



Changes in the Rock-Eval signature of soil organic carbon upon extreme soil warming and chemical oxidation - A comparison

Christopher Poeplau^{a,*}, Pierre Barré^b, Lauric Cécillon^{b,c}, François Baudin^d, Bjarni D. Sigurdsson^e

^a Thünen Institute of Climate-Smart Agriculture, Bundesallee 68, 38116 Braunschweig, Germany

^b Laboratoire de Géologie de l'ENS, PSL Research University, CNRS UMR 8538, 75005 Paris, France

^c Normandie University, UNIROUEN, IRSTEA, ECODIV, 76000 Rouen, France

^d Sorbonne Université, CNRS, Institut des Sciences de la Terre de Paris, 75005 Paris, France

^e Agricultural University of Iceland, Hvanneyri, IS-311 Borgarnes, Iceland

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ABSTRACT

Soil warming can increase soil organic carbon (SOC) mineralization, triggering a positive climate-carbon cycle feedback loop. Globally, many soil warming experiments have examined losses of bulk SOC, but few have assessed changes in quality. Accurate knowledge of the latter is required for an in-depth understanding and improved prediction of SOC feedback to climate change. In this study, we used Rock-Eval thermal analysis (RE6) to characterize shifts in SOC thermal stability and bulk chemistry after six years of geothermal warming by 0.6 °C, 1.8 °C, 3.9 °C, 9.9 °C, 16.3 °C, 40 °C, and 80 °C in an Icelandic grassland topsoil (0–10 cm). We also used the strong warming-induced depletion of SOC (up to 92% in the 80 °C soil) in comparisons of chemical oxidation-resistant and biogeochemically resistant SOC, which are generally assumed to be similar in nature. Sodium hypochlorite (NaOCl) and hydrogen peroxide (H₂O₂) were used for oxidation. Warming-resistant SOC was strongly depleted in hydrocarbons and enriched in oxygen, confirming that SOC oxidation state, and thus energy content, is an important driver for biogeochemical stability. This was supported by findings that thermal stability, i.e., the amount of energy (temperature) necessary to pyrolyze or oxidize SOC, strongly increased with warming intensity. Of the 31 RE6 parameters tested, the most warming-sensitive were hydrogen index (HI, $\rho = -0.84$), oxygen index (OI_{RE6}, $\rho = 0.83$), proportion of total pyrolyzed carbon released as hydrocarbons at 200–650 °C (S2/PC, $\rho = -0.86$), and the temperature at which a certain proportion of CO₂ evolved during pyrolysis ($\rho > 0.8$). Chemical oxidation of unwarmed soil caused average relative SOC losses of 61% (NaOCl) and 91% (H₂O₂) and shifts in RE6 properties that differed strongly from warming-induced shifts at comparable SOC losses. Chemical oxidation-resistant SOC was more enriched in oxygen, but slightly enriched in hydrocarbons, and less thermostable than comparable naturally depleted SOC at the same time. A certain overlap, especially for NaOCl-treated soils, is likely, while H₂O₂-oxidized soils showed very distinct RE6 properties. We concluded that i) soil warming leads to strong shifts in SOC bulk chemistry and thermal stability and ii) H₂O₂ should be avoided in isolation of a slow SOC kinetic pool.

1. Introduction

Soil warming is observed to lead to rapid and severe losses of carbon (C) from soil organic matter (SOM) due to catalyzed microbial activity (Davidson et al., 2000; Lu et al., 2013). According to recent conservative estimates, warming-induced soil organic carbon (SOC) losses will account for 12–17% of total expected anthropogenic greenhouse gas emissions by 2050 (Crowther et al., 2016). Such losses can be expected also to lead to shifts in SOC quality, with relative enrichment of more biogeochemically resistant SOC (Knorr et al., 2005). The

temperature sensitivity of older and more stabilized SOC is often reported to be higher than that of labile SOC (Lefevre et al., 2014), which is in line with kinetic theory (Davidson and Janssens, 2006). However, the large gradient in turnover times across different components of the bulk SOC pool will most likely lead to enrichment of more resistant SOC under soil warming (Conant et al., 2011). Such shifts in SOC quality have rarely been investigated, however, leading to lack of knowledge regarding the biogeochemical nature of warming-resistant SOC. This gap in research may be because i) total SOC stock changes have been the main focus of in situ warming experiments and ii) many warming

* Corresponding author.

E-mail address: Christopher.poeplau@thuenen.de (C. Poeplau).

experiments have been too short or too moderate to allow any strong shifts in SOC chemical composition and/or energetic status.

Since the SOC response to warming is one of the major uncertainties in global earth system models (Friedlingstein et al., 2006), an in-depth understanding of the mechanisms driving C losses from the soil with quantification and characterization of warming-resistant SOC are critically important. The response of different compartments or pools of SOC to warming, and inclusion of these in models, is currently being strongly debated (Conant et al., 2011), due to contradictory results in field and laboratory incubation studies and lack of mechanistic understanding.

Characterizing SOC and understanding its stabilization in the soil have always been challenging, due to the extremely diverse chemical nature of SOC (Kögel-Knabner, 2017) and to complex interactions with the mineral phase of the soil matrix (Kleber et al., 2005; Sollins et al., 1996). During the past two decades, it has been reported that selective preservation of recalcitrant organic molecules has only limited effects on the long-term persistence of organic matter in soils (Dungait et al., 2012; Rasse et al., 2006). Moreover, it is widely acknowledged, that SOM persistence is largely driven by organo-mineral interactions (Sollins et al., 1996), aggregation (Six et al., 2002), large distances between substrate and potential decomposers (Don et al., 2013), and specific environmental conditions such as energy, oxygen, and nutrient limitation (Barré et al., 2016; Fontaine et al., 2007; Schmidt et al., 2011; Wild et al., 2014).

Thermal analysis techniques such as thermogravimetry, evolved gas analysis, and differential scanning calorimetry have been applied, more or less successfully, to characterize the biogeochemical stability of SOC (Plante et al., 2009; Schiedung et al., 2017). Such studies are mainly based on the notion that the energy demand of thermal oxidation is a good proxy for the energy demand of biological oxidation (Barré et al., 2016). One emerging thermal analysis technique to characterize SOC is Rock-Eval (RE), a standard method in oil and gas exploration in sedimentary basins to assess the hydrocarbon potential of a prospect (Lafargue et al., 1998). Rock-Eval is a two-step approach, with ramped heating pyrolysis followed by ramped heating oxidation. Previous studies have demonstrated the potential of RE to characterize SOC stability and decomposition stage by relating it to respiration measurements and SOC fractions (Gregorich et al., 2015; Saenger et al., 2015), H:C ratio and O:C ratio (Espitalié et al., 1977), SOC in soil diagnostic horizons (Disnar et al., 2003) and different depth layers (Soucémariadin et al., 2018), and long-term SOC losses in bare fallow experiments (Barré et al., 2016). Especially the latter were useful to elucidate, that RE thermal stability cannot only be linked to chemical, but also to biological stability of OM, since RE properties shifted consistently with length of bare-fallow period. Thus, OM that resisted enzymatic decay over decades was characterized by a higher RE thermal stability. Several RE indices have been developed, which can be linked to chemical SOM properties (Disnar et al., 2003) or SOC dynamics (Sebag et al., 2016). It has been concluded that the RE method is sensitive to changes associated with SOC biogeochemical processes and could have the potential for landscape-scale applications due to its time- and cost-effectiveness (Saenger et al., 2013).

Fractionation of SOM is a frequently used tool to isolate functionally distinct units of SOM, such as labile and stabile SOC pools (von Lützow et al., 2007). The most stable pool is often isolated using strong oxidizing agents such as sodium hypochlorite (NaOCl) or hydrogen peroxide (H₂O₂) to remove the oxidizable, i.e., more labile, SOC. This is an attempt to mimic strong enzymatic decay, which is largely an oxidative process, and thus isolate a biogeochemically resistant SOC pool that is functionally linked to what is called the 'inert' or passive pool in turnover models (Zimmermann et al., 2007). For example, the remaining fraction after NaOCl oxidation is often found to be correlated with poorly crystalline minerals, which are unaffected by this form of chemical oxidation (Siregar et al., 2005) and assist in stabilizing organic matter (Mikutta et al., 2005a). In fact, NaOCl-resistant SOC has

been found to be much less responsive to land-use changes (Poeplau and Don, 2013), less enriched in modern C after C3-C4 vegetation change (Poeplau and Don, 2014), and older (Helfrich et al., 2007) than bulk SOC. However, despite this general link to biogeochemical stability, it is not clear whether the approach of mimicking enzymatic decay is justified, i.e., whether chemical oxidation-resistant SOC has similar properties to long-term biogeochemically resistant SOC. This can only be directly inferred from comparing soils that are naturally extremely depleted in SOC with chemically oxidized reference soils.

In this study, we used a thermosequence of naturally warmed soil (from 0 to 80 °C), with SOC losses of up to > 80% of the initial SOC (Poeplau et al., 2017), in order to study gradual shifts in RE properties. The main objectives of the study were to 1) determine whether soil warming leads to a shift in SOC quality as revealed by RE signature, 2) identify the properties of SOC that determine its resistance to extreme soil warming, and 3) determine whether chemical oxidation with NaOCl or H₂O₂ yields SOC that is comparable to warming-resistant SOC in terms of quality.

2. Materials and methods

2.1. Study site, soil sampling and basic analysis

The study site with the natural soil warming gradients is located in southern Iceland, close to the village of Hveragerdir (64°00'01"N, 21°11'09"W, 83–168 m a.s.l.), where an earthquake on 29 May 2008 affected geothermal channels close to the surface and shifted their location, in some cases to previously unwarmed areas (O'Gorman et al., 2014). This created strong gradients in permanent soil warming within small distances (< 100 m). Since 2011, several research plots have been established on previously unwarmed soil covered with a plantation of Sitka spruce (*Picea sitchensis* (Bong.) Carr.) and unmanaged treeless grasslands dominated by common bent (*Agrostis capillaris* L.), common meadow grass (*Poa pratensis* L.), meadow horsetail (*Equisetum pratense* L.), and meadow buttercup (*Ranunculus acris* L.). In this study, only the grassland sites were investigated. Mean annual air temperature at the closest weather station (Eyraðakki, 9 km south of Hveragerdir) was 5.2 °C between 2003 and 2015 and mean annual precipitation was 1457 mm. The soil is classified as a Brown Andosol (Arnalds, 2015) and has a silty loam texture (6% clay, 53% silt, 41% sand), with pH_{H2O} 5.7, SOC content 5.4%, and C:N ratio ~10.9 in the unwarmed reference soil (0–10 cm depth) (Sigurdsson et al., 2016). Since the geothermal channels underlie and warm the bedrock, the root zone is chemically uncontaminated by geothermal waters (O'Gorman et al., 2014). On the grassland sites, five transects of permanent plots have been established along two main gradients, which represent the following average warming treatments as measured hourly from spring 2013 to spring 2015: 0 °C (unwarmed reference), 0.6 °C, 1.8 °C, 3.9 °C, 9.9 °C, and 16.3 °C. Three of these transects run downhill (unwarmed reference at the top), and two run uphill on a different slope (Sigurdsson et al., 2016). This natural randomization precludes potential effects of slope position to mask the temperature effect on SOC. For this study, we also sampled a ~40 °C warmed soil in all five transects and ~80 °C warmed soil in one transect (temperature only measured occasionally by hand). Sampling was conducted in December 2014, i.e., six and a half years after the earthquake, using a thin auger (2 cm diameter). Five auger cores (0–10 cm soil depth) were taken in direct proximity to each permanent plot and pooled to one soil sample per plot. These samples were immediately dried at 40 °C and then sieved (2 mm mesh). After ball-milling, all samples were analyzed for total C and nitrogen (N) by dry combustion in an elemental analyzer (EuroEA3024, Eurovector, Milan, Italy).

2.2. Chemical oxidation

Two commonly applied oxidizing agents were used to isolate an

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