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Factors influencing the molecular composition of soil organic matter in New Zealand grasslands

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ABSTRACT

Few studies have attempted to simultaneously link multiple environmental factors to the composition of soil organic matter (SOM). This knowledge gap challenges the ability to predict the response of SOM to environmental changes and make recommendations for effective land-based C sequestration strategies. In this study, topsoil samples from the New Zealand National Soils Archive, of different soil orders and obtained from different climatic regions, land-uses, and positions in the landscape, and taken at two sampling times (one from 1960s to early 1990s and the other after 2004) were analysed for SOM composition using Pyrolysis-GC/MS after being treated with HF to minimise the interference of the soil mineral fraction. Principal component analysis and redundancy analysis were used to screen out major environmental factors that impact on SOM composition. Ordination of SOM composition generally followed two gradients (canonical axes):decomposition and fresh input, and was significantly explained by the C to N ratio and total C (Monte Carlo permutation test, $P < 0.01$) with other factors, such as average annual temperature, average annual rainfall rate, total N and HF-removable C being somehow redundant with total C. Soil order, landscape type and land-use type further contributed to the explanation of the variability of SOM composition, although they were largely redundant with the above-mentioned factors. Overall, sampling time showed little effect on SOM composition. Given the large variation of SOM composition for different soils (e.g. Allophanic soils having a larger fraction of decomposed organic matter compared to other soil orders) and different mechanisms governing SOM stabilisation, effective C sequestration strategies should be case-specific for New Zealand grasslands.

1. Introduction

Soil organic matter (SOM) plays an essential role in maintaining soil functions, such as water infiltration and retention, and regulation of carbon (C) cycling and greenhouse gas emissions among others, and thus contributing to key ecosystem services (Schmidt et al., 2011). The global soil C pool-including 1550 Gt of soil organic C (OC) and 950 Gt of soil inorganic carbon (IC)-represents the largest terrestrial C reservoir (Lal, 2004). This explains that small changes in soil OC may severely impact the global C budget and long-term ecosystems sustainability (Schipper et al., 2007). Therefore, a thorough understanding on SOM and the key factors controlling its cycling is required before appropriate C sequestration strategies can be adopted.

Many factors such as the quality of organic inputs, mineralogy, soil biota, soil aeration, nutrient availability and climate factors (rainfall and temperature regimes) (Wickland and Neff, 2008; Mambelli et al., 2011; Rabbi et al., 2015) can influence the size and turnover dynamics of SOM. Direct effects of these factors on SOM stabilisation have been widely investigated by short-term laboratory incubation studies under controlled conditions (Saggar et al., 1999; Sanderman et al., 2014). However, prediction errors may arise from their extrapolation to field conditions and long-term effects (Percival et al., 2000). Correlations between these factors and soil C content using large soil databases are commonly carried out to infer their effects at larger spatial and time scales (i.e. field conditions and long-term effect). This has revealed the key role of specific soil physicochemical properties, such as clay content, and short-ranged aluminosilicates (e.g., allophane, imogolite) and Al and Fe oxy-hydroxides, in influencing OC storage in temperate soils (Percival et al., 2000) through chemical (i.e., binding to mineral surfaces) and physical protection (mainly within aggregates) (Buurman et al., 2007a; von Luetzow et al., 2008).

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New Zealand has been suggested as an ideal and unique location to examine the influences of multiple factors on SOM cycling (Schipper et al., 2010) due to its large range of climates and soils and pastoral grazing-dominated agriculture. Land-use shift from grazing lands to other land-cover categories in recent years (e.g., since 1990) and more intensive pastoral management practices have induced significant OC losses of some soils (Percival et al., 2000; Schipper et al., 2007; Schipper et al., 2010). In order to reverse this situation, effective C sequestration strategies based on a mechanistic understanding of factors influencing OC stabilisation are needed to put in place so that their effects are long-term. That is, they should promote the increase of long-term stable OC forms and not only that of a transient increase in total OC stocks.

Previous large-scale SOM surveys mainly focused on the total OC stocks and their fluctuations over time, but few studies has focussed on their changes at the molecular level. Given that soil OC is highly heterogeneous in quality, an improved understanding of the composition of OC at a molecular scale is needed to better understand the stabilisation mechanisms under different conditions (i.e., different soil types, land-use and farming practices). Pyrolysis (Py)-GC/MS involves thermal decomposition of OC into various pyrolysis products, chromatographic separation of these components and mass spectral determination for each component (Kögel-Knabner, 2000; Derenne and Quenea, 2015). This powerful tool has been widely used to (i) study insoluble organic macromolecules in SOM, as it enables detailed qualitative and semi-quantitative measurements of individual SOM constituents (Buurman et al., 2007a; Suárez-Abelenda et al., 2015), and (ii) have an in-depth understanding of the processes driving SOM genesis and storage (Buurman et al., 2007a; Suárez Abelenda et al., 2011). However, few studies on SOM characterisation using this equipment (Schulten et al., 1996) have been carried out in New Zealand soils. In this study, top soils of grasslands obtained from the New Zealand National Soils Archive, varying in soil orders, sampling sites, soil properties, climatic factors and sampling times, were analysed for SOM composition using Py-GC/MS. Soils were treated with 1% HF-1% HCl solution to minimise interference of minerals on pyrolysis of SOM (Zegouagh et al., 2004). Multivariate analyses (e.g. principal component analysis and redundancy analysis) were adopted to relate environmental factors to SOM composition features. The objective of this study was to find out factors that may influence SOM cycling in New Zealand grassland soils so that long-term effective and sustainable C sequestration strategies could be established.

2. Materials and methods

2.1. Soil samples

A total of 82 soil samples from the New Zealand National Soils Archive (Landcare Research, Palmerston North) were used. All soils were sampled from the surface horizon of pasture lands (0–8 cm to 0–20 cm depending on sites; sampling sites are shown in Fig. 1). They were classified into 7 major soil orders, including Allophanic, Brown, Gley, Melanic, Pallic, Semi-arid, and Ultic soils, according to the New Zealand soil classification system (Hewitt and Dymond, 2013). The equivalent Soil Taxonomy soil orders (Soil Survey Staff, 2006) are provided in the supporting information Table S1. These soil orders occupy >70% of New Zealand land. Soils from the same site were collected twice, one from 1960s to early 1990s and the other after 2004 as described by Schipper et al. (2007). All soils were initially passed through a 5 mm mesh to remove coarse roots and other litter materials, air-dried, then sieved through 2 mm and ground to <100 μm using a ring grinder. The total C and N in these soils were determined using an elemental analyser (Elementar, Vario MACRO, Germany). Information of soil pH, Olsen P content, elevation, land average temperature, land-use type, soil order, and mineral composition were retrieved from the New Zealand National Soils Archive (Landcare Research, Palmerston North). A summary of sample information is provided in the supporting information Table S2.

2.2. Pre-treatments of soils for Py-GC/MS

To minimise the interference of mineral composition on the pyrolysis of SOM, soils were treated with 1% HF-1% HCl before their Py-GC/MS analysis. Briefly, ~3 g of soil were weighed into a centrifuge tube. Thereafter, 30 ml of 1% HF-1% HCl were added and shaken on an end-over-end shaker for overnight. The soil suspension was then centrifuged at 23000*g* force for 10 min (Thermo Scientific, with S34 head) and the supernatants were removed by a syringe or a water aspirator. The process was repeated for 6 times followed by a thorough rinse with deionised (DI) water (at least 6 times until the supernatant pH >5) to remove residual acid. Thereafter the soil residue was re-suspended with DI water, completely transferred into pre-weight plastic bakers and dried at 45 °C in an oven for one week. The treated soils were ground <100 μm using a ring grinder for elemental composition analysis (Elementar, Vario MACRO, Germany) and Py-GC/MS characterisation. The recovery of C in the soil residue after the pretreatment was calculated. The HF-removable C, which is the C fraction solubilised by HF and calculated as (100% – C recovery%), is shown in Fig. S1 grouped by soil orders. Previous studies (Schmidt et al., 1997) showed the bulk chemical composition of OM was not significantly affected by the HF treatment. This is probably true for surface horizons (unpublished results). In fact, only a slight change was found in C to N ratio (C/N) with this treatment (Fig. S2). We thus used the molecular composition of HF recovered OM as a proxy of overall SOM composition. “SOM composition” in this study refers to that of the HF recovered OM unless otherwise stated.

2.3. Py-GC/MS analysis

Pyrolysis of samples was carried out using a Multi-Shot Pyrolyser (EGA/PY-3030D, Frontier Lab) equipped with an auto-sampler (Frontier Lab). About 0.5 mg to 3 mg of soil, depending on the C content of samples, was weight in an Eco-cup (6 mm height, Frontier Lab) and pyrolysed at 550 °C for 12 s. The pyrolysis unit was connected with a GCMS (GCMS QP2010 Ultra, Shimadzu). The GC column was a stainless steel capillary column [Ultra Alloy UA-5 (MS/HT), 30 m long, 0.25 mm i.d. and coated with 5% diphenyl-95% dimetyl-polysiloxane with a film thickness of 0.50 μm] purchased from the Frontier Lab. High purity He gas was used as the carrier gas with a column flow rate of 1 ml min^{-1}. The split ratio for the GC (i.e. GC spilt injection mode) was set as 30. The GCMS analysis was carried out following Buurman et al. (2007a) and Kaal and Rumpel (2009). The initial oven temperature was 40 °C and held for 12 s (same as the pyrolysis time), and then ramped up to 320 °C at a rate of 5 °C min^{-1}. The final column temperature was 320 °C and held for 20 min. The temperature of ion source was 230 °C. The ionisation energy was set as 70 eV, mass range m/z 45–650 and a cycle time 0.5 s.

Peaks from the chromatograms were identified referring to a NIST mass spec. library and semi-quantified using GCMSsolution software (Shimadzu, Japan). Given the complexity of SOM, the software is prone to picking up the wrong compounds when using the “similarity search” function. Therefore, the compound lists provided by Buurman et al. (2007a) and Sáiz-Jiménez and De Leeuw (1986) were used as references. Only major peaks were identified as minor peaks did not contribute much to the total ion