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Linking organic matter chemistry with soil aggregate stability: Insight from ^{13}C NMR spectroscopy

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ABSTRACT

Soil aggregation is considered as a crucial process in agro-system sustainability due to the role in soil physical, chemical and biological dynamics. Here we tested the hypothesis that the initial chemical traits of organic matter (OM) may help to explain the variability of soil aggregation dynamics after organic amendment. We characterized ten OM types (alfalfa litter, biochar, cellulose, glucose, green compost, maize litter, manure compost, meat powder, sawdust, and solid digestate) by ^{13}C-CPMAS NMR and elemental chemical features to investigate the effects of amendment quality on soil aggregation. In a manipulative factorial experiment, dry samples (200 g) of three soil types (S1, S2 and S3) with different texture, high pH (7–9), and similar OM content, were incorporated with 4 g (2% w/w) of dry, 2 mm-grounded OM, incubated in mesocosms for 300 days under controlled temperature (18 ± 2 °C night and 24 ± 2 °C day), and sampled at 4 dates for measuring aggregation index (AI), based on water stability of soil aggregates (WSA). We found that meat powder and alfalfa litter induced a rapid initial increase of AI, exceeding that of the controls by one to two orders of magnitude, likely acting as a C source for microbes. Biochar incorporation in soil barely affected AI, with intermediate effects with other OM types. Considering C bond types corresponding to OM ^{13}C-CPMAS NMR spectral regions, carbonyl C was only correlated to early AI, possibly due to overlapping signals of amide structures; *O*-alkyl C and di-*O*-alkyl C (carbohydrate fraction) were positively associated to AI, indicating a promoting effect on soil structure, while aromatic C fractions showed an opposite pattern, possibly related to aggregate protection by coatings associated to water repellency, or to direct aggregate internal binding. This study demonstrates that OM chemical quality plays an important role in soil aggregation process, with the molecular composition defined by ^{13}C-CPMAS NMR spectroscopy being more predictive of aggregation dynamics compared to classical elemental features. As such, this study provides a significant novel contribution to clarify the relationships between OM chemistry and soil aggregation.

1. Introduction

Soil aggregation is an important ecosystem process leading to the formation and stabilization of soil structure, i.e. the resulting matrix of soil aggregates and pore spaces (Rillig et al., 2015). Aggregates can form by rearrangement, flocculation and cementation of mineral and organic particles (Bronick and Lal, 2005). Soil structure facilitates gas and water diffusion, promoting microbial function, root penetration and growth, and reducing soil susceptibility to erosion (Annabi et al., 2011; Six et al., 2004). Therefore, soil aggregation is considered as a crucial aspect of soil quality and a keystone for a sustainable management of agro-ecosystems.

The factors that affects soil aggregation have been well documented and reviewed (Amezketa, 1999; Bronick and Lal, 2005; Six et al., 2004). Soil biotic community and biological mechanisms play a vital role in the stabilization of soil structure (Degens, 1997), as well as known destabilizing agents (Oades, 1993). Soil biota is involved in the aggregation process either by producing effective biological binding agents (e.g. microbial polysaccharides and mucilages that promote the formation of aggregates), or by mechanically holding soil particles together, as shown for fungal hyphae, mycelium, and plant roots (Rillig et al., 2015). Furthermore, soil lipids as well as other organic

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substances (e.g. alkanes, fatty acids and waxes) synthesized from living or decomposing plants or microorganisms enhance soil water repellency. Hydrophobicity aids aggregate stability either by reducing water infiltration capacity (Doerr et al., 2000) or by concentration of free lipids and other hydrophobic compounds, forming a hydrophobic coating around the soil organic matter (SOM), which acts as a nucleus of aggregate formation protected from microbial decomposition (de Blas et al., 2010). Organo-mineral interactions may lead to aggregations of clay particles and OM, which stabilize soil structure and C compounds within the aggregates (Oades, 1988). These organo-mineral interactions rely on cation bridges, where cations provide a link between negatively charged clay surface and negatively charged organic functional groups (Muneer and Oades, 1989). Moreover, organo-mineral interactions and mineralogical influences on soil aggregation revealed that the occlusion of iron oxyhydroxides provides a cementation of other minerals directly in contact with OM (Keil and Mayer, 2014), and iron oxyhydroxides act as binding agents in some aggregates, particularly in highly weathered soils.

Soil texture, clay mineralogy, cation content, and OM are considered as the crucial determinants for soil aggregation. OM can either directly act as a binding agent (Piccolo and Mbagwu, 1999; Spaccini et al., 2002) or indirectly promote soil microbial activity, thus enhance aggregate formation and stability maintenance (Murphy, 2015). In fact, a variety of organic substances that promote aggregate stability can be produced by fungal and bacterial activity (Hendrix et al., 1990), or released during OM decomposition (Schmidt et al., 2011). The controlling role of OM on aggregate stability is especially important because its amount and properties can be modified trough agronomic management. A wide range of non-humified organic materials are routinely used as soil amendments, including crop residues, composts, peats, and organic wastes from agro-industries. Most of the published studies on this matter have assessed the immediacy of organic amendment effects on soil aggregate stability, generally reporting a positive effect. However, beside successful applications of organic amendments (Abiven et al., 2007; Annabi et al., 2011; Six et al., 2004) inconsistencies about their ameliorating effect have also been reported (Albiach et al., 2001; Spaccini et al., 2002). On the other hand, the use of humified organic matter extracted from carbon-rich sources such as lignite or oxidized coal were proved not only to increase soil aggregate stability but also to reduce run-off erosion (Piccolo et al., 1997). In fact, different amendment types at varied rates and bioclimatic conditions, can lead to infinite combination of results in soil, highlighting the need to progress in the knowledge of the mechanisms involved in soil aggregation, and in the specific role the different OM structural domains in the resulting aggregation.

The first step in this direction was made more than 50 years ago by Monnier (1965), who proposed a conceptual model describing aggregate stability dynamics after the organic amendment in soil with different quality. In particular, easily decomposable amendments (e.g. green manure) had an intense effect on aggregate stability at the very short term (week to month), which peaked at progressively later stages for lower quality materials (e.g. on a monthly scale for wheat straw). Differently, more recalcitrant amendments (e.g. decomposed manure) had a low initial effect progressively increasing over time. Later, a meta-analysis based on 48 empirical studies Abiven et al. (2009) qualitatively validated such conceptual model, but also indicated the need for effective predictors of OM quality and aggregate stability, in order to properly translate the model into effective agronomic practices. Indeed, in the Monnier's model the amendment quality is largely assumed by simply naming the organic input (i.e. green manure *vs* straw *vs* decomposed manure), which is possibly advantageous for application purpose, but cannot provide accurate predictions of the effect magnitude and dynamics, in terms of aggregate stability. In this context, some studies used the well known C/N ratio as predictor of OM quality, but reported inconsistent relationships with aggregate stability (Martens and Frankenberger, 1992; Sonnleitner et al., 2003).

Few efforts (Álvarez et al., 2013; Recio-Vazquez et al., 2014) in search of chemical indicators to consistently describe OM chemistry and predict aggregate stability is surprising, especially considering the recent advance in chemical analytic techniques. In this perspective, several throughput methods have been applied to directly characterize OM chemistry, including pyrolysis-gas chromatography/mass spectrometry (Huang et al., 1998), near infrared reflectance spectroscopy (Gillon et al., 1999), and ^{13}C-cross-polarization magic angle spinning (CPMAS) nuclear magnetic resonance (NMR) spectroscopy (Kögel-Knabner, 2002). In detail, ^{13}C-CPMAS NMR has been proven useful to relate the characteristics of SOM to soil aggregate stability (Piccolo et al., 2005; Spaccini et al., 2006) and provide a description of chemical composition of plant litter (Kögel-Knabner, 2002), and its relationships with decay rate (Bonanomi et al., 2013) and plant growth (Mazzoleni et al., 2015).

In this study, we combined a detailed OM characterization by ^{13}C-CPMAS NMR, in solid state with a manipulative experiment of soil incubation in mesocosms to investigate the link between OM carbon distribution and soil aggregation stability of 300 days observation period. In detail, we tested the capability of 10 organic amendments, spanning over a wide range of chemical quality, to induce soil aggregation in three soil types with different texture. Specific aims of the study were to:

(i) assess the magnitude and timing of aggregation stability induced by different organic amendment types and describe their effects 300 days after OM incorporation in soils;
(ii) explore the relationships between soil aggregation dynamics and organic amendment quality, as defined by ^{13}C-CPMAS NMR spectroscopy and standard chemical features;
(iii) identify the ^{13}C-CPMAS NMR spectral regions and corresponding organic C types more predictive of organic amendment effects on soil aggregate stability.

2. Materials and methods

2.1. Chemical characterization of organic amendments

Ten types of organic amendment were selected, as representing a wide range of OM with different chemical composition and biochemical stability (Table 1). They were characterized for total C and N content by flash combustion of micro samples (5 mg of sample) in an Elemental Analyzer NA 1500 (Fison 1108 Elemental Analyzer, Thermo Fisher Scientific). All organic amendments were analyzed by solid state ^{13}C-CPMAS NMR, thus allowing a comparative and detailed characterization of molecular properties. The NMR spectra were recorded on a Bruker AV-300 instrument (Bruker Instrumental Inc, Billerica, MA, USA), equipped with a magic angle spinning (MAS) probe with wide-bore of 4 mm, using specific calibrated acquisition features: 2 s of recycle time; 1H-power for CP 92.16 W: 1H 90° pulse 2.85 μs; ^{13}C power

Table 1
Initial C, N content and C/N ratio of 10 different organic materials used in the soil aggregation experiment.

Organic matters	Nitrogen	Carbon	C/N
Alfalfa litter	3.9	38.2	9.7
Biochar	0.5	74.5	149.1
Cellulose	0.1	50.1	500.1
Glucose	0.0	43.0	–
Green compost	1.5	31.1	20.3
Maize litter	0.4	40.3	82.4
Manure compost	2.0	34.3	17.1
Meat powder	8.2	43.8	5.3
Sawdust	0.1	49.8	453.4
Solid digestate	1.9	43.8	22.9

* Biochar was primed from corn stalks, by pyrolysis at 550 °C for 5 h in a muffle furnace.