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2 Bulk and water-extractable organic matter from compost: evaluation of the
3 selective dissolution in water using infra-red absorbance ratios
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Abstract

Land application of composts affects concentration and composition of dissolved organic matter (OM) which plays important roles in soil functioning and may have effects on spreading of environmental pollution. Linking between the compositions of bulk compost OM and its water-soluble fraction may, therefore, allow better understanding and prediction of environmental impact of compost land use. The objectives of this study were to (i) examine compositional links between bulk compost OM and its water-extractable OM (WEOM), and (ii) evaluate and quantify selectivity of bulk compost OM dissolution, based on infra-red (IR) absorbing functional groups. For that, 8 different composts and their freeze-dried WEOMs were characterized by mid-IR transmission spectroscopy. Compositions of compost OM and WEOM were characterized in terms of ratios (R) defined on the basis of both areas and heights of specific IR bands in relation to absorbance by aliphatic CH groups. A simple novel approach is suggested, whereby selective dissolution of compost OM components is quantified by relating the R values determined for WEOM to those associated with compost OM. Significant similarities of IR spectra found in a series of WEOMs (and, to a lesser extent, in a series of compost OMs) suggest significant contributions of OM carboxylic groups to various bands. WEOM composition (characterized by the R values) is associated, to a certain extent, with compost OM composition expressed by similar type indices. The WEOM aromaticity estimated by specific UV absorbance correlated strongly with some R values determined for bulk OM.

Keywords: compost, water-extractable organic matter, fractionation, FTIR, SUVA₂₅₄, DOM, selective dissolution

Introduction

Land application of composted organic matter (OM) is a well-known practice for improving soil properties, adding nutrients and assisting in disposal and utilization of organic wastes (Serra-Wittling et al. 1996; Ros et al. 2006; Hargreaves et al. 2008). Water-extractable organic matter (WEOM) is an active fraction of composts, and the changes in WEOM are commonly associated with changes in bulk compost material and compost maturity (Zmora-Naum et al. 2005; Said-Pullichino et al. 2007; He et al. 2011; Lv et al. 2013). Consequently, following compost application, the concentration of dissolved organic matter (DOM) in the soil environment increases (Leifeld et al. 2002; Sharma et al. 2017; Buchmann and Schaumann 2018). It is generally recognized that DOM participates in multiple biogeochemical processes both in soil and water phases, including C cycling, promoting biological activity, adsorption to soil minerals, reactions with pollutants and agrochemicals and subsurface transport of bound organic and inorganic chemicals (Aiken et al. 2011; Bolan et al. 2011; Huang et al. 2016).

Compost WEOM is a complex mixture of humic-like substances, amino- and carboxylic acids, carbohydrates, amino-sugars, polyphenols, enzymes and soluble lignin fractions (Caricasole et al. 2010; Wei et al. 2014; Monda et al. 2017). Fats, resins, proteins, hemicellulose and cellulose are detected, among others, in composts by chemical fractionation and colorimetric methods (Serra-Wittling et al. 1996). Dignac et al. (2005) reported composts to have variable chemical composition, which, depending on its source, contained different proportions of lignin, polysaccharides, N-containing products, polystyrene, limonene and chlorophyll-derived compounds. Municipal solid waste compost contains also C12–C18 fatty acids (Dignac et al. 2005). Zmora-Nahum et al. (2007) examined 37 commercial composts from different sources including

manure, urban biowaste, green waste, coffee berries, wastes of olive oil press, and different countries (France, Greece and the Netherlands). They concluded that at the end of a complete composting process, the C functionalities were rather uniform for a variety of source materials, with aliphatic C ranging from 18.6% to 26%; polysaccharide C, 39–43%; aromatic C, 18–27%; carboxyl C, 9–12%. The humic-acid to fulvic acid ratio may vary in composted materials (Goyal et al. 2005) with the core structure of humic substances coated by polysaccharides, simple phenols and peptides (Chefetz et al. 1998). In addition, humic acids extracted from composted materials may have smaller molecular sizes than those extracted from fossil or soil samples (Zbytniewski and Buszewski 2005). The organic matter in mature composts is quite stable, such that half of the compost C is stabilized for a long time in the soil (van der Wurff et al. 2016). A variety of compost constituents are expected to undergo selective dissolution from the source bulk material, which may contribute to differences in chemical composition between bulk compost OM and compost-derived WEOM. The understanding of such selective dissolution and the subsequent compositional differences between compost OM and compost-derived WEOM may help in establishing relationships between (i) compost composition (and maturity), (ii) its potential to increase DOM concentration in the soil environment and (iii) DOM composition and its physico-chemical properties, and finally, the DOM involvement in various soil biogeochemical interactions.

The composition of bulk compost OM has been characterized by various methods, including nuclear magnetic resonance (Inbar et al. 1989; Chefetz et al. 1996; Martín-Mata et al. 2016), mass spectrometry (Dignac et al. 2005; Smidt et al. 2005), thermogravimetry and differential thermal analysis (Baffi et al. 2007; El Ouagoudi et al. 2015), solid-phase fluorescence (Muller et al. 2011; Albrecht et al. 2015) and

thermochemolysis coupled to GC–MS (Amir et al. 2006; Spaccini and Piccolo 2007). Multiple characterizations of bulk compost OM were also performed with infrared (IR) spectroscopy (Inbar et al. 1989; Hsu and Lo 1999; Martínez-Sabater et al. 2009; Higashikawa et al. 2014). Presence of humic and fulvic fractions in composts were examined by using basic extraction (Veeken et al. 2000; Polak et al. 2009).

Compost WEOM was typically characterized in solutions by determining dissolved organic C (DOC) concentration, absorbance in UV-visible range (e.g., at 254 nm, Abs₂₅₄) and the DOC-normalized (specific) UV-absorbance (SUVA) (He et al. 2011; Wang et al. 2013), fluorescence spectroscopy (Senesi et al. 1991; Vieyra et al. 2009; He et al. 2013), NMR spectroscopy (Monda et al. 2017), and by fractionation on resins (Hunt et al. 2006; Said-Pallicino et al. 2007; Avneri-Katz et al. 2016). In addition, various functional groups in freeze-dried compost-derived WEOM were examined by means of IR spectroscopy (He and Ohno 2012; He et al. 2013; Lv et al. 2013; Chiang et al. 2016).

However, less attention was paid to quantitative characterization of chemical composition of both bulk compost OM and compost-derived WEOM, by using the same experimental methodology that is sensitive to certain functional groups. Such a characterization would allow to better elucidate compositional differences between bulk OM and WEOM and the selective dissolution of WEOM components. The use of the same methodology may not be always easy since some experimental methods such as UV-visible absorption and fluorescence spectroscopy are typically applicable to solutions but not to bulk compost (although some studies on solid state fluorescence spectroscopy of composts have been reported (Muller et al. 2011; Albrecht et al. 2015). Mid-IR spectroscopy seems to be well suitable for such comparative examination of

bulk compost OM and the compost-derived WEOM albeit that WEOM characterization requires freeze-drying as a preparation step. Such type of study was made by He and Ohno (2011), in which mid-IR spectra were obtained for both manure OM and its freeze-dried WEOM. However, compositional differences between bulk manure OM and WEOM, based on the IR spectra, were not examined in quantitative terms (He and Ohno 2012). Wang et al. (2013) studied IR spectra of sewage slug compost and its freeze-dried WEOM, yet, the rise of the content of carbonyl, hydroxyl, carboxyl and C=C groups in WEOM, relative to that in the bulk compost, was only qualitatively mentioned. Therefore, quantitative description of the compositional differences between the two pools of compost OM, i.e., its bulk matter and WEOM, using IR spectroscopy, and examining the correlations between attributes from the two types of compositions, will be a novel contribution. In turn, this would lead to a better understanding, on a quantitative level, how composition of DOM in natural soil environment may be affected by external organic matter input.

Hence, in this study, we have used absorption FT-mid-IR spectroscopy to characterize a series of composts and their freeze-dried WEOMs, for the purpose of (i) examining whether quantitative links may be established between the composition of bulk compost OM and that of WEOM, and (ii) evaluating changes in chemical composition of OM during its (partial) aqueous dissolution and estimating the selectivity of this dissolution for certain functional groups active in IR spectra.

Materials and Methods

Compost sampling and primary characterization of bulk materials and aqueous extracts

Eight composts were used in this study (Table 1), five of which were commercial products sold by different producers (composts 2-6, Table 1) and three composts were taken at three different stages of composting, after 1 , 3 and 6 months of composting (composts 1a-c, Table 1). All compost samples were air-dried, ground with a porcelain mortar and pestle and sieved (<2mm). Moisture content was determined by 24 h oven-drying at 105 °C to constant mass. Total organic C (TOC) and total N (TN) were measured with the Thermo Finnigan Flash EA 1112 Series elemental analyzer. Ash content was determined by burning compost samples in air at 400 °C to constant mass. The completeness of burning was checked by the TOC analysis of ash. In Table 1, TOC, TN and ash contents (% , w w⁻¹) are provided on 105 °C dry weight basis.

Aqueous compost extraction was performed by mixing water with compost at the 10:1 mass ratio (for compost dry mass), for 2 h at room temperature on a horizontal Edmund Buhler 7400 Tubinger shaker, at 145 min⁻¹ frequency. Then, the mixture was centrifuged for 15 min (2360 G) and double-filtrated (with glass-microfiber 1.2 µm MGC Sartorius filters and then with 1 µm paper filter Sartorius 293). Filtered extracts were characterized for pH and electric conductivity (EC). The Abs₂₅₄ of aqueous extracts (diluted with double distilled water, by a factor of 20-50, depending on an optical density of initial solutions) was measured in a 1 cm quartz cuvette on a Genesys 10UV spectrophotometer, and then, the determined absorbancies were multiplied by the corresponding dilution factor. Concentrations of dissolved organic C (DOC) in the extracts were determined using a Shimadzu TOC-Vcpn analyzer. SUVA₂₅₄ (L mg⁻¹ m⁻¹) was calculated by dividing Abs₂₅₄ by DOC concentration (mg L⁻¹) and the optical length (1 cm) and multiplying by 100. The data for pH, EC, DOC, Abs₂₅₄ and SUVA₂₅₄ of the aqueous extracts are reported in Table 1. All the attributes presented in Table 1

were made in four replicates. Then, a portion of each compost extract was freeze-dried at 4 Pa and -51°C by Freeze Dryer FreeZone 2.5 Labconco.

FT-IR measurements

Absorption mid-IR spectra were collected using KBr pellets for the composts, ash after burning the bulk compost material and freeze-dried WEOMs. The amounts of added materials per 0.3 g of KBr (FT-IR grade by PIKE) were as following: 0.006-0.008 g of compost (or its ash) and 0.002 g of freeze-dried WEOM. The mix was ground with agate mortar and pestle and pressed under 10 tons cm⁻² using a PIKE Technologies Evacuatable Pellet Press. The FT-IR spectral measurements were performed with Tensor 27 Bruker, in the 4000- 400 cm⁻¹ wave number range with 64 scans and a 4 cm⁻¹ resolution. OPUS 6.5 software was used for baseline, CO₂ and H₂O atmospheric corrections, min-max normalization and spectra integration. IR spectral measurements of composts and WEOM were replicated by preparing from 4 to 6 and 2 different pellets, respectively.

In order to describe OM in the compost samples, subtraction of ash spectrum from the "bulk compost" spectrum for each compost sample was performed using Microsoft Excel. In order to perform this subtraction the spectrum of a compost sample was first normalized to a height of a distinct peak at 873 cm⁻¹ associated with carbonates (Miller and Wilkins 1952; NIST Chemistry WebBook). It was assumed that these carbonates are evenly distributed in any given sample and do not decompose at 400 °C (Halikia et al. 2001; Xu et al. 2014). Ash IR spectral measurements showed very good repeatability and were made in duplicates. Then, for a given type of compost, each ash spectrum was also normalized to a carbonate peak height at 873 cm⁻¹, the two replicate

spectra were averaged and subtracted from each replication of the calcium carbonate-normalized compost spectrum.

Further quantitative analysis of the compost OM and WEOM spectra included absorbance integration within a selected wavenumber range producing band area and determination of peak heights. The computation was performed using the OPUS 6.5 software with selecting zero baseline, except for integrating bands linked to symmetric and asymmetric stretching vibrations of aliphatic CH bonds in methyl and methylene groups. The latter both appear as small bands on the tail of broad absorption of O-H stretching bond in water, carboxyl and hydroxyl groups so that the tail was extrapolated to the area of CH bond absorption and used as the baseline.

Results and Discussion

IR absorption band assignment

Typical absorption IR spectra for the bulk compost (#3, Table 1), its ashed form, the resulting spectrum from the subtraction of the ash spectrum from the compost spectrum, and the freeze-dried WEOM spectrum are shown in Fig 1. Absorption IR spectra of the all compost OM's studied (after subtraction of the corresponding ash spectrum from each individual OM spectrum), and of the freeze-dried WEOMs are shown in Figs. S1,S2 (Supplementary Material). The band assignments are summarized in Table S1 (Supplementary Material). The sharp narrow peak at 873 cm^{-1} associated with presence of carbonates is clearly seen in the spectrum of the whole compost (I) and that of its ashed form (II) (Fig. 1). This peak was used for spectrum normalization in the subtraction procedure (Materials and methods). Calcium carbonate was evident also in small yet distinct peaks at 2513 , 1796 and 716 cm^{-1} in spectra I and II (Nguyen et al. 1991;

Ravisankar et al., 2011; Tinti et al., 2015). In the ash spectrum II, calcite contributes also by intensive CO_3^{2-} vibrations at 1427 cm^{-1} (Hay and Myneny 2007; Margenot et al. 2017). The broad band with the maximum around 3435 cm^{-1} in the compost ash (II) corresponds to OH-stretching in phyllosilicates (Margenot et al. 2017), with the kaolinite OH-stretching at 3696 and 3620 cm^{-1} seen both in the ash and the whole compost (Nguyen et al. 1991; McKissock et al. 2003). The quartz absorbance appears at 797 and 779 cm^{-1} (Muller et al. 2012; Bernier et al. 2013).

Comparing the spectra of the compost (I) and ash (II) with the ash-subtracted spectrum (III) clearly reveals that the straightforward use of the compost IR absorbance at $950\text{-}1450\text{ cm}^{-1}$ for characterization of OM without ash-subtraction step would be significantly biased by inorganic components. In the ash-subtracted spectrum of compost OM (III) (Fig. 1) several regions of distinct IR absorption may be detected. Strong broad band with maximum near 3400 cm^{-1} is commonly related to stretching of hydroxyl groups in water, hydroxyl and carboxyl present in OM and strongly affected by variously bound residual water (Ellerbrock and Gerke 2004; Simkovic et al. 2008); therefore, it was not used in further analyses. The band denoted A appears in the $3020\text{-}2780\text{ cm}^{-1}$ wavenumber range on the tail of water/hydroxyl absorption. This band is typically related to symmetric and asymmetric stretching vibrations of aliphatic CH-bonds in methyl and methylene groups (Ellerbrock and Gerke 2004; Simkovic et al. 2008). The absorption in the $1975\text{-}1500\text{ cm}^{-1}$ wavenumber range with the typical broad band having a maximum about 1640 cm^{-1} (tagged B), is indicative of the C=O in ketones, amides, carboxylic acids and of asymmetric stretching vibrations of carboxylate-ion (Silverstein and Webster 1997; Ellerbrock and Gerke 2004; Smidt and Schwanninger 2005; Calderon et al. 2011). Hay and Myneny (2007) observed the C=O vibrations at 1720 cm^{-1} and asymmetric stretching

frequencies of C-O bond in carboxylates between 1580 and 1540 cm^{-1} . The C=C groups conjugated with another C=C group or an aromatic ring may absorb in this region (Silverstein and Webster 1997). Band C (the 1590-1170 cm^{-1} interval) in the compost OM and WEOM spectra may be contributed by symmetric stretching vibrations of COO^- groups (Hay and Myneni 2007) and the aliphatic C-H bending vibrations (Silverstein and Webster 1997). Also, C-N stretching vibrations associated with amide III band may appear at 1265 cm^{-1} (Smidt and Schwanninger 2005). Finally, band D (1250-900 cm^{-1}) represents C-O stretching and O-H deformation vibrations in alcohols, phenols, carboxylic acids, aryl esters and polysaccharides (Smidt and Schwanninger 2005; Tinti et al. 2015). Also Amir et al. (2005) attributed the maximum at 1140 cm^{-1} to ester/ether linkages of fulvic acid. Moreover, C-N stretching vibration of primary amines may appear at 1340-1020 cm^{-1} (Calderon et al. 2011).

Spectra of freeze-dried WEOM samples, exemplified in Fig. 1 (IV) were examined in terms of bands A, B, C and D similarly to that made for ash-subtracted OM. Inorganic carbonates, nitrates and sulfates extracted from the composts could contribute to measured absorbance values of WEOM samples. Since no characteristic peaks at ~2500 and ~873 cm^{-1} associated with presence of carbonates (Miller and Wilkins 1952; Margenot et al. 2017) were detected in the IR spectra of WEOMs (in contrast, for example, to the compost spectrum I, Fig. 1), the contribution of inorganic carbonates to measured WEOM absorbance was considered minor. Sulfates are known to absorb at 1110 cm^{-1} (Miller and Wilkins 1952). Nitrate absorbs at 1384–1350 cm^{-1} (Linker et al. 2005; He et al., 2011) and yields also two weak absorbance peaks at 835-825 and 1790-1740 cm^{-1} (Miller and Wilkins 1952; Yildirim et al. 2015). Indeed, these two weak nitrate peaks were noted in the WEOM spectrum (Fig. 1, IV); a small peak at 831 cm^{-1} and a

1766 cm^{-1} maximum on the tail of band B. In three of the eight WEOM samples studied (Fig. S2, Supplementary Material), these 831 and 1766 cm^{-1} peaks appeared simultaneously thus supporting their relation to nitrate. Therefore, absorbance of some inorganic anions could contribute, to a certain extent, to absorbance of bands B, C and D. However, maximum of band B seems to be minimally affected by the commonly found inorganic anions similarly to that observed in the compost spectrum.

WEOM and compost OM: compositions characterized by absorption IR spectra

The absorption IR spectra of the freeze-dried WEOMs of the all composts studied (Fig. S2, Supplementary Material) demonstrated, in general, similar patterns associated with the presence of small band A standing separately from bands B, C and D. Foremost, these similarities reflect, in a qualitative manner, the fact that the multiple absorbing chemical functionalities contributing to bands A-D are found in different organic materials, but possibly in different proportions. In fact, based on a large number of samples differing in origin and by geographic locations, a matured compost OM is expected to demonstrate a uniform C functionality, with aliphatic C varying between 18.6% and 26%, polysaccharide C in the 39–43% range, aromatic C between 18 and 27% and the carboxyl C in the 9–12% range (Zmora-Nahum et al. 2007). In order to characterize the composition of WEOM, the ratios (R) of the area of band B, C and D to the band A area were calculated, i.e., $R_{B/A}$, $R_{C/A}$ and $R_{D/A}$, respectively. Each such ratio is considered proportional to the ratio between concentrations of the functional groups contributing to the bands B, C or D and the concentration of aliphatic CHs represented by the area of band A. Unlike absolute band areas, these ratios may be compared between different samples.

Similarities between WEOM of different origin are supported by results of a linear regression analysis between $R_{C/A}$ and $R_{B/A}$, and $R_{D/A}$ and $R_{B/A}$ derived from the different WEOMs (Fig. 2a,b, respectively). Considering the variable compost sources (Table 1), one explanation for these strong correlations could be ascribed to the significant contribution of absorption from carboxylates associated with inorganic cations to the band areas B, C and D, i.e., by asymmetric COO^- , symmetric COO^- and C-O stretchings, respectively (Silverstein and Webster 1997; Ellerbrock and Gerke 2004; Hay and Myneny 2007; Tinti et al. 2015; Margenot et al. 2017). As expected, $R_{C/A}$ and $R_{D/A}$ also demonstrated a statistically significant correlation (Table 2).

In addition, the ratios between maximal heights associated with bands B, C and D and band A area were also calculated. These seemingly unusual height to area ratios are deemed useful in order to test whether the relations presented in Fig. 2a,b are affected by multiple functionalities contributing to a certain band area, band overlapping and the wavenumber ranges selected to calculate band area. No use of peak heights was employed for band A due to that it represents the different aliphatic CH vibrations (which may lead to a complicated shape of the whole band).

For isolated bands each one representing a certain oscillating bond, use of integrated band areas and the maximal absorbances should lead to the same trends. When vibrations of various chemical bonds in different surroundings contribute to the band shape, as in the case of the B, C and D bands, the relative contributions of those chemical groups to the maximal absorbance (height) and the whole calculated band area can be different. Therefore, we compared the correlation coefficients determined for the pairs of $R_{C/A}$ with $R_{B/A}$, $R_{D/A}$ with $R_{B/A}$ and $R_{D/A}$ with $R_{C/A}$ obtained for the WEOM samples, when bands B, C and D were quantified by maximal peak absorbance (band A was quantified

by area) to correlation coefficients obtained for the same abovementioned pairs when band areas were used all round (Table 2). Our results suggest that use of ratios based on peak heights for bands B, C or D or those based fully on band areas led to correlations of comparable strengths (Table 2). This implies that relative contributions of different vibrations to a band do not change significantly across the array of the composts studied.

The ratios of band areas $R_{B/A}$, $R_{C/A}$ and $R_{D/A}$ were also calculated for the bulk compost OM, using absorption IR spectra after ash subtraction (Fig. S1, Supplementary Material). For the compost OMs, a significant relation was noted between band area-based $R_{C/A}$ and $R_{B/A}$ (Fig. 3) showing a trend comparable to that noted in the analogous analysis for the WEOM (Fig. 2a). This significant relation may be perceived as an indication to the dominant concurrent contribution of carboxylates by different vibrations to bands B and C. In addition, use of the peak absorbances (i.e., maximal heights) associated with bands B and C in the compost OMs, instead of the band areas, in the ratios to band A area led also to a significant strong correlation similar to that obtained in the case of band area-based ratios (Table 2).

However, unlike the results for the compost-derived WEOM, in the case of the compost OM, for any type of analysis, using either areas or peak heights associated with bands B,C and D, no correlations were found with $R_{D/A}$ (data not presented). This difference between the compost OM and WEOM indicates that evidently different components contribute to the band D area of the compost OM as compared with the compost-derived WEOM.

Finally, the area-based ratios $R_{B/A}$ and $R_{C/A}$ determined in WEOM showed a meaningful relation with the $R_{B/A}$ ratio computed for compost OM (Fig. 4; Table 2), indicating that the WEOM composition associated with bands A,B and C "follows", to a

certain degree, the compost OM composition expressed in the $R_{B/A}$ ratio. The slope of the linear regression line shown in Fig. 4a (5.25) is meaningful, as both in the WEOM and the compost OM the R ratios of the same bands, B and A, are used. This significant highly >1 slope can be interpreted in terms of preferable aqueous dissolution of the OM components contributing to band B over the dissolution of the components including aliphatic CH bonds and associated with band A. Selective dissolution of compost OM components in water involves OM fractionation (Said-Pullicino et al. 2007, Wang et al. 2013). However, when using the peak height-based ratios $R_{B/A}$ and $R_{C/A}$, no significant correlations between WEOM and OM compositions were found (Table 2), which apparently indicates that the above-suggested constancy of relative contributions of different vibrations to a band across the compost series is not sufficiently strong in this type of comparison.

Estimating compost OM fractionation caused by selective dissolution of its components in water

The compost OM fractionation caused by selective dissolution of its components in water may be described by using ratios derived from IR-spectroscopic determinations. This approach is illustrated by an example considering carboxylate groups and aliphatic CHs as possibly the major groups that contribute to bands B and A, respectively:

$$\frac{R_{B/A}(WEOM)}{R_{B/A}(OM)} = \frac{\left(\frac{[COO^-]}{[CH]}\right)_{WEOM}}{\left(\frac{[COO^-]}{[CH]}\right)_{OM}} = \frac{[COO^-]_{WEOM}}{[COO^-]_{OM}} / \frac{[CH]_{WEOM}}{[CH]_{OM}} \quad (1)$$

The ratios appearing in Eq. (1), i.e., $R_{B/A}(WEOM)$ and $R_{B/A}(OM)$, are determined from IR spectra, using either band areas or peak heights, for WEOM and OM, respectively. As mentioned earlier (section 3.2), each such ratio is proportional to the ratio of

concentrations of the functional groups specified further in the brackets, in WEOM or in the compost OM, i.e., $R_{B/A}(WEOM)$ is proportional to $\left(\frac{[COO^-]}{[CH]}\right)_{WEOM}$ and $R_{B/A}(OM)$ is proportional to $\left(\frac{[COO^-]}{[CH]}\right)_{OM}$. A coefficient of such a proportionality is the ratio of specific absorptivities of the relevant functional groups. It is assumed to be similar both for WEOM and OM. This assumption seems to be reasonable since spectra of both freeze-dried WEOM and OM were obtained in essentially OM-rich surrounding in the same KBr matrix.

The k coefficients in Eqns. 2 and 3 are introduced to relate concentrations of a certain group in WEOM to its concentration in compost OM and, therefore, to describe distributions (*dis*) of functional groups between the different phases.

$$k_{dis}^{COO^-} = \frac{[COO^-]_{WEOM}}{[COO^-]_{OM}} \quad (2)$$

$$k_{dis}^{CH} = \frac{[CH]_{WEOM}}{[CH]_{OM}} \quad (3)$$

In this example, $k_{dis}^{COO^-}$ and k_{dis}^{CH} are used to describe the concentration ratios of COO^- and aliphatic CH groups, respectively, between WEOM and OM. Finally, a ratio of the k_{dis} coefficients of the two types of functional groups may be determined from IR-spectroscopic data (Eq. 4):

$$\frac{k_{dis}^{COO^-}}{k_{dis}^{CH}} = \frac{R_{B/A}(WEOM)}{R_{B/A}(OM)} \quad (4)$$

Since during compost extraction all the WEOM components are dissolved in the same solution volume, the ratio of the k_{dis} values in Eq. 4 may be used in a straightforward manner, to compare quantitatively the distribution of one group (e.g., COO^-) between the aqueous WEOM phase and compost OM with that for aliphatic CHs. When this k_{dis} ratio

in Eq. 4 exceeds 1, it indicates that there is a greater tendency for carboxylate (carboxylic) groups to move into the WEOM phase from the compost OM than that for the aliphatic CH groups.

These k_{dis} ratios were calculated using the band area-based $R_{B/A}$, $R_{C/A}$, $R_{D/A}$ values and also by quantifying bands B, C and D with the peak heights (Table 3). It is clear that in general multiple functionalities might contribute to the areas/maximal heights of the bands B, C and D. The functionalities contributing to these bands are typically more hydrophilic as compared with aliphatic CHs and, in the current context, they are expected to be significantly contributed by one type, at least in the case of bands B and C (as supported with Figs. 2 and 3) which are most probably carboxylate (carboxylic) groups.

All the k_{dis} ratios in Table 3 exceed 1 which clearly demonstrates that the tendency for the components contributing to absorbance in bands B, C and D to dissolve in water and be found in WEOM is greater than that of the aliphatic CH groups represented by band A. In ~50% of the comparisons, the area-based k_{dis} ratios did not differ, within the errors, from those obtained using peak heights (Table 3). In the rest of the cases, the value of the area-based k_{dis} ratio was either lower or higher than that determined using peak heights for quantification of bands B, C and D. Identical k_{dis} ratios are expected when the bands are contributed by a single chemical functionality, without interference of neighboring bands. In reality, the k_{dis} ratios based on band areas and peak heights seem to differently represent functional groups. Nevertheless, the k_{dis} ratios shown in Table 3, either based on band areas or on peak heights, quantify the same phenomenon, which is a preferential dissolution of hydrophilic compost OM components as compared with aliphatic CHs.

This phenomenon may be helpful in explaining the strong relations that were found between area-based $R_{B/A}$ and $R_{C/A}$ values of compost OM and the WEOM property associated with the fraction of aromatic substances in the whole DOM, i.e., $SUVA_{254}$ (Fig. 5; Table 2). Even stronger relations with $SUVA_{254}$ were obtained when peak height-based $R_{B/A}$ and $R_{C/A}$ values were used, i.e., the correlation coefficients being 0.983 and 0.848, respectively (Table 2).

The relations shown in Figure 5 could be rationalized in the following simplified way. Compost OM contains aromatic oxidized matter with multiple functional groups and, specifically, carboxyls. The extent of aqueous extraction/dissolution of aromatic oxidized hydrophilic matter containing carboxylic groups is expected to be higher than that of OM components containing CH groups, i.e., more "fatty" constituents. This expectation is supported by preferable distribution of carboxylate/carboxylic groups as compared to the CH groups from compost OM to water (Table 3). Aromatic water-soluble compounds make a significant part of WEOM as can be deduced from the positive relation between Abs_{254} and DOC (Fig. S3a, Supplementary Material). Conversely, an increase in TOC content in the composts demonstrated a significant negative relation with $SUVA_{254}$ (Fig. S3b) suggesting that OM-rich composts are augmented by aliphatic matter which leads to an increase in its presence, as compared with aromatic matter, in the WEOM. Therefore, accumulation of hydrophilic aromatic components in WEOM, expressed in terms of $SUVA_{254}$ values, could reflect the increase in the proportion of these substances in the whole compost OM, as characterized by the R values relating concentrations of hydrophilic chemical functionalities to aliphatic CHs, thus leading to the relations depicted in Fig. 5. The actual scenario is obviously more complicated, and it appears that aqueous release of mostly carboxyl-containing aromatic organic matter

might be associated with dissolution of that part of OM which is rich by aromatic constituents with other hydrophilic groups, foremost hydroxyls. In addition, release of short-chain aliphatic acids that may be found in composts (Himanen et al. 2004; Zmora-Nahum et al. 2007; He et al. 2019) might contribute to WEOM. Those may be the reasons why no significant correlations were found between the R ratios in WEOM and $SUVA_{254}$, and $R_{B/A}$ (WEOM) was correlated negatively with Abs_{254} (Table 2; the area-based R values).

Conclusions

The composition of WEOM, characterized by the area- and peak height-based ratios between certain IR bands associated with hydrophilic groups and that of aliphatic CH groups, accompanies, to a certain extent, a similar index of compost OM composition. Moreover, the extent of WEOM aromaticity expressed as $SUVA_{254}$ exhibited a strong relation with IR-spectroscopic ratios connecting areas (or peak heights) of some bands representing hydrophilic components in bulk compost OM with aliphatic CH absorbance. Use of band areas to characterize OM is not equivalent to the use of peak heights because each contains different information, regarding major functional groups contributing to measured intensity.

Compost OM fractionation caused by selective dissolution of its components in water may be simply described by using double ratios, i.e., calculating area- (or peak height-) based ratios that characterize a certain band in relation to that linked to aliphatic CH groups and normalizing such a ratio obtained for WEOM to that associated with bulk compost OM. In this way, a quantitative assessment of the selective dissolution of

compounds containing carboxylic groups, compared with that of the aliphatic CH-containing components, was attained.

The performed analysis of IR-spectral data yielding correlations between bulk OM and WEOM compositional indices, as well as measures for preferential dissolution of OM components in water, may provide a way to predict the properties of released water-soluble OM, using the IR spectroscopy-based characterization of bulk compost OM.

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Table 1. Characteristics^a of the composts studied

#	Compost source	TOC ^b	TN ^c	Ash ^d	pH	EC ^e	DOC ^f	Abs ₂₅₄ ^g	SUVA ₂₅₄ ^h
		%	%	%		dS/m	mg L ⁻¹		L mg ⁻¹ m ⁻¹
1a	Raw cattle manure with added plant wastes (15%); 1 month composting (kibbutz Sde Eliyahu)	26.2	3.4	61.1	8.1	6.7	4400	96.1	2.18
1b	Raw cattle manure, with added plant wastes (15%); 3 month composting (kibbutz Sde Eliyahu)	20.8	2.0	61.3	7.9	8.7	1832	49.1	2.67
1c	Raw cattle manure, with added plant waste (15%); 6 month composting (kibbutz Sde Eliyahu)	18.5	1.7	67.8	8.1	7.9	1348	44.7	3.31
2	Toilet waste (from Hava&Adam eco-farm)	27.9	2.2	44.0	7.3	3.5	519	13.8	2.74
3	Kitchen waste (from Hava&Adam eco-farm)	21.7	2.1	59.0	7.2	3.6	335	9.4	2.65
4	Vermicompost (from kibbutz Dovrat)	15.7	1.4	64.6	8.6	6.8	886	26.1	2.94
5	Cattle manure compost (from MAHLUF)	14.2	1.9	75.5	7.3	6.1	585	24.0	4.10
6	Cattle manure compost (kibbutz Sde Eliyahu; commercial product)	26.2	2.1	52.1	8.1	6.4	2058	60.4	2.93

^aAll the analyses were performed with four replicates of compost samples; the percentages are based on the 105°C dry compost mass. ^bTOC - total organic C. ^cTN - total N. ^dAfter burning in air at 400 °C to constant mass. ^eEC - electrical conductivity. ^fDOC - dissolved organic C in aqueous extracts (1:10 w/w). ^gAbsorbance of extracts measured at 254 nm. ^hSpecific UV Absorbance at 254 nm.

Table 2. Coefficients of correlations with R ratios: bands B, C and D are quantified using (i) peak absorbance and (ii) area.

Pairs of correlated properties ^a	Correlation coefficient	
	Quantification of bands B, C, and D	
	Peak absorbance	Band area
$R_{C/A}(\text{WEOM}) - R_{B/A}(\text{WEOM})$	0.8970 ^b	0.9757 ^b
$R_{D/A}(\text{WEOM}) - R_{B/A}(\text{WEOM})$	0.7889 ^b	0.8443 ^b
$R_{D/A}(\text{WEOM}) - R_{C/A}(\text{WEOM})$	0.8033 ^c	0.7539 ^c
$R_{C/A}(\text{OM}) - R_{B/A}(\text{OM})$	0.8987 ^b	0.8730 ^b
$R_{B/A}(\text{OM}) - \text{SUVA}_{254}$	0.9830 ^b	0.7136 ^c
$R_{C/A}(\text{OM}) - \text{SUVA}_{254}$	0.8480 ^b	0.8157 ^c
$R_{B/A}(\text{WEOM}) - \text{Abs}_{254}$	-0.6370 ^d	-0.7397 ^c
$R_{B/A}(\text{OM}) - R_{B/A}(\text{WEOM})$	0.6478 ^d	0.7315 ^c
$R_{B/A}(\text{OM}) - R_{C/A}(\text{WEOM})$	0.4576 ^d	0.7222 ^c

^aBand A is quantified by its area. ^bSignificance <0.01; ^cSignificance <0.05; ^dSignificance >0.05.

Table 3. Selective dissolution of compost OM components in water: the k_{dis} ratios defined using Eqs. (1-4) and based on the areas of bands B, C and D as well as their peak heights. Compost numbering corresponds to that in Table 1.

Compost #	$R_{B/A}(WEOM)/R_{B/A}(OM)$		$R_{C/A}(WEOM)/R_{C/A}(OM)$		$R_{D/A}(WEOM)/R_{D/A}(OM)$	
	Area-based	Height-based	Area-based	Height-based	Area-based	Height-based
1a	4.2±0.1 ^a	3.9±0.3	3.9±0.2	6.8±0.5	5.6±0.3	4.5±0.6
1b	5.6±0.5	6.7±1.0	6.5±2.0	12.8±4.0	27.1±3.5	24.8±4.7
1c	6.2±1.9	3.3±0.6	4.7±0.6	3.3±1.1	17.6±5.4	10.5±5.5
2	4.8±1.3	3.4±0.5	6.5±3.4	8.9±1.5	9.8±2.4	5.1±1.1
3	7.9±0.6	4.9±0.4	13.9±4.2	8.5±0.8	18.8±5.3	21.0±5.5
4	3.7±2.1	9.0±1.5	5.2±3.8	17.5±5.3	58.1±28.0	16.0±3.9
5	5.8±1.9	6.9±0.7	9.1±3.7	9.0±0.6	28.3±13.1	35.0±2.3
6	3.5±1.1	3.9±0.2	3.1±1.3	3.8±0.7	5.2±0.9	3.8±0.5

^a standard deviation

Fig. 1 IR absorption spectra for the kitchen waste compost (#3, Table 1). I - air-dried compost, II - the ashed compost (spectra I and II were normalized by carbonate absorbance at 873 cm^{-1}), III - the spectrum obtained from subtracting the ash spectrum from that determined for the compost, IV - WEOM. Black area in spectra III and IV represents integration used to quantify absorbance of aliphatic CH groups

Fig. 2 Relations between various band area ratios in WEOM. The solid lines represent linear regressions: (a) $R_{C/A}(\text{WEOM}) = 1.16 \times R_{B/A}(\text{WEOM}) - 19.95$, (b) $R_{D/A}(\text{WEOM}) = 1.09 \times R_{B/A}(\text{WEOM}) - 6.95$. r is the correlation coefficient, and p is statistical significance. Each compost-derived WEOM is represented in the plots by two measurements made in different KBr pellets. The symbols in the legend are associated with the numbers of source composts presented in Table 1

Fig. 3 The relation between the band area ratios $R_{C/A}(OM)$ vs. $R_{B/A}(OM)$, both obtained from the bulk compost OM. The solid line represents the linear regression: $R_{C/A}(OM) = 0.63 \times R_{B/A}(OM) - 0.83$. r is the correlation coefficient, and p is statistical significance. The symbols in the legend are associated with the numbers of the source composts presented in Table 1. Each compost OM is represented by 4-6 measurements made in different KBr pellets

Fig. 4 Relations between band area ratios in the compost OM and WEOMs. The solid lines represent linear regressions: (a) $R_{B/A}(WEOM) = 5.42 \times R_{B/A}(OM) + 0.93$, (b) $R_{C/A}(WEOM) = 6.42 \times R_{B/A}(OM) - 23.07$. r is the correlation coefficient, and p is statistical significance. The symbols in the legend are associated with the numbers of source composts presented in Table 1. The R values associated with WEOM are the averages of 2 measurements made in different KBr pellets, whereas the R values representing bulk compost OM are the averages of 4-6 measurements

Fig. 5 The relations between SUVA₂₅₄ and band area ratios in the compost OM. The solid lines represent the linear regressions: (a) $SUVA_{254} = 0.13 \times R_{B/A}(OM) + 1.72$, (b) $SUVA_{254} = 0.20 \times R_{C/A}(OM) + 1.81$. r is the correlation coefficient, and p is statistical significance. The symbols in the legend are associated with the numbers of source composts presented in Table 1. The R values representing compost OM are the averages of 4-6 measurements and SUVA₂₅₄ are the averages of 4 measurements

Supplementary Material

Bulk and water-extractable organic matter from compost: evaluation of the selective dissolution in water using infra-red absorbance ratios

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Fig. S1 Absorption IR spectra of compost OMs. Numbering of the spectra corresponds to the numbering of the composts in Table 1. The presented OM spectra were obtained by normalizing the IR spectrum of each compost by its calcium carbonate absorbance and subtracting the similarly normalized corresponding spectrum of ash

Fig. S2 IR absorption spectra of the freeze-dried compost-derived WEOMs. Numbering of the spectra corresponds to the numbering of the composts in Table 1

Table S1. IR band assignments

	Inorganic component			Organic component		
Wavenumber interval (cm ⁻¹)	Peak position (cm ⁻¹)	Mineral	Vibration assignment	Peak position (cm ⁻¹)	Organic group	Vibration assignment
3800-2700	3697&3622 ^a	kaolinit	O-H stretching	3600-3400 ^b	water, carboxyl and hydroxyl groups	Stretching O-H bond
	3750-3400 ^c	phyllosilicate	O-H stretching	2920 ^b	CH3 and CH2 group	C-H asymmetric stretching
	3800-2800 ^c	allophane & imoglite	O-H stretching	2860 ^b	CH3 and CH2 group	C-H symmetric stretching
	3400-3000 ^c	Fe oxide	Fe-O of FeO-H absorbance			
2700-2400	2500 ^d	calcite, dolomite	overtone/combination band CO ₃ ²⁻			
1800-1500				1740-1675 ^e	aldehydes, ketones, esters	C=O stretch
	1700-1550 ^c	allophane and imogolite	O-H stretching	1650-1515 ^f	amides in protein	NH ₂ and NH bending
				1650-1640 ^g	amides	C=O stretching vibration (amid I band)
				1650-1540 ^h	carboxyl	Asymmetric stretching vibration of COO-

				1540 ^b	double bond	stretching vibrations of C=C
				1650-1600 ⁱ	aromatic and unsaturated ketones, carboxylic acids and amides	aromatic ring, conjugated C=C groups
1500-1300	1450-1430 ^g	calcite	CO ₃ ²⁻ vibration	1450-1430 ^g	CH ₃ and CH ₂ group	C-H bending vibration
				1420-1330 ⁱ	carboxyl	Symmetric stretching vibrations of COO ⁻
1300-900	1120-950 ^c	different silicates like kaolinite, halloysite, beidellite, montmorillonite, Illite	Si-O stretch and OH absorbance	1340-1020 ^k	Primary amines	C-N stretching
				1265 ^e	Amid III	C-N stretching
	1030-1020 ^c			1255-1195 ^l	carboxyls, aryl ethers and phenols	C-O stretching and OH deformation
	1010 ^c			1250-900 ^m	polysaccharide, carbohydrates, cellulose	C-O, C-O-C vibration
900-600	950-915 ^c	layer silicates	Si-O	900-675 ^g	aromatic compounds	out of plane aromatic ring C-H
	873 ^{c,h}	calcite and dolomite	CO ₃ ²⁻	800-666 ^g	amides	out-of plane NH wagging
	715-712 ^c	calcite	CO ₃ ²⁻			

^a McKissock et al. (2003); Nguyen et al. (1991); Ravisankar et al. (2011); Simkovic et al. (2008). ^b Ellerbrock and Gerke (2004). ^c Margenot et al. (2017). ^d Nguyen et al. (1991); Ravisankar et al. (2011); Tinti et al. (2015). ^e Smidt and Schwanninger (2005), Kowalski et al. 2018. ^f Silverstein and Webster (1997); Ellerbrock and Gerke (2004); Calderon et al. (2011). ^g Silverstein and Webster (1997). ^h Hay and Myneny (2007). ⁱ Silverstein and Webster (1997); Hay and Myneny (2007). ^k Calderon et al (2011). ^j Ellerbrock and Gerke (2004); Margenot et al. (2017); Silverstein and Webster (1997). ^l Tinti et al. (2015). ^m Smidt and Schwanninger (2005); He et al. (2006), Rumpel et al. (2001).

Fig. S3 The relations between (a) Abs_{254} in WEOM solutions and DOC content (expressed in %, $w w^{-1}$), and (b) $SUVA_{254}$ of WEOM and compost TOC content (in %, $w w^{-1}$). In both plots the % ($w w^{-1}$) is provided per dry bulk compost mass. The solid lines represent the linear regressions, i.e., $Abs_{254} = 21.11 \times DOC + 8.71$, and $SUVA_{254} = -0.078 \times TOC + 4.64$. r is the correlation coefficient, and p is statistical significance. The symbols in the legend are associated with the numbers of the source composts presented in Table 1 of the paper

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