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Title :

UV-Visible and Fluorescence Green Waste Composts Monitoring: Material Dependency

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Abstract :

The most frequent way to survey green waste composts is to monitor the temperature during the composting process. However, if the temperature is a good index for global biological processes, it is not for the chemical stability. In order to identify a reliable index, this work investigates water extraction coupled to spectroscopic indexes such as E_2/E_3, E_4/E_6 and $SUVA_{254}$ ratios, and fluorescence indexes such as Kalbitz, Milori, CP/PARAFAC and Fluorescence Region Integration. The measurements of these indexes are carried out with six samples from different sites with different green waste material composition. The results show that most indexes depend on the green waste origin more than the composting time; some depend mostly on the material origin while others on compost age. A comparison of these results indicates that the biochemical

process occurs more rapidly than expected by the compost producers. The combination of these indicators gives useful information on the processes that take place during composting.

1. Introduction

The composting process is based on two phenomena; firstly on bio-oxidation reactions in the aerobic environment and secondly on molecular reorganization leading to a partial humification of the organic matter. After an optimum rest time, the result is humified compost. Composting is also defined as a controlled process of degradation of organic constituents of plant and animal origin, by a succession of microbial communities evolving under aerobic conditions, resulting in a rise in temperature, and development of stabilised humified organic matter. The resulting product is called compost (de Bertoldi et al., 1983). Degradation of organic matter through composting is needed to improve the biological, chemical and physical properties of soil. These composts can be used to 1) improve soil structure, 2) increase organic matter in soil, and 3) provide nutrients to plants for accelerating their growth (Bernal et al., 1998). Furthermore, composts can be used for remediation of soils contaminated with toxic organic compounds (Amine-Khodja et al., 2006). Composts can be made from different sources of waste such as animal manures, water treatment plant mud, alimentary waste and vegetation waste. Grass clippings, dead leaves and pruning branches are distinguished from the others as green wastes. Only mature compost is of interest for agriculture since unstable or immature compost is prone to problems such as deprivation of nitrogen for plants along with phytotoxicity by competition of oxygen (Bernal et al., 1998; Gómez-Brandón et al., 2008). In order to evaluate the maturity and chemical

stability of compost, time consuming measurements have to be performed. These include processes such as respirometry, carbon and nitrogen content determination and germination tests. As a result, they are difficult to apply to real time surveys or large sets of data (Bernal et al., 1998). To overcome this, the optical properties of the extracted organic matter have been investigated to find a proxy for the evaluation of chemical stability. Indeed, compost management is often done only after temperature stabilisation, or after an empirical time defined by the compost producers. Several studies were done based on various types of input (cattle manure, green waste and winery waste), and these are often used as co-compost with green wastes (Wei et al., 2014). Only a few studies have investigated the best way to monitor compost evolution. One example that stands out is the usage of fluorescence spectroscopy to define a multivariate optical formula to assess the maturity of various animal manure or industrial organic final products (Yu et al., 2010). Fluorescence and UV-Visible spectroscopy have also been used to monitor the process of composting, generally for a duration of three or four months, until the temperature of the compost has decreased and stabilised (Li et al., 2014; Marhuenda-Egea et al., 2007; Sellami et al., 2008; Tang et al., 2011). For winery waste and animal manure it is generally observed that the carbon to nitrogen ratio (C/N ratio), percentage of carbon (%C) and protein fluorescence decreases while the humic acid (HA) over fulvic acid (FA) ratio increases at the same time at their fluorescence signal (Domeizel et al., 2004; Marhuenda-Egea et al., 2007; Tang et al., 2011). The same results were observed on vermicompost by fluorescence spectroscopy using fluorescence regional integration (FRI) and the E_4/E_6 index (Zhang et al., 2015) and on cattle manure (He et al., 2013). Until now, only a few studies have been done solely on green waste composts (Domeizel et al., 2004; Khalil et al., 2008),

as these types of waste are often used as co-composting material (Jouraiphy et al., 2005). However, it is important to study the maturation of this type of compost to help compost producers in compost permutation and turnover during production because green waste inputs are highly heterogeneous and season-dependent. The present work uses the optical properties of water extractable organic matter (WEOM, Said-Pullicino et al., 2007a; Shao et al., 2009) and extractable organic matter (EOM, Fuentes et al., 2006) to determine rapid and reliable indexes of process ending. Experiments were done on seven exclusive green waste composts (GW) located on six producer sites that were sampled monthly over a period of six months. The organic matter of the composts was extracted with a water (1 h, WEOM) and sodium hydroxide (NaOH) solution (24 h, EOM) and extracts were analysed using the UV-Visible technique (Guo et al., 2012), 3D fluorescence spectroscopy (Tian et al., 2012), pH and dissolved organic carbon. Various parameters such as ultraviolet-visible (UV-vis) spectra, the E_2/E_3, E_4/E_6 ratios and $SUVA_{254}$ were measured. The E_2/E_3 ratio is used as an indicator of humification and of the molecular weight of humic substances (Peuravuori and Pihlaja, 1997; Duarte et al., 2003; Li et al., 2009). The E_4/E_6 ratio is widely used for the characterisation of humic substances (Chen et al., 1977; Senesi et al., 1991). $SUVA_{254}$ is widely used as an index for aromatic structures within dissolved organic matter (DOM) (Weishaar et al., 2003; Shao et al., 2009; Pifer and Fairey, 2012; Zhang et al., 2016). The Canonical Polyadic/PARAFAC (CP/PARAFAC) decomposition and FRI of excitation-emission matrix spectra is widely used (Chen et al., 2003; Marhuenda-Egea et al., 2007; Yu et al., 2011; Zhou et al., 2012; Pype et al., 2013) to assess the compost maturity. The Milori index (Milori et al., 2002), the Kalbitz index (Kalbitz et al., 1999), the Hx index (Zsolnay et al., 1999) and the $R_{a,c}$ (Mounier et al., 1999) were also investigated.

2. Materials and methods

2.1. Sampling and pre-treatment

The GW used in this study were collected on various organic waste composting sites in an aerobic environment, located in the south of France. They were from the cities of Agde (43.288551, 3.514246), Marsillargues (43.661910, 4.178902), Signes (43.288648, 5.852698) and Fréjus (43.440724, 6.707701). Each composting site was fuelled by different types of green waste, mainly consisting of dead leaves, pieces of wood, tree and herb prunings from individuals and municipal cleaning. All these vegetable wastes were produced and deposited on a soil to form a 50 to 5 x 2 x 2 m windrow, depending on the site. In order to maintain the aerobic conditions during the composting process, the swath was returned using a windrower. The temperature was measured every month at a depth of 80 cm at different locations of the swath. Samples were taken monthly. Each sample was divided into four parts. Two quarters were merged and distributed again to obtain four new sub-samples. From one of the last sub-samples, ten grams (10 g) were sampled to measure moisture by weight loss at 100 °C, and the remainder was frozen for storage. The dried sample was used to measure the total organic carbon (TOC) of the solid sample in triplicate. The three remaining sub-samples were sampled and used for individual spectroscopic measurement. The obtained vlaues were averaged to obtain the field experimental variability.

2.2. Extractions

All the extractions were done at maximum 2 hours after sampling. The fresh samples were placed in a 50 mL plastic corning. WEOM was obtained by extracting samples with Milli-Q water (solid to water ratio of 1:10) and EOM was obtained by extracting with a 0.1 $mol.L^{-1}$ solution of NaOH (pH = 12) with the same w/v ratio. The cornings were gently shacken for 1 hour (WEOM) and 24 hours (EOM) at 7 rpm using a rotary shaker HeildophReax at room temperature. The suspensions were then centrifuged at 2.012 $m.s^{-2}$ for 30 min. A pH measurement was carried out at the end of the centrifugation (pH_{WEOM} of pH_{EOM}), and before filtration, with a HannaLab pHmeter after electrode calibration.

Then, extracts were filtered on cellulose nitrate filters (0.22 µm) by means of an online filtration system (Sartorius stedim®). Filtrates (5 mL) were collected in two glass tubes previously burned at 450 °C during 12 hours. The samples were then divided into two groups.

For the first group, the WEOM and EOM were preserved with 100 µL of 1 $mol.L^{-1}$ sodium azide (NaN_3 > 99%, Aldrich) and stored at 4 °C in the dark in order to measure the non-purgeable organic carbon (NPOC) and take spectroscopic measurements. The second group was frozen at -20 °C in order to measure the total dissolved nitrogen (TDN).

2.3. Spectroscopic measurements

UV-Visible spectra were recorded from 200 to 800 nm at medium speed on a double beam UV-1800 (Shimadzu). Milli-Q water (C.E: 18 MΩ.cm at 25 °C) or NaOH (0.1 mol.L^{-1}) solutions were used as references for WEOM and EOM respectively.

The E_2/E_3 ratio was calculated from the quotient between absorbance at 250 and 365 nm, The E_4/E_6 ratio was calculated by dividing respectively absorbance at 465 and 665 nm, and $SUVA_{254}$ was the ratio of the absorbance at 254 nm (Abs 254) by UV cell path length (l) measured in (m), and the concentration of dissolved organic carbon (DOC) measured in milligrams per litre (mg.L) was calculated from these spectra as proxy of spectral slope and molecular size (Stevenson, 1982; Summers et al., 1987), humification and degradation (De Haan, 1983) and aromaticity respectively (Weishaar et al., 2003).

The same quartz SUPRASIL® cells were used for absorbance and fluorescence measurements. Excitation-emission matrix fluorescence (EEM) measurements were made with a HITACHI® F4500 spectrofluorimeter. Samples were diluted with a sodium bicarbonate $NaHCO_3$ solution to obtain the same pH conditions until absorbance at 254 nm < 0.1 to avoid an inner effect (Luciani et al., 2009). Raman spectra (Ex/Em = 350/395 nm) were recorded daily in order to verify excitation lamp calibration. The Raman fluorescence intensity variability was less than 5% during all the measurements. 2D fluorescence wavelengths were used to follow several parameters: speed-scan of 240 nm.min^{-1}, response mode auto, PMT 700 V, excitation and emission slit at 5 nm and 10 nm respectively and wavelength range to measure $R_{a,c}$ (λ_{ex} = 200-400 nm, λ_{em} = 420 nm) (Mounier et al., 1999), Kalbitz (λ_{ex} = 300-520 nm, λ_{em} = λ_{ex} + 55 nm) (Kalbitz et al., 1999) and Milori (λ_{ex} = 440 nm, λ_{em} = 350-650 nm) (Milori et al., 2002). The 3D parameters of the spectrofluorimeter were set at (λ_{ex} = 200-550 nm, λ_{em} = 200-600 nm, excitation and emission slit at 5 nm, scan-speed at 2,400 nm.min^{-1}, and response mode

at 0.1 s, PMT 700 V). Excitation-emission matrices were extracted from the 3D spectra every 5 nm for excitation and emission by the FLSolution HITACHI software. Rayleigh and Raman diffusion were suppressed by the direct cut and numerical method before decomposition (Zepp et al., 2004). Fluorescence regional integration (FRI) was done directly on EEM (Chen et al., 2003) and has been used successfully in previous work (Chen et al., 2003; Wang et al., 2009) to characterise different organic matters and even to define compost maturation indexes (Tang et al., 2011; Yu et al., 2010). The best model of CP/PARAFAC decomposition was the one giving the higher number of component and CONCORDIA over 60%, was chosen. In order to define green waste indexes, all the results were obtained by averaging the triplicate values, meaning that for each time and site, the index value was calculated as the average of the field sample triplicate.

2.4. Chemical analysis

The NPOC, after acidification (HCl, reagent grade), and TDN were measured using a Shimadzu TOC-V from the samples with and without NaN_3 poisoning respectively. Calibration was done each day with a phthalic acid solution. When necessary, the sample was diluted to bring it into the calibration range. Total solid carbon, (TC) and total solid nitrogen (TN), were measured with a Shimadzu-CN instrument by introducing a small amount (mg) of sample in a 950 °C furnace. Calibration was done daily using L-Aspartic chemical and solid reference material of known C and N content.

3- Results and discussion

To determine what indicators statistically vary with time or with origin of the green waste matter (site), an analyse of variance (ANOVA) study was done for sites and time for all the measured indexes. The results are reported in Table 1.

Table 1

The time and site (TS) group showed significant differences during maturation time and sites, meaning that they had potential to be good indexes for monitoring both compost maturation and raw material origin. The fourth index from FRI calculation (QIV) is the unique in the time dependent group (T) because it is more sensitive to the maturation time than to the sites. This is potentially a good indicator for maturation or stabilisation monitoring. In the site dependent group (S), the indexes show variations depending on green waste origin. Most of the indexes are located in the N group, meaning that they present a too high variability to identify any significant trend during compost maturation or to define the composition of the compost. It is important to keep in mind that the ANOVA is not a correlation test, but it gives useful information to choose indexes that could be good candidates for monitoring purposes as it reveals differences between times and sites. Whatever their group membership, the indexes are described later in this work as chemical stability compost indicators. Based on the ANOVA description, the boxcar plot was chosen to represent time variation in the different indexes.

3.1. The composting process

The variations in temperature recorded during the composting process (Fig. 1) followed an almost similar pattern to many composting platforms for organic waste (Mustin,

1987, Tomati et al., 1995). Two phases were represented in this process. An initial phase was characterised by an increasing average temperature up to 50-70 °C (Agde (68 °C), Fréjus (57 °C), Marsillargues (59 °C) and Signes (70 °C)) in the first four months. This increase was mainly due to the different microbial populations that degraded green waste organic matter (Zhao et al., 2013). The increase in temperature made it possible to clean up the compost by killing most pathogens (Khalil et al., 2011; Nafez et al., 2015) and a large proportion of the weed seeds (Larney and Blackshaw, 2003). Then, during the maturation phase, the average temperature decreased (Agde (50 °C), Fréjus (46 °C), Marsillargues (44 °C) and Signes (58 °C), during the sixth month) over time. This reduction can be considered as stabilisation of the active humification of the organic matter with molecular recombinations allowing the humic compounds to appear.

Fig. 1- Temperature variations

For both extraction protocols, the pH_{WEOM} and pH_{EOM} increased from the start to the end of maturation time and reached an average stabe maximum of nine before decreasing on the last month (Fig. 2). One can notice that for EOM, even though the pH of the extracting solution was at 12 (0.1 $mol.L^{-1}$ of NaOH), the measured pH_{EOM} values reached systematically lower values of around pH = 9. The pH_{WEOM} or pH_{EOM} increase might be due to the degradation of fatty acids or the release of ammonia during the alkalinisation phase during the composting process. Thus a plateau was reached after month 4 for the green waste composts. An explanation for the reduction of the pH in month 6 was that even if process details were given by the producers, at the end of the commercial process, it happened that some mixing occurred with different fresher

composts, to reach an normed value allowing commercialisation. This pH behaviour was different from the co-composting or manure compost: in the case of green wastes, it seemed that the pH reached a higher value (around 8.5) instead of 6-7.5 for other type of inputs (Marhuenda-Egea et al., 2007; Tang et al., 2011; Zhang et al., 2015). The global increase was continuous, without an intermediate decrease as already observed (Tang et al., 2011). However, a higher pH could be observed in mature green waste compost (Wei et al., 2014).

Fig. 2 – pH variation

The average TC variation is given in Fig. 3. The C content was relatively constant (35 g of C.kg^{-1}) during the first three months and then suddenly decreased to 30 g of C.kg^{-1}. TDN_{EOM} and TDN_{WEOM} seemed to be constant, oscillating between 25 µmol.L^{-1} to 10 µmol.L^{-1}. $NPOC_{EOM}$ and $NPOC_{WEOM}$ also decreased from 600 to 100 µmol.L^{-1} and from 650 to 200 µmol.L^{-1} respectively. This trend was permanently observed for all compost types, due to mineralisation of the biomaterial (Said-Pullicino et al., 2007b). The C/N ratio of the extracted EOM and WEOM decreased as previously observed in manure and sludge co-composting. The reached values were consistent with those found for other types of compost (Wei et al., 2014; Zhang et al., 2015). However, the values were much higher than those found for WEOM of grape pomace compost (near 0.32) at the final stage (Bernal et al., 1998). It is obvious that for the present set of green waste composts, the variability of the value drastically decreased with time, meaning that whatever the input, the same final value was reached.

Fig. 3 – TC and TN variations

UV-Visible indexes E_4/E_6 and E_2/E_3 ratio are presented in Fig. 4. A trend towards an increase in the E_4/E_6 ratio for WEOM could be described, from 4 to 6, but for EOM there was high heterogeneity and no particular trend. These values had a similar trend to those observed for sludge co-composting, but with a decrease from 7.6 to 4.5 during the maturation time (Zhang et al., 2015). The same trend was observed for the E_2/E_3 index. These UV-Visible indexes were not enough dependent on both site, i.e. green waste origin and maturation time to be proxies of compost stabilisation.

Fig. 4 – UV-Visible variation

The average $SUVA_{254}$ (Fig. 5) showed an increase for WEOM and EOM until the third month, and stayed at around a value of 0.03 for WEOM and 0.04 for EOM. However, once again the variability was high and showed a high dependency on the input matter. This trend was also observed for cattle manure for the first 40 days (He et al., 2013) and waste city co-composting (Said-Pullicino et al., 2007b). This behaviour was attributed to an increase of the phenolic moieties due to higher biodegradability of the hydrophilic compounds.

Fig. 5 – $SUVA_{254}$ Variation

The average $R_{a,c}$ index of WEOM and EOM increased but with high heterogeneity for the latter (Fig. 5). This index variation was opposite to those observed for cattle manure

(He et al., 2013). In this work, the $R_{a,c}$ increased from 0.8 to 1.4, while it decreased from 1.66 to 1.55 in the case of cattle manure (He et al., 2013). In both cases, the 1.4 value seemed to be a common limit. For a green mature compost a value of 0.91 was observed in a 24-hour water extracted sample (Wei et al., 2014). During composting the quantity of FA should decrease while the quantity of HA increases. This was determined comparing initial and final composting processes. In this study, sampling was made during the maturation time and on different green wastes. The $R_{a,c}$ increased probably due to a more rapid production of fulvic acid-like compounds than humic ones, revealing differences in kinetic production process. When the equilibrium process is reached the $R_{a,c}$ index remains constant. Thus, $R_{a,c}$ of WEOM was potentially a good index for biochemical stabilisation and maturation monitoring.

The Milori index (Fig. 6), $H_{FIL,WEOM}$, decreased a little from the first month to the third, and increased until the sixth month. $H_{FIL,EOM}$ showed a high variation compared to $H_{FIL,WEOM}$. The Milori index was not a good candidate for the green compost stabilisation, $H_{FIL,EOM}$ was more dependent on inputs than $H_{FIL,WEOM}$ because its variability was much higher.

Fig. 6 – Milori index variation

The average Kalbitz indexes (Fig. 6) of WEOM and EOM clearly decreased during time composting from 10 to 4. Surprisingly, the more sensitive Kalbitz index to input quality was the EOM one. Stabilisation of the Kalbitz signal was reached at the fourth month.

PARAFAC components and their variations with composting time are presented in Fig. 7. Decomposition was done on the 6 months x 6 sites x 3 triplicates x 2 extractions protocol = 236 EEMs and a three-component model was selected with a 94% CONCORDIA, and no outliers were observed. Component 1 (C1), component 2 (C2) and component 3 (C3) were respectively represented on lines A, B and C in Fig. 7. C1 presented a maximum peak at the Ex/Em wavelength of 325/415 nm and it could be related to the humic-like compounds in the region of the peak C (Coble, 1996; Parlanti et al., 2000). The C2 presented a double peak emission at 475 nm for 275 and 375 nm of excitation and could be related to more humificated or ligneous compounds. Finally, the C3 component peak was located at an Ex/Em wavelength of 275/350 nm which was the protein-like-compound position corresponding to biological activity. The stability of the C1 contribution of EOM and WEOM, and the increase of average $C2_{WEOM}$ and $C2_{EOM}$ were consistent with the degradation of simple and biolabile molecules into humic-like compounds. However, humic acids with high molecular weight were produced and conserved preferentially to fulvic acids. This AH/AF ratio evolution was opposite to the $R_{a,c}$ one which increased with time, but could be explained by the redshift of the C2 position while the $R_{a,c}$ index was calculated with the same emission wavelength, 420 nm. Hence, during composting the fluorescence intensity at an Ex/Em wavelength of 250/415 nm decreased less rapidly than the C1 maximum. $R_{a,c}$ and CP/PARAFAC gave complementary information on the extracted organic matter process: high molecular humic acid-like compounds were degraded or transformed preferentially, and it was the ligneous compounds that remained preferentially. Thus CP/PARAFAC in combination with other indexes was useful for monitoring molecular changes of compost.

The decrease of the C3 (Fig. 7, line C) was important for one month and after, it slowed down at a consistent rate. The proteins' fluorescent response was more important in the first month due to bacterial activity. Thus, high microbial activity during the first month was confirmed in concordance with other works using 3D fluorescence (Coble, 1996; Parlanti et al., 2000; Baker, 2001; Baker, 2002; Stedmon et al., 2003). The dependency on the input material was higher for the C1 and C2 components than for C3. As for the C/N ratio, it seemed that dependency was important at the beginning, in the first month, and reached exponentially an asymptotic response .

Fig. 7 -PARAFAC component variations

Based on the 3D fluorescence response, FRI was calculated for all the samples. The QI and QII fractions were related to simple aromatic proteins, such as tyrosine and tryptophan, while QIII was related to recently degraded organic matter. QIV was related to fulvic acid presence and QV to humic acid. To compare the variation of the QI, QII, QIII, QIV and QV values in this work, the time set values were normalized to the value of the first sample (T1) for WEOM and EOM, corresponding to the raw material, and the mean of each normalized FRI region was calculated with corresponding standard deviation, using WEOM and EOM together as they were highly correlated ($R^2 = 0.89$). The obtained results are presented in Fig. 8. The QI and QII fractions showed a slight increase for two months (T1 to T3) and had stabilised by the end of the experiment. The increase of QI and QII during this period was not in agreement with the variation observed by Tang et al. (2011) for swine manure, rice husk and straw, or that observed by Tian–et al. (2012) from dairy manure and rice chaff, or by Marhuenda-Egea et al.

(2007) for winery and distillery residues. Concerning the QIII fraction, once again the behaviour was contrary to those found for swine manure, rice husk and straw (Tang et al., 2011), but in accordance with dairy manure, where it stayed constant, or with winery and distillery residues where it increased. The QIV and QV fractions stayed constant in this work. In other work, for swine manure, QIV and QV increased during the first month (Tang et al., 2011), while for dairy manure and winery and distillery residue, QIV decreased while QV increased (Marhuenda-Egea et al., 2007). QIV and QV were related to humic and fulvic acid but in our case, the contribution to fluorescence of extractable OM did not vary. On another way, the QI, QII and QIII increased until the second month and stayed stable.

Fig. 8 – FRI variations.

4. Conclusions

The critical information during compost production is to know when the compost reaches stability or maturity. The fast and common is the inside pile temperature which should be related to microbial activity but is not necessarily good parameter. This work on green waste composts showed that the pH and the $R_{a,c}$ fluorescent indexes were potentially good indexes to determine the compost biochemical stabilisation by their behaviours during maturation time and related to WEOM. Both the pH and $R_{a,c}$ of WEOM were fast measurements that could be done on site. Measurement on water-extracted organic matter was efficient, and showed a stabilisation after three months of composting.

This work also demonstrated that most of the indexes developed in the past and in this work were highly dependent on the input material. This indicated that it would be difficult to define the maturity, stabilisation or age of a compost by measuring only one value or a universal parameter. Results showed that the non-dependent parameters on green compost inputs were the C/N ratio, Kalbitz and the CP/PARAFAC C3 component, at the end of the time process. Finally, the $R_{a,c}$ and pH measurements were highly negatively correlated to the C/N ratio, which was a time-consuming chemical parameter. To monitor the compost chemical stabilisation with an on-site rapid, low cost and time-saving method, the best way is to combine the inside pile temperature, pH and $R_{a,c}$ index of the WEOM.

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