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Review

Methods for determination of coal carbon in reclaimed minesoils: A review

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ABSTRACT

Organic carbon (OC) of the minesoils reclaimed from coal mining often contains carbon (C) associated with coal particles from mining and the reclamation activities. This C, collectively referred to as geogenic OC (formed as a product of geological processes), must be quantified in order to accurately determine the pools and sequestration potential of OC that originates from recent vegetation input. Reclaimed mined lands can provide significant sink for atmospheric carbon dioxide (CO_2) through C assimilation in vegetation biomass, formation and accumulation of SOM. However, the validity of the reported C sequestration potentials in minesoils reclaimed from coal mining activities is questionable due to inability to quantitatively determine the different C sources that may be present in these soils. Due to its high C content, coal particles present in these soils may lead to overestimation of pools and sequestration rates, and can also represent a large C background against which small changes in recent OC must be measured. This is a methodological challenge which must be overcome in reclaimed minesoils (RMS). Standard procedures for quantifying soil organic C (SOC) cannot distinguish geogenic C and recent OC from plant biomass. Appropriate soil C analysis in RMS must differentiate between inorganic C (carbonates), geogenic OC and recent OC from decomposition of plant biomass. Therefore, the purpose of this review is to collate and synthesize the available information on the existing techniques for separating geogenic and recent OC, and quantifying these OC fractions in RMS. Methods for quantifying geogenic OC in RMS have been grouped into microscopic, thermal, chemical, spectroscopic, isotopic, and combination of some of these methods. The major limitation of thermal and chemical methods is the overlap in sensitivity between some types of coal and recent OM fractions. Most of the spectroscopic techniques are semi-quantitative, and generally yield less accurate estimates of geogenic OC. Radiocarbon analysis is one of the most reliable methods for quantifying geogenic OC in RMS. However, the need for specialized instrumentation, advanced computational skills, and high analytical costs precludes its adoption for routine soil analysis. Additional research is needed to further evaluate the existing techniques, develop some reliable and cost-effective methods, and ultimately propose standard geogenic OC quantification methods that can be widely adopted.

Contents

Abbreviations: SOC, soil organic carbon; OC, organic carbon; RMS, reclaimed minesoils; OM, organic matter; SOM, soil organic matter; TOC, total organic carbon; TC, total carbon; IC, inorganic carbon; BC, black carbon; EC, elemental carbon; TG, thermogravimetric; DTG, derivative thermogravimetric; CPMAS NMR, cross polarization magic angle spin nuclear magnetic resonance.

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1. Introduction

Minesoil are soils formed on landscapes altered by surface mining activities. Sometimes referred to as spoils or anthropogenic soils (Sencindiver and Ammons, 2000), these drastically disturbed soils exhibit profile characteristics, physical, chemical, and biological conditions that reflect anthropogenic perturbations rather than natural soil forming processes (McSweetney and Jansen, 1984). Minesoils are often characterized by heterogeneous mixtures of rock fragments and sediment materials. Compared to native soils, the volume of rock fragments in minesoils can be as high as 67% of the total soil volume (Ashby et al., 1984; Ciolkosz et al., 1985; Thurman and Sencindiver, 1986).

In addition to recent organic carbon (OC) from humification of plant residues, minesoils formed from reclamation of surface mining of coal often contain varying quantities of coal particles distributed throughout the soil profile depending on mining and reclamation techniques (Insam and Domsch, 1988; Roberts et al., 1988; Rumpel et al., 1998a,b; Schafer et al., 1980; Schmidt et al., 1996; Stroo and Jencks, 1982; Ussiri and Lal, 2008a). The organic carbon (OC) of coal particles is termed geogenic OC (i.e., OC which has been subjected to geological processes). Microbial decomposition of recent soil organic matter (SOM) from plant litter and other pedogenic processes lead to mixing of recently formed SOM with coal particles. For minesoils developed on calcareous parent materials (siltstone, sandstone, and limestone), inorganic C may also occur in significant quantities. Therefore, total carbon (TC) in reclaimed minesoils (RMS) can be a mixture of: (1) inorganic carbon (IC) originating from parent material, (2) geogenic OC from coal particles incorporated during mining and reclamation operations, and (3) plant-derived recent soil organic carbon (recent OC). Because of the dark color of humus and its intimate mixing with fine coal particles, these two sources of carbonaceous materials cannot be distinguished by visual means.

RMS can be a significant sink for atmospheric carbon dioxide (CO_2) through CO_2 assimilation into aboveground biomass and accumulation of recent SOM. Soil organic carbon (SOC) sequestration rates ranging between 0.45 and 3.0 Mg C ha^{-1} yr^{-1} during the first two decades following reclamation have been reported (Akala and Lal, 2001; Shukla et al., 2004; also see reviews by Shrestha and Lal, 2006; Shrestha et al., 2009; Sperow, 2006; Ussiri and Lal, 2005). Other reports have shown that SOC storage in RMS sometimes exceeds that of the adjacent undisturbed soils (Fettweis et al., 2005; Shukla et al., 2005; Ussiri et al., 2006a). However, the accuracy of SOC pools and sequestration rates which have been reported is questionable due to failure, in many studies, to account for the contribution of coal C to the total SOC pools in RMS. Standard SOC determination methods such as dry combustion do not distinguish between recent and geogenic OC, and may lead to overestimation of SOC pools and sequestration rates in RMS. Quantifying recent SOC accrued from biochemical processing of plant materials (litter, dead roots, and root exudates) is crucial to understanding SOC dynamics, and accurate determination of SOC pools and sequestration rates in RMS. Therefore, development of reliable analytical techniques capable of overcoming these challenges is urgently needed.

In this review, geogenic OC collectively represents lithified plant debris at different degrees of coalification formed by biological and geological processes over millions of years. It differs from "elemental C" (also called black carbon (BC) in atmospheric studies, Andreae and Gelencser, 2006) in that BC results from incomplete combustion (i.e., pyrogenic processes) of biomass and fossil fuel (char) and its condensates (soot) (Elmquist et al., 2006). Although geogenic OC and BC have some chemical and structural similarities (Currie et al., 2002; Gustafsson et al., 2001) and also can co-occur in soil and sediment samples (Goldberg, 1985), it is important to stress their differences based on their origin. A comprehensive review on the geochemistry of BC and measuring techniques was published (Masiello, 2004), and an inter-laboratory comparison of methods using reference materials has been conducted recently (Hammes et al., 2007). Therefore, methods exclusive to BC quantification will not be covered in the present review.

Geogenic OC occurs in soils at specific sites associated with coal mining and utilization activities (Rumpel et al., 1998b; Ussiri and Lal, 2008a), including deposition of airborne coal particles near coal processing and coal fired power plants (Schmidt et al., 2000), and soils ameliorated with coal combustion ash (Schmidt et al., 1999). Coal is formed from peat by diagenetic processes in geologic time scale. It is a continuum representing different chemical structures and reactivity ranging from lignite to anthracite and graphite. Similar to pyrogenic BC, there are no generally accepted and standardized methods for quantifying geogenic OC in the environment.

Research effort to quantify the contribution of geogenic C to the SOC in RMS remains limited (Jacinthe et al., 2009; Maharaj et al., 2007a; Rumpel et al., 1998a,b; Ussiri and Lal, 2008a). During the last few decades, several methods have been proposed for separating and quantifying geogenic OC content in soils and sediments. These include methods based on microscopic, spectroscopic, and isotopic analyses of samples, and methodologies that rely on the resistance between coal and recent OC to thermal and chemical oxidation to distinguish geogenic from recent OC and quantify geogenic OC (Jacinthe et al., 2009; Maharaj et al., 2007a; Rumpel et al., 1998b, 2001; Ussiri and Lal, 2008a). The objectives of this review are to collate, summarize and synthesize available information on methods for quantifying coal C, its distribution in RMS, and identify research priorities for developing and standardizing coal C quantification techniques in RMS. First, we will briefly describe general properties of coal and its geology to distinguish it from pyrogenic BC and recent OC that evolved from decomposition of recent vegetation biomass. We will also briefly describe mining and land reclamation techniques in order to provide the proper context to understand the formation and unique properties of RMS, including contamination by coal particles. The bulk of the review will focus on available techniques for geogenic C quantification. The last section will outline