mg O_2 g^{-1} DM h^{-1}; OFMSW, one sample of DS and CM can be classified as moderately biodegradable wastes since they present a DRI between 2 to 5 mg O_2 g^{-1} DM h^{-1} and the rest of the materials are wastes of low biodegradability, which have a DRI below 2 mg O_2 g^{-1} DM h^{-1}. Both DS samples were the only ones analyzed twice with significantly different stability degrees.

Samples collected after biological treatment (except one sample of DS) presented a low DRI, as it is expected for final products. Also PW had a low DRI and it is classified as a waste of low biodegradability. The PW composition could be assimilated to the typical fiber composition of the woody matter presented by Haug (1993). According to that study, the wood composition is ranging from 30 to 60% of cellulose, 19 to 30% of hemicellulose and 10 to 20% of lignin. In this case, it has been observed a slow degradation rate (Solano et al., 2001), since it is a complex polymer and it also provokes a delay in the cellulose decomposition and in the released carbon dioxide.

3.3. BOC

Figure 1 shows, as example, the evolution of BOC degradation during the anaerobic and aerobic assay for the case of MSW. Anaerobic and aerobic BOC values for each sample analyzed are shown in Fig. 2.

3.3.1. Aerobic Assessment (BOC_{AE})

Each sample has a different assay time according to the threshold established to finish the process. Only the pruning assay was stopped before the limit because it was found to be a really slowly biodegradable material and it was considered that in 90 d the assay could be stopped. Actually, the DRI obtained for PW was 0.9 mg O_2 g^{-1} OM h^{-1}, whereas after 90 d the oxygen uptake rate measured was 0.11 mg O_2 g^{-1} OM h^{-1}, i.e. 12% of DRI and the lowest value observed for the different wastes analyzed.

As expected, most of the samples obtained after an anaerobic digestion and/or composting treatment had lower BOC_{AE} values than raw materials since in both biological treatments the BOC is degraded. However, no significant correlation between DRI (expressed as mg CO_2 g^{-1} DM h^{-1}) and BOC_{AE} could be established in order to investigate if a shorter time test could be representative of the BOC_{AE}. In fact, two different samples could present a similar BOC_{AE} and very different DRI depending on their biochemical composition and organic matter nature. For instance, PW and both RS presented a similar BOC_{AE} (around 18% on dry basis) while the DRI of the former was much lower according to the lower rate of decomposition of fibers. In this sense, the characterization of BOC into easily and slowly degradable fractions would be of special interest (Tremier et al., 2005). Ponsá et al. (2011c) have recently related the DRI with the rapidly biodegradable fraction of solid wastes and its kinetic constant of biodegradation (k_R). In the same way, the values of BOC of all the samples obtained at different times of analysis were compared with the total BOC_{AE}. Figure 3 shows the variation with time of the average $BOC_{AE,n}/BOC_{AE}$ during the first 25 d of assay found for all the samples analyzed and excluding PW because it was the only waste where the degradation rate remained practically constant during the test. All the BOC_{AE} data after 2 d of analysis correlated with the BOC_{AE}. According to the Fig. 3, the BOC_{AE} obtained at 2, 3, 4, 5, 7, 10, 15, 20 and 25 d accounts for the 17, 26, 34, 38, 47, 57, 73, 82 and 89% of the total BOC_{AE}, respectively. From the 4th d of analysis the BOC_{AE} could be estimated with a correlation coefficient of 0.962. However, a longer analysis does not increase the correlation coefficient. Data in Fig. 3 could be well fitted to the exponential model (Eq. 3) ($p < 0.0001$ and $r^2 = 0.998$). Model parameters obtained were a = 0.96 and b = 0.10 d^{-1}. These results were obtained with 15 samples of different typologies and should be confirmed by analyzing more samples.

$$\frac{BOC_{AE,n}}{BOC_{AE}} = a\left(1 - \exp^{-bn}\right) \tag{3}$$

where: $BOC_{AE,n}/BOC_{AE}$ is the ratio of BOC obtained at time n (d) to the total BOC content; a is the ratio of the ultimate BOC potential (dimensionless) and b is the maximum degradation rate of BOC_{AE} (d^{-1}).

3.3.2. Anaerobic Assessment (BOC_{AN})

As occurred in the aerobic results, BOC_{AN} was higher for raw materials than for previously treated materials. The disadvantage of this analysis is the long period of time required to determine the final biogas production. In order to shorten the analysis length, and considering the studies presented by Ponsá et al. (2008b) and Ponsá et al. (2011b) about MSW anaerobic indices, all the biogas potentials obtained at 21 and 50 d were correlated with the final potential determined after 100 d. In this work, an acceptable correlation between biogas production at 21 and 100 d was obtained ($GB_{21} = 0.62GB_{100} + 39.4$; $r^2 = 0.776$; $p = 0.0017$). Nevertheless, a better correlation was obtained using the biogas potential obtained at 50 d ($GB_{50} = 0.84GB_{100} + 23.38$; $r^2 = 0.923$; $p < 0.0001$). Therefore, a general correlation among GB_{50} and GB_{100} could be established for the all the typical solid wastes studied. Probably, the BOC_{AN} could be more precisely estimated if correlations were calculated for each kind of waste since different biodegradation kinetic rates are expected depending on the nature of the organic matter of the waste (Ponsá et al., 2011a).

3.3.3. Comparison between BOC_{AE}, BOC_{AN} and TOC

Figure 2 shows the TOC, BOC_{AE} and BOC_{AN} values of the organic wastes that are expressed on DM percentages. All data are presented jointly with the standard deviation of its replicates, which in general was much higher in the TOC determination. Raw wastes presented a

BOC_{AE}/TOC ratio between 31 to 57% and a BOC_{AN}/TOC ratio between 19 to 56% on DM basis. As expected, results show an important reduction of BOC content after biological treatment. Nevertheless, the reduction of TOC is far from that observed for BOC and in many cases the TOC content (%) remains almost constant. As this is not possible because BOC is a part of TOC and thus TOC should decrease along the assay, this confirms the unsuitability of using the chemical C/N ratio in biological processes. For example a raw material as OFMSW and a completely processed material as F-OFMSW have the same TOC/N ratio but contrarily they present a totally different BOC_{AE}/N ratio (Table 2).

As predictable, different BOC_{AE} and BOC_{AN} values were obtained for each sample. In general, raw wastes showed higher BOC content under aerobic conditions. This can be explained because not all the aerobically biodegradable OM can be degraded under anaerobic conditions due to the presence of different microbial communities. For instance, the PW has a high content of lignocellulosic compounds that are resistant to direct enzymatic hydrolysis because of two major hindrances related to the compact cellulose structure and the lignin barrier surrounding cellulose (Mansfield et al., 1999; Yu et al., 2004). In general, the hydrolysis has been reported in literature as being the limiting factor in some anaerobic digestion processes (Ponsá et al., 2008a; Walker et al., 2009). However, lignocelluloses can be degraded under aerobic conditions at slow degradation rates (Tuomela et al., 2000). Under anaerobic conditions, this could be changed by using an adapted inoculum for anaerobic digestion once the waste biochemical composition is precisely known. Although this is out of the scope of this work, this procedure has demonstrated to be a successful strategy for anaerobic digestion (Fernández et al., 2005; Martín-González et al., 2010). The results of the final samples showed different trends depending on the type of biological treatment selected.

3.4. Chemical C/N ratio and Biodegradable C/N ratios

Table 2 shows the results obtained on the chemical C/N ratio and the biodegradable C/N ratio obtained under aerobic and anaerobic conditions for the studied samples.

The difference between C/N and both types of BOC/N ratios can be mainly attributed to the different fractions of carbon considered since the nitrogen content is always chemically determined. In relation to nitrogen content it has been assumed that TN corresponds to the really bioavailable nitrogen content as the other forms of nitrogen (humic substances) are slowly biodegradable and its nitrogen is not detected in mineral form (Bernal et al., 2009). Thus, (BOC/N)/(C/N) ratios were equivalent to the BOC/TOC ratios. The variation found between the biodegradable and total carbon contents supports the literature recommendations of using the BOC to determine the C/N ratio (Sánchez, 2007).

All results showed that the samples analyzed had a BOC/N ratio below the optimal ranges established under aerobic and anaerobic conditions i.e., 25-30 and 20-30, respectively. Only the PW ratio was in the wide range proposed by Haug (1993) for an optimal composting process (15-30). Obviously, most of the treated samples presented a very low BOC/N ratio (< 4), since BOC is the nutrient most biodegraded along these biological processes. In sludge samples the low BOC/N ratio was caused by the usual high nitrogen content in the wastewater sludge. Regardless the high BOC content of the farm wastes and RS, a low ratio was calculated due to their high nitrogen content. On the other hand, the BOC/N ratios found for both OFMSW were around 13, similar to that reported by Kayhanian and Tchobanoglous (1992). On the contrary, BOC/N ratios determined for MSW in this work were half of the ratio reported by the same authors. This could be explained by a different presence of biodegradable carbonaceous materials such as paper, which are recycled in Spain at a high ratio and thus, mostly absent in MSW.

Particularly from a composting point of view, the lower and higher BOC_{AE}/N ratios of the raw samples were found for the RS and the PW, respectively. In addition, the RS had high moisture content (around 70%) and a high bulk density. Because of this, to carry out the sludge composting process it is necessary to mix the sludge with an appropriate bulking agent. In fact, the most widely used materials as bulking agents are pruning wastes or wood chips (Larsen and McCartney, 2000; Ponsá et al., 2009), since both have a high water retention capacity, they avoid matrix compaction and they are abundant and cheap wastes. However, despite the high organic carbon content of both bulking agents, they are not believed to be significantly biodegraded under composting conditions. In the present work, it has been determined that 43% of TOC PW could be aerobically biodegraded, although its respirometric assay confirmed the slow rate of biodegradation of this material (Solano et al., 2001; Zhu, 2007). Accordingly, a progressive degradation of BOC can be observed, which increases the BOC_{AE}/N ratio of the composting mixtures in the long term.

In general, except for the PW, all the wastes presented in this work had a low BOC_{AE}/N ratio, below 15. It suggests that nitrogen does not limit the biological reactions but it can be lost by volatilization during the composting process, which generates odors and atmospheric pollution (Pagans et al., 2006). Low BOC_{AN}/N ratios (all below 20) have also been obtained, which can cause the ammonia accumulation during the anaerobic digestion. On the contrast, the 50% of chemical C/N ratios calculated were over 15.

Despite these differences and the previous recommendations proposed in several works, most of the studies about nitrogen emissions or the performing of the composting process still consider the C/N ratio in chemical terms. Some researchers insist that a high C/N ratio does not necessary correspond to an effective prevention of nitrogen loss (Eklind and Kirchmann, 2000; Liang et al., 2006; Ogunwande et al., 2008). More recently, de Guardia et al. (2010) confirmed lower ammonia emissions at higher C_{bio}/N_{bio} ratio in composting mixtures. Additionally, Matsumura et al. (2010) has concluded that the biodegradability of carbon-rich compounds added on the reduction of nitrogen emissions is more important than the C/N ratio attained after the mixing process.

The BOC/N ratios presented in this work reinforce literature conclusions and explain multiple observations of ammonia losses in composting processes of mixtures with a theoretical C/N in the recommended range. In consequence, the mixing of different substrates to balance C/N ratio in the composting and anaerobic digestion processes should consider BOC as well as the easily biodegradable BOC fraction instead of the traditional TOC measure. Moreover, optimal mixtures for composting and anaerobic digestion should be reformulated when considering the results obtained in this study.

4. Conclusions

Values from 31 to 57% of BOC_{AE} and 19 to 56% of BOC_{AN} on TOC were obtained in all the raw wastes. These values are crucial for the design of future waste treatment plants.

All the samples presented a BOC/N ratio significantly different to the chemical C/N ratio and below the optimal range defined in other studies for waste biological treatment. Only the PW has a near-to-optimal composting ratio due to its very high percentage of BOC_{AE}, which is slowly biodegradable. The C/N ratio used to carry out a biological treatment must be defined in biodegradable terms, i.e. BOC_{AE} for composting and BOC_{AN} for anaerobic digestion instead of chemical total carbon content, which is difficult to be accurately determined in organic samples, especially raw wastes. The BOC_{AE} and BOC_{AN} degraded at different time test correlated well with the total content of both parameters. The $BOC_{AE,4}$ is a good alternative to estimate in a short period of time the BOC_{AE} of the most wastes analyzed. The biogas potential calculated during 50 d correlated well with the ultimate production.

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Figure Legends

Figure 1. Evolution of Biodegradable Organic Carbon (BOC) during anaerobic (a) and aerobic (b) assays of MSW. Different time scales are represented due to the different thresholds established to stop each assay. The sampling time in aerobic assay was 15 minutes while in anaerobic assay it was between 1 and 2 days.

Figure 2. Values of Total Organic Carbon (TOC) with aerobic and anaerobic Biodegradable Organic Carbon (BOC_{AE} and BOC_{AN}) in the organic samples (% of DM). Average of triplicates is presented jointly with standard deviation. *Anaerobic assay not undertaken.

OFMSW: Organic Fraction of Municipal Solid Waste. C-OFMSW: Digested and Composted OFMSW. F-OFMSW: Mature and Refined C-OFMSW.

Figure 3. Evolution of partial Biodegradable Organic Carbon at time n ($BOC_{AE,n}$) with respect to Biodegradable Organic Carbon content obtained at 25 days for all the samples analyzed excluding Pruning Waste.

Figure 1: Puyuelo et al.

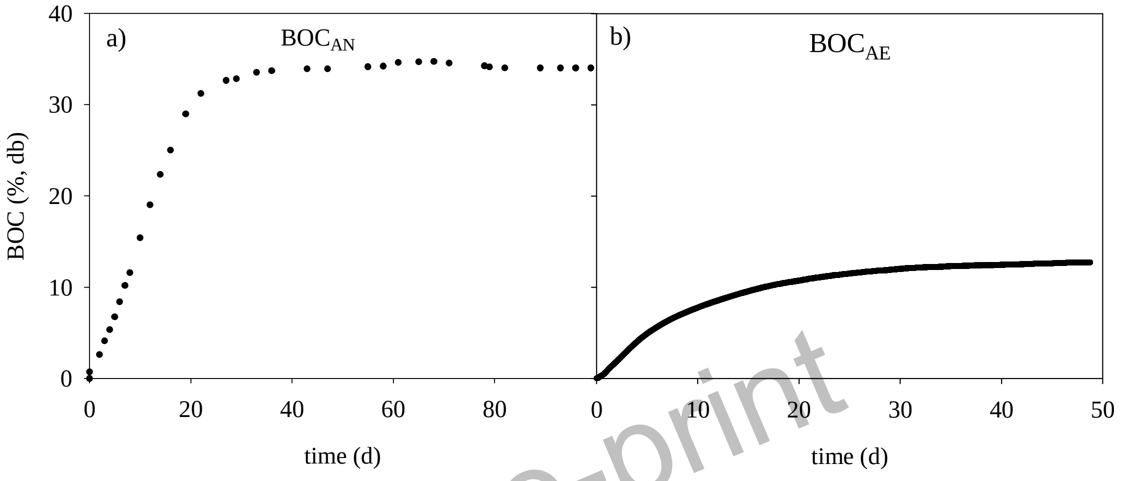


Figure 2: Puyuelo et al.

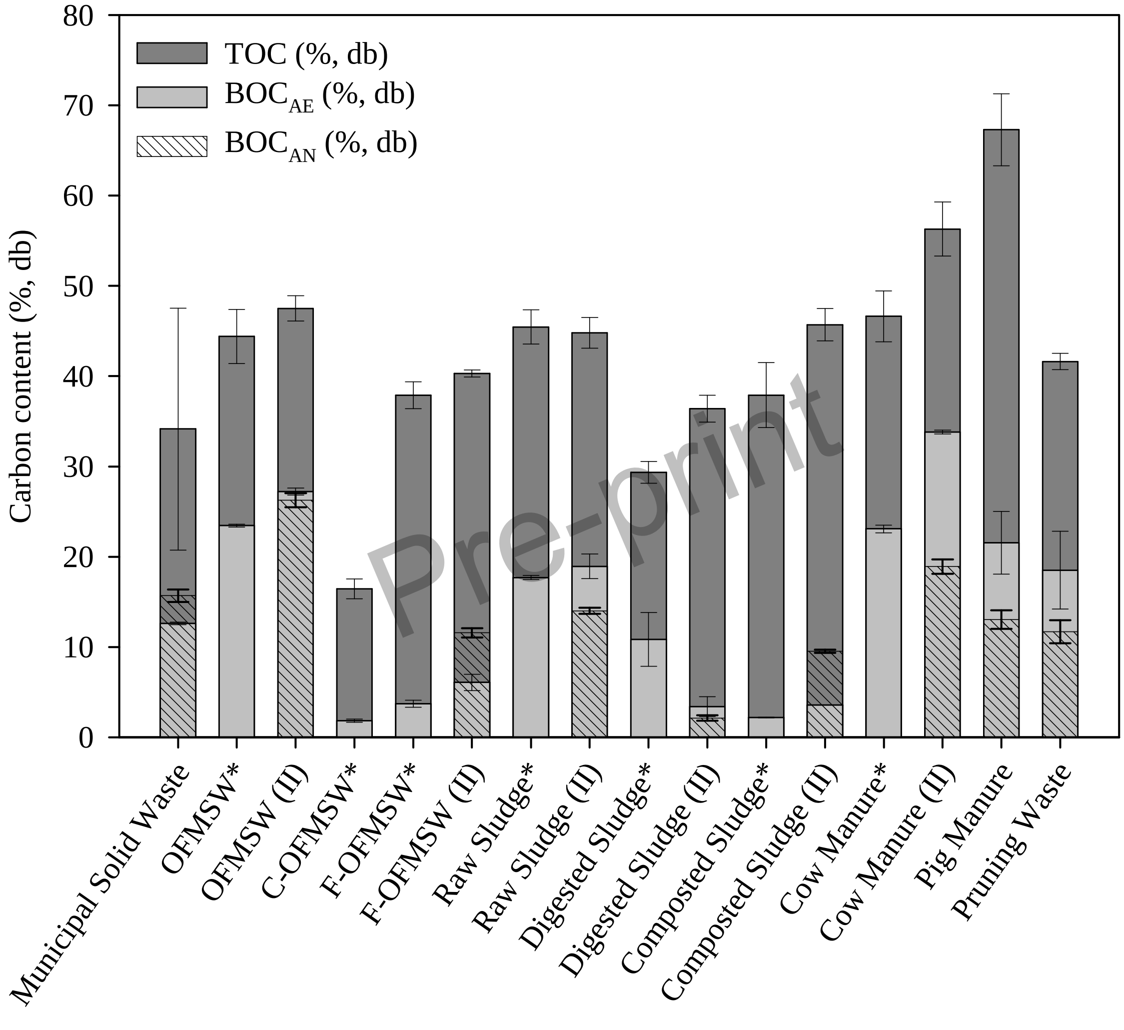
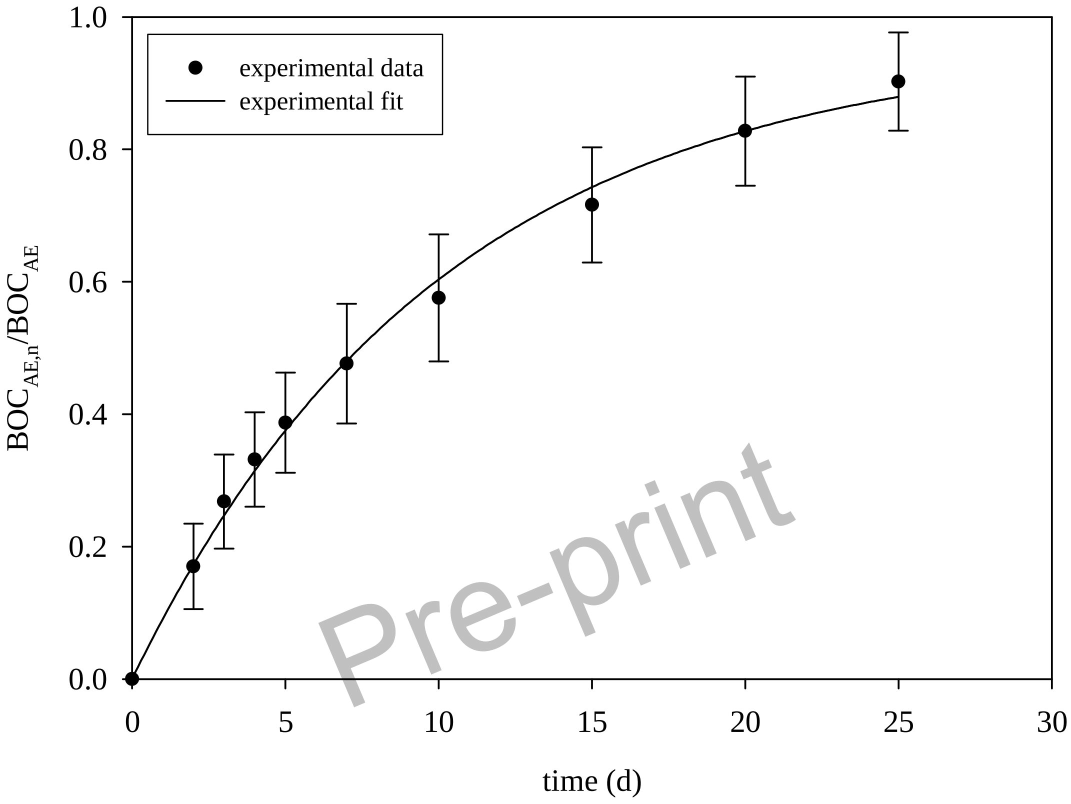


Figure 3: Puyuelo et al.



Tables

Table 1. Main properties of the organic samples studied.

	Dry Matter (%, wb)	**Organic Matter (%, db)**	**TN (%, db)**
Municipal Solid Waste	62 ± 6	37 ± 15	1.0 ± 0.1
OFMSW	29 ± 2	77 ± 3	2.0 ± 0.1
OFMSW (II)	39 ± 2	82 ± 1	1.9 ± 0.2
C-OFMSW	65 ± 2	28 ± 3	1.7 ± 0.1
F-OFMSW	50.2 ± 0.8	33.3 ± 0.9	1.9 ± 0.1
F-OFMSW (II)	75.1 ± 0.3	63.8 ± 0.4	3.0 ± 0.2
Raw Sludge	29.4 ± 0.8	77.1 ± 0.9	7.2 ± 0.1
Raw Sludge (II)	17.9 ± 0.4	75.7 ± 0.1	7.1 ± 0.4
Digested Sludge	19.6 ± 0.1	54.8 ± 0.1	4.3 ± 0.1
Digested Sludge (II)	18.9 ± 0.7	62.7 ± 0.1	4.2 ± 0.1
Composted Sludge	57.4 ± 0.4	65 ± 1	4.3 ± 0.1
Composted Sludge (II)	69.7 ± 0.4	77 ± 4	4.9 ± 0.3
Cow Manure	23.5 ± 0.2	84.9 ± 0.9	2.7 ± 0.1
Cow Manure (II)	21.1 ± 0.5	88.0 ± 0.6	2.5 ± 0.1
Pig Manure	12.7 ± 0.3	85.1 ± 0.4	2.3 ± 0.2
Pruning Waste	60 ± 1	92 ± 1	0.8 ± 0.2

Results from triplicates are presented as mean ± standard deviation. OFMSW: Organic Fraction of Municipal Solid Waste. C-OFMSW: Digested and Composted OFMSW. F-OFMSW: Mature and Refined C-OFMSW. TN: Total Nitrogen; wb: wet basis; db: dry basis.

Table 2. Biological and chemical characterization of the wastes analyzed.

	DRI	**C/N ratio based on**		
	(mg O_2 g $^{-1}$ OM h^{-1})	**TOC**	**BOC_{AE}**	**BOC_{AN}**
Municipal Solid Waste	4.00 ± 0.09	34.0	12.6	15.7
OFMSW	5.32 ± 0.06	22.0	11.7	-
OFMSW (II)	4.2 ± 0.2	24.7	14.3	13.8
C-OFMSW	0.78 ± 0.06	9.4	1.1	-
F-OFMSW	1.7 ± 0.2	20.0	1.9	-
F-OFMSW (II)	1.42 ± 0.03	13.4	2.0	3.9
Raw Sludge	8 ± 1	6.3	2.4	-
Raw Sludge (II)	9.3 ± 0.3	6.3	2.7	2.0
Digested Sludge	6.0 ± 0.5	6.7	2.6	-
Digested Sludge (II)	1.64 ± 0.01	8.6	0.7	0.5
Composted Sludge	0.22 ± 0.06	8.8	0.5	-
Composted Sludge (II)	0.49 ± 0.01	9.4	0.7	1.9
Cow Manure	3.17 ± 0.04	17.4	8.6	-
Cow Manure (II)	4.6 ± 0.1	22.4	13.5	7.6
Pig Manure	6.2 ± 0.6	29.1	9.1	5.7
Pruning Waste	0.9 ± 0.1	52.0	22.5	15.0

Results from triplicates are presented as mean ± standard deviation. OFMSW: Organic Fraction of Municipal Solid Waste. C-OFMSW: Digested and Composted OFMSW. F-OFMSW: Mature and Refined C-OFMSW. OM: Organic Matter. DM: Dry Matter. DRI: Dynamic Respirometric Index; TOC: Total Organic Carbon; BOC: Biodegradable Organic Carbon; AE: aerobic. AN: anaerobic.