



## Compositional characteristics of organic matter and its water-extractable components across a profile of organically managed soil



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### ARTICLE INFO

#### Article history:

Received 17 July 2016

Received in revised form 12 October 2016

Accepted 15 October 2016

Available online xxxx

#### Keywords:

Soil profile

Compost

Organic matter

FTIR

Fluorescence

PARAFAC

### ABSTRACT

Soil organic matter (SOM) plays a dominant role in the functionality of agricultural soils and particularly so in organic farming. Yet, there is limited knowledge on the effect of organic management in which the soil is subjected to incorporation of a variety of organic residues on the composition of SOM and water-extractable organic matter (WEOM) in top and sub-surface soil layers. The general objective of this study was to quantify depth-related changes in the composition of SOM and WEOM in an organically managed soil subjected to multiple compost applications, using spectroscopic techniques requiring no or minimal soil sample pre-treatment. We collected soil samples across the top 60 cm on October 2012 from an existing field experiment initiated in late 2009, which was organically fertilized by means of compost and green manure incorporation. Compost was applied at levels of 0 (control), 20, 40 and 60 m<sup>3</sup> ha<sup>-1</sup>, with the control treatment being fertilized with urea and amended with green manure. The collected samples were then used to characterize (i) SOM by FTIR absorbance associated with hydrophilic SOM functional groups and aliphatic CHs, total organic C and N contents, and (ii) WEOM by dissolved organic C (DOC) concentration, UV–VIS absorbance and fluorescent components identified following parallel factor analysis. In general, for all the studied attributes the core data tended to (i) increase after compost addition, although differences among the compost doses could not always be identified, and (ii) decrease with soil depth for all compost doses as well as the control treatment. Compost addition enriched soil by hydrophobic organic matter and water-extractable aromatic and, specifically, humic-like components. In the compost-amended soil, SOM became depleted of hydrophilic groups and enriched by hydrophobic aliphatic CH-rich substances. However, the content of hydrophilic organic matter in SOM was elevated with increasing depth.

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### 1. Introduction

Soil organic matter (SOM) has been considered a good indicator of a healthy soil system (Haynes, 2005) as it plays an important role in a wide range of soil properties and processes such as maintenance of soil structure (Oades, 1993), water-retention capacity (Lado et al., 2004), nutrient cycling (Goulding et al., 2000) and stimulation of biological activities (Jimenez et al., 2002). The addition of organic residues to soil increases SOM content over time (Schulten et al., 1992; Gregorich

et al., 1996), modifies the chemical, physical and biological properties of the soil (Nardi et al., 2004; Adani et al., 2007) and increases its total N content (Marschner et al., 2003; Blackshaw et al., 2005) and C storage (Cabrera et al., 2009; Powlson et al., 2012), with the latter occurring directly from C inputs by amendments and indirectly from increased plant production (Eghball and Power, 1999; Ryals and Silver, 2013).

The role of SOM may become even more meaningful under organic management, as organic farming practices minimize chemicals inputs and rely on periodic incorporation of various organic residues and on reduced or no tillage, which in turn enhance SOM content (Doane and Horwath, 2004; Raviv, 2010). Increased SOM content enhances the activity and diversity of macro and microorganisms which are critical for the reduction of plants susceptibility to pests when pesticides are avoided (Raviv, 2010), as well as for successful crop nutrition that is based on nutrient cycling (Watson et al., 2002).

Concerning SOM-related biological functionalities, it is relevant to investigate labile soil organic C pools such as water-extractable organic

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matter (WEOM), microbial biomass and particulate organic matter that turn over quickly and can respond more rapidly to soil management practices (Haynes, 2005; Liang et al., 2011). Earlier studies have reported that organic matter extractable from soil is sensitive to the use of organic amendment (Leinweber et al., 1995; Chantigny et al., 2000). The application of composts to soil increased the stable organic matter content (Franko et al., 1997; Watson et al., 2002), and enhanced the activity and size of soil microbial communities (Saison et al., 2006).

Although the studies on the effects of organic amendments on organic matter dynamics in soils often focused on the upper soil layer (0–20 cm) (West and Post, 2002), some studies also looked at depth distribution of SOM and its components in relation to land use and management, concluding that deeper soil horizons are capable of sequestering SOM due to its increased recalcitrance and turnover time (Lorentz and Lal, 2005; von Lütow et al., 2008). Subsoil horizons (below 20 cm) are considered to contain large (and even major) amounts of soil organic C within the 0–3 m depth thus affecting global C storage and dynamics (Jobbagy and Jackson, 2000; Janzen, 2005). A long term study of tillage effects in the 0–60 cm soil profile reported a greater soil organic C in the upper 0–10 cm layer under no tillage than under conventional tillage, but no effects on the labile C fraction below 10 cm (Liu et al., 2014). Conversely, a long term application of manures increased dehydrogenase activity and organic C pools in 0–60 cm depth relative to control (Liu et al., 2014; Simon and Czako, 2014). Several field studies have shown that concentration and fluxes of dissolved organic matter (DOM) in soil solution decrease significantly with soil depth (Kalbitz et al., 2000a). Subsoil SOM may be contributed more significantly by microbial-derived organic matter as compared with plant-derived material, and its degradation can be suppressed by SOM interactions with minerals, occlusion in soil aggregates and, possibly, unfavorable temperature, supply of nutrients and energy (Rumpel and Kögel-Knabner, 2011). Formation of organo-mineral complexes and occlusion in soil aggregates are important SOM protection mechanisms at different soil depths, but degradation dynamics of root litter may be different in top and subsoil (Sanaullah et al., 2011). Subsoil SOM was found to be horizontally stratified in adjacent compartments which should be taken into account in examining subsoil C sequestration (Chabbi et al., 2009). Yet, the importance of organic C in subsoils is underestimated, and more efforts are needed to better understand the mechanisms of soil organic C storage and turnover (SUBSOM - DFG).

The methodologies used to characterize SOM composition are often destructive (e.g., thermochemolysis and pyrolysis-field ionization mass-spectrometry; Lorentz and Lal, 2005; Erich et al., 2012), and may involve an aggressive pre-treatment, such as HF handling of soil samples for  $^{13}\text{C}$  NMR measurements (Downie et al., 2011; Clouard et al., 2014) or base extraction for recovering humic substances. Alternatively, non-destructive FTIR spectroscopy has been used successfully for SOM characterization in bulk soil samples (Haberhauer and Gerzabek, 1999; Reeves et al., 2001; Tremblay and Gagné, 2002; Demyan et al., 2012; Voelkner et al., 2015). Recently, it was suggested to quantify the accumulation of certain SOM components in non-disturbed soil samples, by relating the absorbance of IR radiation by a given organic functional group to the absorbance by quartz (Bernier et al., 2013). The latter is commonly present in soils, its content is hardly sensitive to soil management and, hence, quartz could be used as an internal reference. Fluorescence spectroscopy is commonly used to examine fluorescing organic matter in aqueous solutions (Senesi et al., 1989; Zsolnay et al., 1999; Kalbitz et al., 2000b; Chen et al., 2003; Borisover et al., 2012; Cohen et al., 2014). Fluorescence spectroscopy (combined with thermal analysis) was used to study the effects of profile depth and organic amendment on the composition of labile and total SOM (Erich et al., 2012). UV-absorbance may provide a proxy for concentrations of aromatic DOM components soluble in water (Zsolnay and Steindl, 1991; Weishaar et al., 2003). Hence, based on ultraviolet-visible (UV/VIS) spectroscopy of WEOM, it was shown that the aromaticity and humification degree of WEOM increased with depth in the top 30 cm of

organic matter-poor sandy soil treated by different amendments (Daouk et al., 2015).

The fate of SOM and its water-extractable components in deeper soil layers may be different under organic management, in which C inputs are typically greater and the biological activity at the upper soil layer may be more intense, than under conventional management. However, the changes in the chemical composition of SOM and WEOM in sub-surface horizons of agricultural soils under organic farming practice have barely been investigated and are, thus, poorly understood. Therefore, examination of the composition of SOM/WEOM across a profile of organically managed soil is required, having the potential to provide original data and new meaningful insight for organic farming.

Thus, the general objective of this study was to quantify depth-related changes in the composition of SOM and its water-extractable constituents in an organically managed soil that was subjected to multiple compost applications. For that, spectroscopic techniques were selected, requiring no or minimal soil sample pre-treatment, including: (a) FTIR-spectroscopic analysis of the whole soil samples (SOM characterization), and (b) UV/VIS spectroscopy and excitation-emission fluorescence of the water-extractable organic matter (WEOM characterization). FTIR-spectroscopic analysis was enhanced by applying a novel approach using quartz as the internal soil reference (Bernier et al., 2013) which allows examining not only the SOM compositional changes but also the accumulation of separate SOM components in the whole soil sample. Examining WEOM fluorescence was carried out by measuring excitation-emission matrices (EEMs) of fluorescence, augmented with parallel factor analysis (PARAFAC) which provides the possibility to identify chemically sounding fluorescent components of organic matter (Smilde et al., 2004; Ohno and Bro, 2006). Consequently, a new set of data that had not been available before was obtained, and a better understanding of depth-related changes in organic matter composition under organic management may be expected.

## 2. Materials and methods

### 2.1. Study site, soil characterization and experimental design

The study used an experimental field platform originally established in late 2009 to examine factors which affect soil fertility under organic management. The experimental field is situated at Newe Ya'ar Research Center, located in the Jezre'el Valley, northern Israel (32°42'N 35°11'E). This region is characterized by Mediterranean climate with cool winter (average minimum of 8–9 °C), warm dry summer (average maximum of 32–34 °C) and average annual precipitation of 570 mm, concentrated mostly between November to March (The Israel Meteorological Service; <http://www.ims.gov.il/IMS/CLIMATE>; accessed at 7.07.2016; temperature averages are for the years 1995–2009, and rain average is for the years 1980–2009).

The soil is a Vertisol-type, classified as Chromic Haploxeret (fine clayey, montmorillonitic, thermic; Antil et al., 2011). Selected properties of the soil up to a depth of 60 cm, determined by standard analytical methods (Klute, 1986; Page et al., 1986), are presented in Table 1. The experimental field platform has a total area of 1 ha which has entirely been managed organically with respect to plant protection (no pesticide use) and to green manure incorporation. The area was sub-divided into twenty plots, 450 m<sup>2</sup> each, to examine the effect of organic fertilization by means of three levels of annual compost application. Four treatments were applied in five replicate plots in a randomized block designed: (i) 20 m<sup>3</sup> compost/ha/yr; (ii) 40 m<sup>3</sup> compost/ha/yr; (iii) 60 m<sup>3</sup> compost/ha/yr; and (iv) control (no compost) which was fertilized with urea according to conventional practice (200 kg urea/ha/yr). No additional fertilizers were used in treatments (i–iii). The compost was obtained from Sde Eliyahu commercial site and considered stable based on heat emission of around 10 J/g dry matter/12 h measured by microcalorimetry (Saadi et al., 2010). The compost characterization is provided in the

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