Changes in the chemical characteristics of dissolved organic matter during the composting process and their influence on compost stability and maturity.

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Introduction

Composting is a well-known system for rapid organic matter (OM) stabilization and humification. The application of compost derived from a wide variety of human activities to arable soils has received worldwide attention because of a potential improvement in soil fertility through the increase in the organic matter content [1]. Although the transformation of OM during the composting process has been widely studied, most reports focused on the NaOH-extracted humic-like fraction and less attention has been devoted to the study of dissolved organic matter (DOM).

Compost DOM is a mixture of specific low-molecular weight compounds (free amino acids and sugars) and chemically heterogeneous, high-molecular weight polyelectrolytes (enzymes, amino-sugar complexes, polyphenols, and humic-like substances) [2]. Since most biogeochemical transformations that form part of the evolution of organic matter during composting occur in solution, DOM represents the most active fraction of compost, both biologically and chemically. It is therefore the organic fraction most subject to change, and as such, should directly reflect the OM transformation process. In actual fact, the chemical transformations that occur in the DOM fraction of compost could provide important indications on the evolution and stabilization processes during composting, as well as on the maturity of the final compost.

The involvement of compost DOM in the chemical and biochemical processes of a soil ecosystem after amendment with compost has a direct implication on the composition of soil organic matter [3] and on the suitability of a compost to support plant growth

[4]. Even if the amount of DOM in compost is small compared to the bulk organic matter, it plays a significant role in the microbial activity in soil and in the transport of nutrients, metals and hydrophobic pollutants [5].

In view of the important role that DOM plays in both the process and the application stages of composting, this research seeks to relate the assessment of compost stability and maturity to the chemical and spectroscopic transformations that occur in the water soluble fraction from fresh feedstock to final compost.

Materials and Methods

Raw materials and composting processes

Three urban waste composts were produced mechanically under aerobic conditions by fast aerobic digestion (28 d) followed by a curing phase. Composts SCOM1 and TCOM1 were produced at a composting plant in Perugia (Italy) while SCOM2 was produced in Milan (Italy). SCOM1 and SCOM2 were produced from a standard mixture of source-separated municipal solid waste and yard trimmings, in a feedstock ratio of 50:50% and 70:30% respectively. TCOM1 was produced from an experimental feedstock composed of source-separated municipal solid waste (55%), yard trimmings from pruning activities (30%) and foliage residues from the tobacco agro-industry (15%). The changes in the chemical characteristics of the feedstock with composting time were studied by collecting and analysing compost samples at different times.

Extraction and fractionation of dissolved organic matter

Compost dissolved organic matter samples (SDOM1, SDOM2 and TDOM1) were obtained from the urban waste composts (SCOM1, SCOM2 and TCOM1) by overnight extraction with deionized and degassed water (extraction ratio of 1:10 on a dry weight basis) at room temperature, followed by centrifugation and filtration of the supernatant through a 0.45 micrometers membrane filter.

Fractionation of the DOM extracts into the hydrophilic (HiDOM) and hydrophobic (HoDOM) fractions was carried out using an Amberlite XAD-8 resin (Rohm and Haas, Philadelphia, Pa) [5]. All fractions obtained were purified and freeze-dried.

Chemical properties of composts and dissolved organic matter

Changes in some of the chemical properties of the feedstocks during composting were determined following standard procedures. Analysis involved the determination of total organic carbon content by dichromate oxidation, total Kjeldahl nitrogen [6] as well as the determination of total and labile polysaccharides [7]. Analysis of DOM extracts involved the determination of dissolved organic carbon (DOC), hydrophilic and hydrophobic carbon, dissolved organic nitrogen (DON) and total water soluble phenol

concentration by reaction with the Folin-Coicalteau reagent followed by spectrophotometric quantification [8].

Spectroscopic analysis

The FT-IR spectra of the HiDOM and HoDOM fractions were obtained for a wavenumber range of 4000 to 400 cm^{-1}. Pellets were prepared by mixing 100 mg of dried KBr with 2 mg of the lyophilized substance and then gradually compressing up to 10 tons under vacuum for a total time of 10 min.

The ^{1}H-NMR spectra were recorded on a Bruker 400 MHz spectrometer (Bruker, Karlsruhe, Germany) at a temperature of 290 K. For measurement, 50 mg of each freeze-dried sample were dissolved in 1 mL of 0.5 M NaOD/D$_2$O. The spectra were performed using 5-mm sample tubes using homonuclear presaturation for solvent suppression, 1.16 s acquisition time, 1 s delay time and 2 Hz line-broadening factor. Chemical shifts were given relative to the resonance of tetramethylsilane. The signal areas were calculated by electronic integration.

Respirometric analysis

The specific oxygen uptake rate (SOUR) was determined by measuring the rate of oxygen consumption in the liquid state for the various compost samples, and used as a measure of organic matter stability [9].

Germination Bioassays

The effects of compost maturity on seedling emergence were determined with a cress (*Lepidium sativum* L.) chosen for the bioassay of extracts from compost samples [10]. The extracts were obtained by bringing the water content of fresh samples to 85%, and filtering through a 0.45 micrometers membrane filter. These extracts together with 3 dilutions (25, 50 and 75%) were used as the germination media. The number of germinated seeds and the primary root length were measured and expressed as a percentage of the control. Data were analyzed against concentration of the compost water extract in the growing media and the compost age.

Results and Discussion

The variation in dissolved organic carbon (DOC) with composting time shows similar trends in all three composts, particularly with high DOC values towards the beginning of the process and a general decrease to low values towards the end of the curing phase. The DOC concentration decreased by 72, 64 and 75% for SDOM1, SDOM2 and TDOM1 respectively. The variation in DOC concentration during the process is related to the equilibrium between various reactions which increase or decrease the amount of soluble organic matter. Solubilization through the degradation of the more

labile compounds initially, followed by the more refractory organics that form part of the bulk organic matter, as well as *de novo* biochemical synthesis of low-molecular weight compounds, increase the concentrations of DOC. On the other hand, the reduction in DOC concentrations depends on the continuous mineralization of soluble organic compounds, and re-polymerisation and condensation pathways that lead to the synthesis of humic-like substances that have a lower solubility in water. The contribution of these various reactions during composting changes with process time – the carbon content of DOM during the active phase of composting greatly depends on the nature of the feedstock and composting process used, however, during the curing phase a general decrease in the organic carbon content is observed for the DOM extracts of all three composts.

The changes in dissolved organic nitrogen (DON) with composting time, particularly during the active phase, are more difficult to interpret than the net increase in the total nitrogen content observed and generally reported for most composting processes. The DON is probably influenced by the nature of the feedstock as well as the establishment of various biological and chemical equilibria, also involving inorganic forms of N. The changes are probably a function of variables such as temperature, humidity, oxygen availability, carbon content, production of toxic degradation products, which can influence the fate of organic nitrogen compounds in solution. Results show that TCOM1 has a higher content of dissolved organic nitrogen possibly related to the use of tobacco residues in the feedstock.

The variation in the dissolved organic carbon to nitrogen (DOC:DON) ratio during the process shows a decrease similar to that observed for the total organic carbon to Kjeldahl nitrogen (C:N) ratio of the feedstock for all three composts. However the absolute values obtained for the DOC:DON ratio were generally lower than those obtained for the C:N ratio, only returning to a similar value towards the end of the process. This could be due to the faster degradation of the more labile, soluble carbon compounds as a source of energy for microorganisms with respect to soluble organic nitrogen, especially during the active phase of composting.

Fractionation of the DOM enables the study of the variation of the hydrophobic (HoDOM) and hydrophilic (HiDOM) fractions with composting time. For all three composts the variation in DOC during the active phase was directly related to the concentration of organic carbon in the HiDOM fraction ($r^2 = 0.9731$). In fact during the first 30 days of composting the HiDOM fraction makes up about 80% of the DOC. During the curing phase the concentration of carbon in the HoDOM fraction starts increasing, until the concentration of carbon is actually equal or even greater than that in the HiDOM fraction. This increase could be related to a net effect due to (i) a contribution of hydrophobic constituents from the degradation of ligno-cellulosic materials

occurring during the curing phase, (ii) a faster mineralization of HiDOM moieties with respect to the more refractory HoDOM constituents, and (iii) the transformation of hydrophilic components into hydrophobic moieties by polymerization and condensation reaction as part of the humification process. These changes in the characteristics of DOC have been corroborated by looking at the variations in the concentrations of organic constituents namely polysaccharides and phenolic compounds, as well as by spectroscopic analysis.

The variations in the stability of the feedstock during the composting time are generally studied by means of respirometric analysis. Amongst these, the specific oxygen uptake rate (SOUR), which measures oxygen demand in the liquid state is greatly correlated to the concentration and composition of DOM. For all the three composts, the changes in the concentration of hydrophilic DOM were found to correlate to the SOUR values. Moreover, such a correlation seems to suggest that the reduction in HiDOM with composting time is responsible for the increase in feedstock stability. The lowest values of SOUR were obtained at process times in which the hydrophobic to hydrophilic DOM ratio was greater than 1.

The seed bioassays were used to evaluate changes in compost phytotoxicity during the composting process. The germination indexes (GI) obtained for each sample clearly show a trend of decreasing phytotoxicity with composting time. During the active phase a moderate increase in the GI is evident, however the most significant increase occurred after 60 days of composting. The influence of the water extract concentration in the germination media on the GI was different for samples collected during the active and curing phases. The values obtained for the active phase samples show that maximum toxicity is reached even by the media containing 50% of the extracts and no difference is observed with higher concentrations. The most dilute media (25%) inhibit germination by about 50% with respect to the control. On the other hand, the curing phase samples induce a variation of the GI that seems to be inversely proportional to the concentration of the germination medium over the concentration range studied.

Phytotoxicity or poor plant response can result from several factors the most important of which are a high oxygen demand, the accumulation of toxic compounds such as alcohols, methane, low molecular weight organic acids, ammonia and toxic nitrogen compounds, the immobilization of nitrogen with high C/N ratios, and the presence of heavy metals and mineral salts [11]. Although a significant correlation was observed between the concentration of DOC and the germination indices, further research into the chemical characteristics of the compost DOM with respect to phytotoxicity is foreseen.

References

[1] Giusquiami P.L., Pagliai M., Gigliotti G., Businelli D. and Benetti A. (1995) Urban waste compost: effects on physical, chemical and biochemical soil properties. J. Environ. Qual. 24:175-182.

[2] Chefetz B., Hatcher P.G., Hadar Y. and Chen Y. (1998) Characterization of dissolved organic matter extracted from composted municipal solid waste. Soil Sci. Am. J. 62:326-332.

[3] Gigliotti G., Giusquiani P.L., Businelli, D. and Macchioni A. (1997) Composition changes of dissolved organic matter in a soil amended with municipal waste compost. Soil Science 162(12):919-926.

[4] Cooperband L.R., Stone A.G., Fryda M.R. and Ravet J.L. (2003) Relating compost measures of stability and maturity to plant growth. Compost Science and Utilization 11(2):113-124.

[5] Gigliotti G., Kaiser K., Guggenberger G. and Haumaier L. (2002) Differences in the chemical composition of dissolved organic matter from waste material of different sources. Biol Fertil Soils 36:321-329.

[6] Ministero delle Politiche Agricole e Forestali (2001) Metodi di analisi delle acque per uso agricolo e zootecnico. G. Mecella (ed.) Società Italiana della Scienza del Suolo, FrancoAngeli, Milan, Italy.

[7] Lowe L.E. (1993) Total and labile polysaccharide analysis of soils, In: Carter M.R. (ed.) Soil sampling and methods of analysis. Canadian Society of Soil Science, Lewis Publishers, pp. 373-376.

[8] Lowe L.E. (1993) Water-soluble phenolic materials, In: Carter M.R. (ed.) Soil sampling and methods of analysis. Canadian Society of Soil Science, Lewis Publishers, pp. 409-412.

[9] Adani F., Gigliotti G., Valentini F. and Laraia R. (2003) Respiration index determination: a comparative study of different methods. Compost Science and Utilization 11(2):146-153.

[10] Zucconi F., Monaco A., Forte M. and De Bertoldi M. (1985) Phytotoxins during the stabilization of organic matter, In: Gasser J.K.R. (ed.) Composting of Agricultural and Other Wastes. Elsevier Applied Science Publishers, London, pp. 73-86.

[11] Kapanen A. and Itavaara M. (2001) Ecotoxicity tests for compost applications. Ecotoxicology and Environmental Safety 49:1-16.

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