



An investigation of organic matter quality and quantity in acid soils as influenced by soil type and land use

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ABSTRACT

Knowledge of the molecular composition of soil organic matter (OM) and the interaction of OM with soil minerals is needed to fundamentally understand how the persistence of OM is affected by land use. We investigated organic carbon (C) fractions, content of short-range order constituents (SRO) (i.e., Al and Fe oxy-hydroxides) and OM chemistry of 45 top soils across a range of soil orders and land uses in New Zealand. The objective of the study was to assess the influence of different land uses on the OM quality and quantity of soils that differed in their content of SRO constituents. The C fractions considered were cold + hot water-soluble C (C_{H_2O}), C recovered in the residuum after HF treatment ($C_{HF-residuum}$), and C not so recovered ($C_{HF-mobile}$). Carbon in particulate OM (C_{POM}) was determined in non-Allophanic soils, and C extractable with sodium pyrophosphate (C_p) in Allophanic soils. The chemistry of the HF-residual OM was investigated using pyrolysis-GC/MS. The highest C content was found under grazed grasslands and, among soil orders, in Allophanic soils, which had the largest $C_{HF-mobile}$ and $C_{HF-residuum}$ contents. Yet compared to non-Allophanic, Allophanic soils were more vulnerable to loss of C ($C_{HF-mobile}$ and $C_{HF-residuum}$) when used for cropping. The relative contribution of microbial- vs. plant-derived OM was influenced by soil order and land use: microbial-derived OM increased as the presence of SRO constituents increased, these being more abundant in Allophanic soils; soils under ungrazed grasslands had the largest contribution of fresh plant-derived molecules to OM (and of $C_{HF-residuum}$ to total C) while cropping had a negative impact on the contribution of plant-derived OM, consistent with a decrease in C_{POM} . Overall, the results showed that not only is the ability of New Zealand soils to store C soil-specific, but so too is their vulnerability to losing it when under specific land use.

1. Introduction

In 2015, at the COP21 United Nations Framework Convention on Climate Change held in Paris, a global agreement on the mitigation of climate change was reached to limiting global warming to $< 2^\circ\text{C}$ compared with pre-industrial levels. This accord has been accompanied by an ambitious international research agenda aimed at increasing soil carbon (C) stocks by 0.4% per year (Minasny et al., 2017). Yet to evaluate the feasibility of this target, a better understanding of the fundamental processes involved in the protection of organic matter (OM) in soils is required. Soil OM is a continuum of decomposing organic compounds, from biopolymers to molecules that decrease in size and become more oxidised and water-soluble as decomposition progresses (Hedges and Keil, 1999; Kleber et al., 2015). These organic

compounds retain chemical signatures from which the degree of decomposition of primary plant material and/or the abundance and type of microbial-derived OM can be inferred (Buurman et al., 2007; Suárez-Abelenda et al., 2015). In fact, an important fraction of OM consists of decomposition products of microbes, which themselves turn over, as do plant-derived molecules (Buurman et al., 2007; Liang and Balsler, 2010). The resultant organic species can become chemically protected against further microbial decomposition through interaction with inorganic short-range ordered (SRO) constituents (e.g., aluminium (Al) and iron (Fe) oxy-hydroxides, allophane) (Kögel-Knabner et al., 2008; Kleber et al., 2015). Particulate OM, the fraction of OM that retains some of the original plant structure, can be partially physically protected within soil aggregates (Six et al., 2000; Huang et al., 2002; Dungait et al., 2012). Other forms of C, such as carbonised C, can persist

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longer in soil because they are not the preferred substrates to fulfil microbial energy needs (Lehmann and Joseph, 2015).

Except for carbonised material, the soil C fractions considered to have the longest residence times are those chemically associated with mineral surfaces and metal cations forming organo-mineral complexes (Kleber et al., 2007; Kögel-Knabner et al., 2008; Kleber et al., 2015; Heckman et al., 2018). These organo-mineral associations have been proposed by Kleber et al. (2007, 2015) to follow a discrete zonal sequence, similar to an “onion-type” structure, in which the bonding strength and residence time decreases with increasing distance from the mineral. In the outer zone, also referred to as the kinetic zone, where cations (e.g., Al and Ca) act as bridges between organic ligands (Kleber et al., 2007), the exchange rate of OM molecules tends to be faster than in the inner layer, and oxidative degradation becomes more intense (Kögel-Knabner et al., 2008). This is less the case in acid soils – especially volcanic soils at early stages of weathering, under high precipitation and good drainage (Takahashi and Dahlgren, 2016a) – where Al is able to form inner-sphere complexes with organic ligands (Scheel et al., 2007), increasing OM preservation. However, as pH increases, the preferential formation of Al hydroxides and the weakening of proton bridging between organic ligands (e.g., carboxylic acid functional groups) (Newcomb et al., 2017) increases the vulnerability of OM to decomposition. This explains the observed deleterious effect of management practices that increase soil alkalinity (e.g., liming) on the stability of organo-Al complexes (Verde et al., 2005; Miyazawa et al., 2013).

Land use and management practices also influence soil nutrient status, the quantity and composition of organic detritus entering the soil, and the turnover of soil OM (Chen et al., 2018). In New Zealand, the historic conversion of native forest to permanently grazed pasture led to an increase in soil C content due to greater soil fertility and the denser root system of pasture species (Sparling and Schipper, 2004). Despite this general increase in soil C under pasture systems, the residence time has been shown to decrease as OM decomposition becomes accelerated by the build-up in energy (through increased OM input) and nutrient availability (Sanderman et al., 2016). In contrast, conversion of pasture to cropping causes a loss of soil C mostly through (i) the disruption of aggregates causing the exposure of physically protected OM (Six et al., 1998), (ii) a smaller OM input to soils (Six et al., 1998), and (iii) greater temperature and moisture fluctuations (Verde et al., 2010; De Troyer et al., 2014; Kaiser et al., 2015) in the absence of a permanent plant canopy. Soils of different orders (with different mineralogy and OM chemistry) may respond differently to agricultural management practices. Land use and management may also influence the molecular composition of soil OM, thus impacting the interaction of OM with soil minerals (Rumpel et al., 2009; Wang et al., 2016). Yet limited information is available on this subject, even though such knowledge is crucial to fundamentally understand the persistence of OM as affected by land use and agricultural management.

Recently McNally et al. (2017) have sampled a wide range of New Zealand soils to examine commonly measured characteristics that might indicate the soil C sequestration potential under two major land uses, grazed pasture and continuous cropping. Here in our study – using a subset of these soils and another set, that of ungrazed grasslands, from the same project –, we investigate different organic C fractions stored in these soils and examine the chemical nature of OM. Our main interest is to explore whether different land uses have a common influence on the OM quality and quantity of soils that differ in their contents of inorganic SRO constituents. We preliminary explore the hypotheses that (i) in soils poor in inorganic SRO constituents, total soil C concentration under specific land use is mainly determined by the size of the chemically-unprotected C fraction, whereas (ii) in soils with an abundance of inorganic SRO (i.e., Allophanic soils), the soil C concentration under a specific land use is determined by the size of both the chemically-unprotected and chemically-protected C fractions. To investigate this, we fractionated C and chemically characterised OM for a range of soil

orders (i.e., Allophanic, Brown, Gley, Pallic and Recent) and land uses (i.e., permanently grazed pasture, ungrazed/unmanaged grasslands, annual cropping). We used conventional wet chemical methods to extract C fractions: (i) diluted HF (2%) to estimate mineral-bound C ($C_{HF\text{-mobile}}$) and mineral-unbound C ($C_{HF\text{-residuum}}$), (ii) sodium pyrophosphate (0.1 M) to estimate C bound to Al cation (C_p) (in Allophanic soils), and (iii) water-soluble C (C_{H_2O}). Particulate OM (C_{POM}) was determined in non-Allophanic soils. We also identified OM fingerprints in the HF-residual OM with the use of pyrolysis-gas chromatography–mass spectrometry (Pyrolysis-GC–/MS).

2. Materials and methods

2.1. Soil samples

A representative subset of 45 soils was selected from a larger project in which soils (0–15 cm depth) were collected from New Zealand's major agricultural regions (Auckland, Canterbury, Hawkes Bay, Southland, Taranaki, Waikato; McNally et al., 2017). The locations of the sampling sites are displayed in Fig. 1 of Data in Brief (Shen et al., n.d.) and details on soil sampling are provided in McNally et al. (2017). The subset of 45 soils covered the dominant soil orders in the New Zealand Soil Classification (Hewitt and Dymond, 2013): Allophanic (9 soils), Brown (6 soils), Gley (11 soils), Pallic (10 soils) and Recent (9 soils). The corresponding soil classification following the USDA Soil Taxonomy Classification System is detailed in Table 1 of Data in Brief (Shen et al., n.d.); essentially, Allophanic soils correspond to Andisols, Brown soils to Udepts, Gley soils to soils with aquatic moisture regime, Pallic soils mostly to Alfisols but also Inceptisols, and Recent soils to Entisols. The 45-soil subset represents soils derived from either sedimentary or volcanic parent materials under either permanently grazed pasture (i.e. dairy and drystock; 17 soils), continuous cropping (i.e. arable and vegetable; 17 soils) or unmanaged and ungrazed grassland (11 soils) land uses. An additional subset of 17 Allophanic soils from the same project was included when doing principal components analysis (PCA) of only Allophanic soils to make a total of 26 soils; of these, 17 were permanently grazed pasture, and 8 under continuous cropping. Only one Allophanic soil under ungrazed grasslands was included in the study.

2.2. Soil characterisation

Physico-chemical characteristics (Table 2 of Data in Brief (Shen et al., n.d.)) of the soils were determined as follows: pH was measured at a soil:water ratio of 1:2.5 using a standard glass electrode; the clay ($< 2 \mu\text{m}$) content was measured by sieving and sedimentation using the pipette method (Gee and Bauder, 1986). Total C and N were determined by Dumas combustion (LECO TruMac, Leco Corporation, St. Joseph, MI, USA). Particle size distribution was determined following soil dispersion by sonication (60 s at 64 J s^{-1}) (McNally et al., 2017). The C content of the particulate OM fraction ($> 53 \mu\text{m}$) (C_{POM}) was measured using the same methods. Water-extractable C (C_{H_2O}) was measured as described by Ghani and Rajan (1996), following a sequential extraction: readily soluble OM was extracted with deionised water at room temperature (20 °C; hereafter referred to as cold water extraction) and then removed in a hot-water bath at 80 °C for 16 h (hot water extraction). Organic C in the cold and hot water extracts was determined using a Total Organic Carbon Analyser (Shimadzu TOC-V_{CSH}, Shimadzu Corp, Japan). The C_{H_2O} was defined as the sum of the cold- and hot-water extractable C.

The specific surface area (ADSSA) of each soil was calculated from the water content of air-dried soil as described by Parfitt et al. (2001), where:

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