



Distinguishing „new“ from „old“ carbon in post mining soils

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Introduction

Soils developing on heaped overburden after open pit coal mining near Sokolov, Czech Republic, provide an exceptional opportunity to study sites of different ages (0–70 years) developing on similar substrate under relatively well-known conditions. Soil organic carbon (SOC) is a useful indicator of soil quality and represents an important global carbon pool. Post-mining soils would be a perfect model for long-term study of carbon dynamics. Unfortunately, quantifying SOC in Sokolov post-mining soils is quite complicated, since conventional quantification methods cannot distinguish between SOC derived from plant residues and fossil organic carbon derived from coal and kerogen present in the overburden. Moreover, also inorganic carbon may sometimes bias SOC quantification.

Up to now, the only way to directly estimate recently derived SOC in these soils is radiocarbon dating (Rumpel et al. 1999; Karu et al. 2009). However, this method is costly and thus cannot be used routinely. The aim of our study is to find an accessible method to quantify recently derived SOC. We would highly appreciate ideas of other soil scientists, organic geochemists and sedimentologists on how to solve this challenge.

Methods and hypotheses

A set of 14 soil samples were analysed by radiocarbon (^{14}C -AMS) analysis, near-infrared spectroscopy (NIRS), ^{13}C CPMAS NMR spectroscopy, Rock-Eval and XRD.

For calibration of NIRS, also 125 artificial mixtures were produced by mixing different amounts of claystone, coal and partially decomposed litter.

NIRS (1000–2500 nm) as well as younger mid-infrared spectroscopy has been widely applied to soils (Janik et al. 2007; Vasques et al. 2009; Michel et al. 2009). When combined with multivariate chemometric techniques, it can be used to predict concentration of different compounds. No study has yet focused on NIRS application to soils where fossil carbon is found in two chemically different forms – whereas coal is rather aromatic, kerogen in our study area is highly aliphatic.

^{13}C CPMAS NMR spectroscopy is an analytical technique used for structural characterization of soil organic matter (Preston 1996). Particular regions of NMR spectra can be assigned to alkyl C, O-alkyl C, aromatic C, and carboxylic C (Kögel-Knabner 2000). We hypothesize that recently derived and fossil organic matter will have different relative proportions of signals in these regions and this difference could be used to estimate recently derived SOC in unknown samples.

Rock-Eval pyrolysis is a method used in oil exploration to evaluate the quantity, quality and thermal maturity of organic matter in sediments. Lately, it has been applied also to soils and can bring useful information about soil organic matter (Sebag et al. 2006; Disnar et al. 2003). Particularly, it allows to determine the total organic carbon content (TOC wt.%) and also provides Hydrogen and Oxygen Index values (HI and OI) which are known to correlate with H/C and O/C ratios. Also, pyrolysis and oxidation products (hydrocarbons, CO and CO₂) can be plotted against temperature and give us an idea of thermal stability of their source compounds. We hypothesize that recently derived and fossil organic matter will differ in thermal stability and also in the quantity and quality of pyrolysis products. These differences could allow to quantify both fractions in post-mining soils.

XRD (X-ray diffraction) is an analytical technique used to identify minerals in rocks and soils and give a semi-quantitative estimate of their content. Carbonates (as an inorganic form of carbon, IC) can be source of bias in some organic carbon analyses. Carbonates can be removed from samples by acid treatment but the specific procedure that is required depends on the type (and solubility) of carbonates present in sample (Brodie et al. 2011). Up to now, other methods did not show a significant content of IC in Sokolov soils; however, previous XRD analyses of parent claystones in the area showed that siderite (FeCO₃) represents a highly variable component of the overburden (Table 1 from Křibek et al. 1998). Since siderite is known to be highly insoluble, it is possible it has not been detected by previous IC measurements in soils (Larson et al. 2008).

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