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Quantitative differentiation of coal, char and soil organic matter in an Australian coal minesoil

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ABSTRACT

Organic inputs from plant establishment are part of the rehabilitation process in restoring coal minesoil function. Soil organic matter (SOM) content could therefore potentially be an indicator of rehabilitation success. Rehabilitated coal minesoils contain inherited coal and char that complicate the attribution of measured total C to recent SOM inputs. We provide proof-of-principle tests of ramped combustion thermal analyses combined with chemometrics (multivariate curve resolution–alternate least squares, MCR-ALS) to quantitatively distinguish between geogenic C, pyrogenic C and SOM C in model mixtures and a coal minesoil from Queensland, Australia. MCR-ALS successfully separated coal and char, and initial estimate thermograms improved the model fits. Geogenic C represented a small proportion of total organic C in the tested unknown minesoils (mean = 9.2%), and a larger contribution from pyrogenic C (mean = 32.4%). Trends in SOM were also consistent with Walkley-Black measurements of organic C. Our combined thermal-chemometric approach represents a robust means of quantifying SOM, distinct from coal and char, though resolution could be improved using multi-element thermograms and additional end-members and soils.

1. Introduction

Minesoils are the soils created during the rehabilitation of mined lands, typically covering the newly constructed landforms [1,2]. The landforms created with the overburden must be stabilized and rehabilitated before relinquishment. In particular, opencut mining of coal moves large quantities of overburden and soil. In 2014, ~230 Mt of coal was produced from opencut mines in Queensland, Australia [3] and ~1.5×10^9 bank cubic meters of overburden was moved [4]. Rehabilitated mined lands usually use stockpiled topsoil to spread over spoil and overburden materials, often in a layer no thicker than 0.3 m. Mixing of these different materials, topsoils and spoils, during their reapplication is common. These soils are therefore developmentally young, with little to no organic matter due to losses during stockpiling, disturbance and dilution from mixing with overburden material [1,5].

Incorporation of soil organic matter (SOM) from plant and microbial detritus during plant establishment are part of the rehabilitation process in restoring soil quality and function [6]. Beyond reclamation, direct and indirect measures of SOM content are frequently used in assessments of agricultural soil quality and health [7,8]. Improved soil quality can reduce erodibility and stabilize these landforms, thus fulfilling rehabilitation objectives. Soil organic matter (SOM) derived from the accumulation of recent plant and microbial inputs could therefore potentially be used as an indicator of rehabilitation success. In addition, disturbed minesoils also represent an opportunity to act as an important sink for atmospheric CO_2 as SOM levels increase [9,10], though they likely do not represent a net sequestration of C since they are part of the fossil fuel production process.

The artificial nature of landform construction on a mine site is reflected in a highly uneven distribution of carbon across a mine site creating a high spatial heterogeneity of carbon originating from various sources [11]. Minesoils at coal mines contain variable amounts of inherited coal particles from waste rock removed during mining, and coal dust from aeolian deposition. Coal dust accumulation from nearby operations may also continue after initial reclamation. This complicates the quantification of soil carbon from recent SOM inputs attributable to rehabilitation. The quantification of SOM

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accumulation in Australian coal minesoils is further complicated by the potential presence of pyrogenic C derived from the incomplete combustion of biomass from wildfires. This char, or black carbon (BC), has been investigated for its potential to remain in the soil for centuries [12]. Pyrogenic C is found commonly in soils globally [13–15] and is nearly ubiquitous in Australian soils and especially in Vertisols [13,16]. Vertisols and Solonetzs are the predominant soil types in the coal mining region of interest to this study–the Bowen Basin, Queensland, Australia [17]. Quantifying SOM carbon accumulated in mined lands during rehabilitation therefore requires distinguishing this carbon from that which is inherited from the starting materials used for reclamation.

Ussiri et al. [2] provide a comprehensive overview of the methods for quantifying geogenic C (*i.e.*, coal) in rehabilitated minesoils, which they classify as: optical/microscopic, thermal, chemical, spectroscopic, molecular markers, isotopic, or some combination of these. The most reliable method to quantify geogenic C is radiocarbon analysis, owing to lack of radiocarbon activity due to age, but the analysis is prohibitively expensive for routine use, particularly in cases requiring large sample numbers such as carbon stock assessment in rehabilitated land. ^{13}C NMR spectroscopy has also been used [18], but frequently requires sample pre-treatments and long run times thus also making it time-consuming, expensive, and impractical for high sample numbers. In response, infrared spectroscopy (FTIR, DRIFT) combined with multivariate data analysis (partial least squares (PLS)) was proposed as a more rapid and practical approach [19], but the PLS statistical approach requires large calibration data sets that might be soil-specific or only locally applicable, which represent an expensive and time consuming set of reference measurements. Similarly, methods to quantify pyrogenic char in soils generally involve elemental analysis after removal of more labile organic matter either by chemical or thermal oxidation [20,21], or direct detection by pyrolysis-GC/MS, ^{13}C NMR or thermogravimetry [22]. More recently, Rock-Eval analysis uses ramped pyrolysis and combustion to discern different types of organic materials in soil and sediment samples [23–25], and has been compared to conventional methods for distinguishing BC from SOM [26–28].

As geogenic C, pyrogenic C and soil organic matter C combust at different temperatures, the application of ramped combustion to distinguish among them is an attractive approach. However, each of these components is actually composed of a spectrum of materials that combust over a range of temperatures, making the distinction with a single temperature cut-off challenging. The interpretation of thermograms as the primary result from ramped combustion of carbon-containing substrates may be carried out qualitatively or (semi-)quantitatively. Multivariate curve resolution – alternate least squares (MCR-ALS) is defined as a group of statistical techniques that help resolve mixtures by determining the number of constituents, their response profiles (*e.g.*, spectra) and their estimated concentrations, using a minimal number of assumptions about the nature and composition of these mixtures [29–31]. MCR-ALS has been successfully applied to a variety of biological and chemical processes with near infrared (NIR) spectroscopy [32,33], FTIR spectroscopy [34,35] and discrete data such as concentrations of different pollutants [36]. However, to our knowledge, this technique has not been applied to resolve thermal analysis curves or to the characterization of organic matter in surface soils.

The objectives of this study were to first provide a proof-of-principle test of whether thermal analyses combined with the MCR-ALS chemometric technique are able to distinguish between and quantify proportions of geogenic C, pyrogenic C and soil organic matter C in model mixtures of increasing complexity. A series of experimental mixtures combining various mineral matrix and organic C end-members were subjected to CO_2 evolved gas analysis (CO_2-EGA) during ramped combustion (*i.e.*, thermal analysis). MCR-ALS analyses were applied to the resulting thermograms to generate modeled estimates of the different forms of organic C. A second objective was to test the approach against a set of minesoils of unknown composition to generate estimates of the proportional contributions of geogenic C (coal), pyrogenic (or black) C (BC) and soil organic matter C (SOC) to the total organic C content. The ultimate goal is to provide a robust method for quantifying soil organic matter C accumulations during the rehabilitation of minesoils.

2. Materials and methods

2.1. Reference materials and mixture end-members

2.1.1. Geogenic carbon

Bituminous coal from the BHP Billiton Mitsubishi Alliance Goonyella coal mine (21°45′32″S 147°58′37″E) and from the Anglo American German Creek coal mine (22°54′35″S 148°33′57″E) were selected as the reference materials for geogenic C. As these coal samples originated from mines within the Bowen Basin, they were assumed to be similar to coal particles found in rehabilitated minesoils in the vicinity of the mined resource. The coal samples were collected in July and August 2010 as grab samples from stockpiles. The samples were oven dried at 40 °C, and homogenized by ball milling.

2.1.2. Pyrogenic carbon

Chestnut (*Castanea sativa*) wood char was used as reference material to represent pyrogenic, biomass-derived BC. The char was produced by pyrolysis at 450 °C for 5 h, and has been used in the international BC ring trial [20,37]. Wood char was selected because the historical vegetation cover at the research sites was dominated by Brigalow (*Acacia harpophylla*) scrub, a woody plant that is regularly subjected to fire [38].

2.1.3. Carbon-free mineral matrix

Laboratory grade, acid washed sand was re-washed with 4 *M* HCl solution and heat treated in a muffle furnace at 600 °C for 48 h to remove all organic C, including BC. Sand was ball milled to improve homogeneity of mixtures. While the quartz mineralogy is not necessarily representative of the mineralogy of the regional soils, it is useful as a simplified model mineral matrix.

2.1.4. Coal-free, BC-containing soil matrix

A sandy clay (37% clay) Vertisol soil sample collected from Urrbrae, South Australia [21], previously used in the international BC ring trial [20], was selected as a reference material to represent a natural matrix containing SOM and pyrogenic BC, without containing geogenic coal. The soil was previously found to contain 3–30% of its organic C as pyrogenic BC (depending on the method used), with the remainder as SOM [21]. This soil was selected because Vertisols, as well as other high clay containing soils, are common in the Bowen Basin [17].

2.1.5. Minesoil matrix

Rehabilitated minesoils were collected from the BMA Blackwater coal mine (23°28′0″S 148°46′0″E) in the Bowen Basin in Queensland, Australia, as a reference minesoil matrix for experimental mixtures because of its low organic and inorganic carbon concentrations. The area is in the Brigalow Belt bioregion, which is semi-arid with periods of both intense rainfall and long dryness [39]. Vegetation at the site is dominated by buffel grass (*Cenchrus ciliaris*). Minesoil samples were collected from 0.1 to 0.2 m depth. The soils were oven dried at 40 °C, sieved to pass a 2.0-mm mesh, ground to pass a 0.5-mm mesh for Walkley-Black [40] organic C