

DIFFERENCES IN THE CHEMICAL COMPOSITION OF COLLOIDAL ORGANIC MATTER FROM VARIOUS MUNICIPAL SOLID WASTE COMPOSTS AS STUDIED BY PYROLYSIS/GC/MS

M.-F. Dignac¹, M. Andrades², S. Houot^{3,4}, E. Barriuso³

¹Laboratoire de Biogéochimie des Milieux Continentaux (BioMCo), INRA-CNRS-Univ. Paris VI, 78850 Thiverval-Grignon, France, dignac@grignon.inra.fr

²Dpto Agricultura y Alimentación, Univ. de La Rioja, Av. Madre de Dios, 51. 26006 Logroño, Spain

³Unité Environnement et Grandes Cultures - INRA-INAPG, 78850 Thiverval-Grignon, France

⁴CREED-Veolia group, Environment, Energy and Waste Research Center, 78520 Limay, France

ABSTRACT

Soluble and colloidal organic matter (COM) plays an important role in soil processes. Compost addition increases the proportion of COM in soils, with effects depending on their reactivity in relation with their chemical nature. COM was extracted from soils treated or not with composts and from composts at different maturity degrees with liquid water at different temperatures. Then pyrolysis - gas chromatography - mass spectrometry was used for their chemical characterization. Soil and compost colloids extracted at 20°C were mainly composed of N-containing compounds. The COM extracted from the soils (treated and untreated) yielded very similar pyrolysates. With increasing extraction temperature, relative amounts of polysaccharides increased in the extracts. Lignin-derived products were observed in the pyrolysates of COM extracted from soils at temperatures higher than 125°C. Pyrolysis indicated an important bacterial origin of the immature compost extract. This study underlines the ability of pyrolysis for revealing differences in the organic composition of COM extracted from soils and composts.

INTRODUCTION

Composts contain complex mixtures of partly degraded and humified organic matter (OM). When applied to cultivated soils, a part is degraded and/or transformed by microbial activity. At the same time, a small proportion may contribute to the soil Colloidal Organic Matter (COM), and be transferred down the soil profile, with possible consequence on the increase leaching of other input in agriculture like pesticides. The effect of COM depends on their reactivity which is related to their chemical nature. Works on characterization of compost organic matter are mainly addressed to the evaluation of compost stabilization (Chen, 2003). Only few studies described the chemical composition of composts or their fractions by molecular (Pichler and Kögel-Knabner, 2000; Diné et al., 2001) or spectroscopic techniques (Chefetz et al., 1998). We used pyrolysis coupled to gas chromatography with mass spectrometry detection (pyrolysis/GC/MS), since this technique, for the last decades, has been shown suitable to ascertain the chemical composition of organic wastes and their changes upon composting process (Serés-Aspax et al., 1985; García et al., 1992; González-Vila et al., 2001, Dignac et al., 2004).

The objective of this work was to characterize by pyrolysis/GC/MS the chemical composition of colloidal solutions extracted from soils and composts. Different colloid extraction techniques were used allowing extraction of COM with different chemical nature. Extractions were done with liquid water at subcritical conditions allowing modification of water solvation properties, with decreasing water polarity when temperature increased. We studied agricultural soils

originating from a field experiment in France, which aims at comparing the effects of different compost types on soil properties.

MATERIAL AND METHODS

Sample collection and preparation. Compost samples were collected on industrial composting plants in France, after three (immature) and six (mature) months of composting of green waste and sewage sludge, during the maturation phase. Amended and non amended soils were sampled in a field experiment at Feucherolles, near Paris, France. The “mature composts” were applied three times in October 1998, September 2000 and 2002. Each time, the equivalent of 4 Mg of C ha⁻¹ was applied. Soil coming from a non-amended plot was used as reference. In this soil, the average organic carbon and the average nitrogen amounts were 9.55 g kg⁻¹ and 0.99 g kg⁻¹ respectively, and 150 g.kg⁻¹ of clay, 783 g.kg⁻¹ of silt et 67 g.kg⁻¹ of sand. Colloidal and soluble organic matter (COM) were extracted from soils and from composts by shaking in water at 20°C during 24 h, and by pressurized water extraction at 50, 125 and 175°C, using a Dionex ASE 200 (Accelerated Solvent Extractor). Three replicates of the extraction of each soil and compost samples were realized. The COM solutions were freeze-dried and characterized by pyrolysis/GC/MS.

Pyrolysis-GC/MS. Approximately 0.5–1 mg of sample were loaded in tubular ferromagnetic wires, inductively heated to their Curie temperature of 650°C in 0.15 s (10 s hold) by a pyrolysis unit (GSG Curie-Point Pyrolyser 1040 PSC). Pyrolysis products were separated using a Hewlett Packard HP-5890 gas chromatograph (GC) on a 60 m fused silica capillary column SolGelWax (SGE, 0.32 mm i.d., film thickness 0.5 μm), with He as carrier gas. The temperature program of the GC oven was set with an increase of the temperature from 30 to 280°C at 2°C/min, and maintained at 280°C for 15 min. The GC was coupled to a Hewlett Packard HP-5889 mass spectrometer (electron energy 70 eV). Compounds were identified based on their mass spectra, GC retention times, and comparison with library mass spectra. A number of pyrolysis products were identified from each sample, some of them being specific of a macromolecular source. All chromatograms are displayed with toluene having the same height.

RESULTS AND DISCUSSION

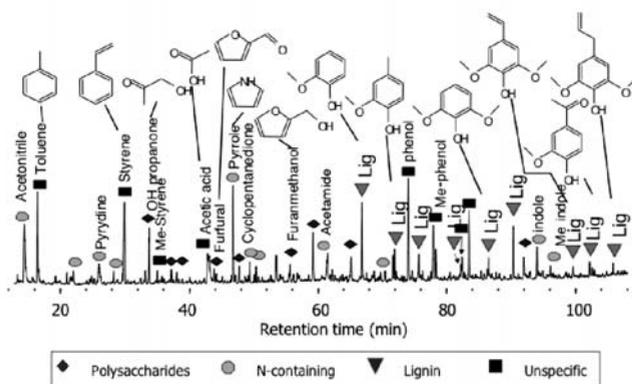


Figure 1. Typical pyrochromatogram of colloidal organic matter: main identified compounds were detailed and also their supposed origin from the specific biopolymers.

A polar capillary column was chosen for GC separation of pyrolysis products, for a better separation of polar compounds originating from sugars, proteins and lignins. The less polar compounds such as alkanes/alkenes are less easily observed on this column, but on an apolar column they represented relatively small peaks compared to the products originating from fresh organic matter (data not shown). A number of pyrolysis

products were identified (Fig.1), some of them being specific of a macromolecular source, like N-containing products (N) derived from proteins and peptides, polysaccharide-derived (PS) from cellulose, or methoxy phenols from lignin (LIG), compounds with isoprenic structure and compounds derived from plastics. Others compounds with unspecific origin were also identified: styrene, phenol, acetic acid,

Extraction with water at 20°C can be assimilated to the leaching in field conditions. Indeed, extracts could represent the materials easily available in soils. In COM recovered at 20°C, mainly N-containing pyrolysis products were observed, with a minor contribution of polysaccharides. COM extracted at 20°C were very similar in the different soils, without a significant influence of compost application on soil COM composition (Fig. 2). However, COM extracted with water at 20°C showed large differences between mature and immature composts (Fig. 2). COM from immature compost was formed by relatively more N-containing compounds, and the large acetamide peak in the COM from immature compost pyrolysate is probably a tracer of the non degraded bacterial materials (peptidoglycans).

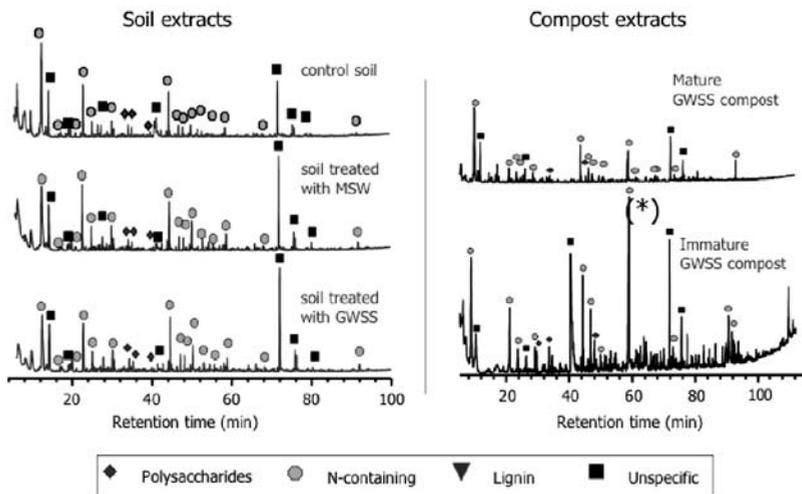


Figure 2. Representative pyrochromatograms of colloidal organic matter extracted at 20°C from (on the left) : soils treated or not with municipal solid waste compost (MSW) and sewage sludge co-composted with green wastes (GWSS); and (on the right): mature and immature GWSS compost. (* signals the peak corresponding to the acetamide).

The use of liquid water at subcritical conditions was an innovative extraction technique based on the modification of water polarity through the decreasing of their dipolar moment with temperature increase. The extraction yields increased with the temperature because of hydrolytic reactions directly related to the water temperature increasing water diffusivity and affinity for hydrophobic compounds. With increasing extraction temperature, the relative amounts of polysaccharides increased in the extracts (Fig. 3). Lignin-derived products were observed in the pyrolysates of COM extracted from soils at temperatures higher than 125°C. Less lignin-derived compounds were observed in the control soil than in the soil treated with GWSS compost. In the pyrolysate of COM extracted at 50°C, some polysaccharide-derived compounds were observed, in addition to N-containing and unspecific compounds.

This study underlines the ability of pyrolysis for revealing differences in the organic compo-

sition of COM extracted from soils and composts. These differences can be used to understand the specific reactivity of COM for organic pollutants present in soils.

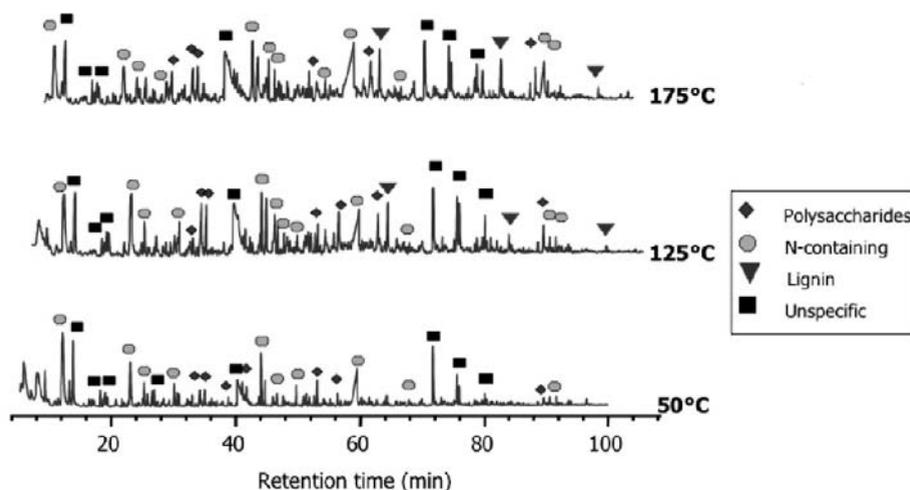


Figure 3. Pyrochromatograms of colloidal organic matter extracted with liquid subcritical water at different temperatures from the sewage sludge co-composted with green wastes (GWSS).

Acknowledgements. Work supported by the INRA-Department of Environment & Agronomy, the Spanish Ministry of Education and CREED-Veolia group that supplied compost and financial and technical support.

REFERENCES

- Chefetz, B., Hatcher, P.G., Hadar, Y., Chen, Y. 1998. Characterization of dissolved organic matter extracted from composted municipal solid waste. *Soil Sci. Soc. Am. J.*, 62: 326-332.
- Chen, Y. 2003. Nuclear magnetic resonance, infra-red and pyrolysis: application of spectroscopic methodologies to maturity determination of composts. *Compost Sci. Util.*, 11: 152-168.
- Dignac, M.-F., Houot, S., Derenne, S. 2004. Pyrolytic study of compost and waste organic matter. *Organic Geochem.*, submitted.
- Dinel, H., Schnitzer, M., Paré, T., Lemée, L., Amblès, A., Lafond, S. 2001. Changes in lipids and sterols during composting. *J. Environ. Sci. Health.*, 36B: 651-665.
- García, C., Hernández, T., Costa, F., Ceccanti, B., Calcinai, M. 1992. A chemical-structural study of organic wastes and their humic acids during composting by means of pyrolysis-gas chromatography. *Sci. Total Environ.*, 119: 157-168.
- González-Vila, F.J., Lankes, U., Lüdemann, H.D. 2001. Comparison of the information gained by pyrolytic techniques and NMR spectroscopy on the structural features of aquatic humic substances. *J. Anal. Applied Pyrolysis*, 58: 349-359.
- Pichler, M., Kögel-Knabner, I. 2000. Chemolytic analysis of organic matter during aerobic and anaerobic treatment of municipal solid waste. *J. Environ. Qual.*, 29: 1337-1344.
- Serés-Aspax, A., Alcañiz-Baldellou, J.M., Gassiot-Matas, M. 1985. Application of pyrolysis-gas chromatography to the study of the composting process of barley straw and pear-tree wood. *J. Anal. Applied Pyrolysis*, 8: 415-426.