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On the rocks: Quantifying storage of inorganic soil carbon on gravels and determining pedon-scale variability

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ABSTRACT

The storage and flux of carbon from soils, the planet's third largest carbon pool, strongly influence the global carbon cycle and are essential, but poorly constrained, parameters for global climate models. An estimated 40% of all soil carbon is stored as inorganic carbonate minerals. Despite a recognition of the importance of soil inorganic carbon (SIC) in soil carbon storage, few studies have quantified pedon-scale variability in SIC storage. We examine different stages of carbonate development and accumulation rates between gravelly and non-gravelly soils. Studies often ignore carbonate coatings on gravels in measurements of soil inorganic carbon (SIC). By quantifying and differentiating the fine (< 2 mm) and coarse (> 2 mm) fractions of SIC in the Reynolds Creek Experimental Watershed in southwestern Idaho, we show that gravel coatings contain up to 44% of total SIC at a given site. Among the 26 soil sites examined throughout the watershed, an average of 13% of the total SIC is stored as carbonate coatings within in the gravel fraction. We measured a high level of pedon-scale field variability (up to 220%) among the three sampled faces of 1 m^3 soil pits. Analytical error associated with the modified pressure calcimeter (0.001–0.014%) is considerably less than naturally occurring heterogeneities in SIC within the soil profile. This work highlights and quantifies two sources of uncertainty in studies of SIC needed to inform future research. First, in gravelly sites, the > 2 mm portion of soils may store a large percentage of SIC. Second, SIC varies considerably at the pedon-scale, so studies attempting to quantify carbon storage over landscape scales need to consider this variability.

1. Introduction

Soil is the third largest global pool of carbon; as such, data on soil carbon storage and its fluxes are essential components for global climate models. Although most research on soil carbon has focused on soil organic carbon, soil inorganic carbon (SIC) constitutes approximately 40% of soil carbon globally and in semi-arid and arid regions is the dominant form of carbon storage (Batjes, 1996; Eswaran et al., 2000). While soil-to-atmosphere flux of soil organic carbon is likely much higher than those of soil inorganic carbon on human timescales, quantifying SIC storage is an essential first step for both quantifying total soil carbon and for ascertaining whether the SIC pool is indeed stable under different land-use and climate conditions.

Soils have very heterogeneous properties, but few studies have quantified the range of variation in SIC accumulation. More often, SIC studies derive their results from single measurements at a single soil site (Batjes, 1996; Rasmussen, 2006; Hirmas et al., 2010). Soil properties are highly variable even at the pedon-scale and we hypothesize that this heterogeneity extends to SIC accumulation within RCEW. Taking a single profile as representative of a location may lead to considerable under- or over-estimation of SIC amounts.

Soil inorganic carbon accumulates by the precipitation of carbonate minerals ($CaCO_3$ and $MgCO_3$) in soils over time; soil-forming factors, including climate, vegetation, parent material and time (e.g. Jenny, 1941; Arkley, 1963; Birkeland, 1999) and dust deposition (e.g. Gile et al., 1966; Machette, 1985) dictate the presence and rate of SIC accumulation in a soil profile. In addition, there are differences in both the rates and characteristics of development between SIC forming around fine soil particles (< 2 mm) and gravel clasts (> 2 mm) (Gile et al., 1966; Machette, 1985; Treadwell-Steitz and McFadden, 2000). However, analyzing carbonate storage on clasts is difficult and time consuming, and many previous studies have removed the gravel fraction before SIC analysis (e.g. Sobecki and Wilding, 1983; Vincent et al., 1994; Treadwell-Steitz and McFadden, 2000; Rasmussen, 2006; Kunkel et al., 2011; Ramnarine et al., 2012; Washbourne et al., 2012; Austreng, 2012). Studies that do include the gravel fraction have processed the soil and gravels together (e.g. Schlesinger, 1985; Reheis et al., 1992; Grinand et al., 2012). These studies of combined soil and gravel SIC

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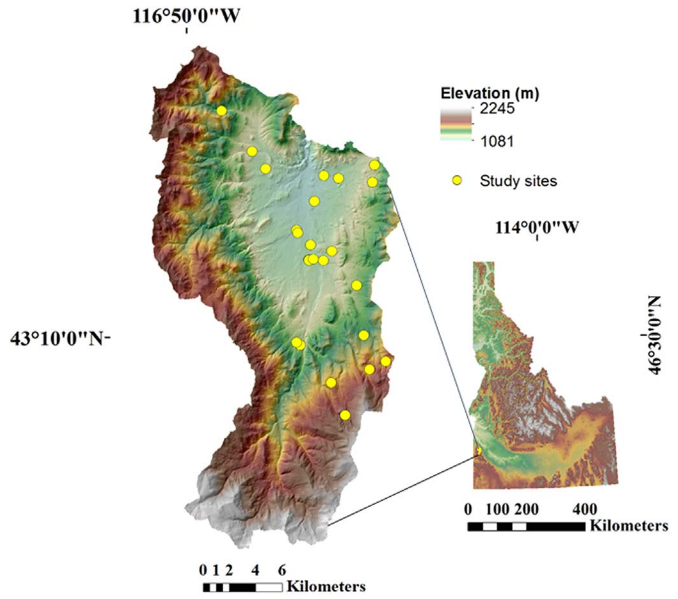

Fig. 1. The Reynolds Creek Experimental watershed (RCEW) in southwestern Idaho. Soil sample sites used for analysis of gravel SIC are marked in yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

provide needed information on total soil SIC; however, it is not clear what the relative storage of SIC is between these different pools. Studies of SIC that do not analyze the gravel fraction are either underestimating SIC or are not fully exploring its complexities. While in many cases the time and cost associated with quantifying carbonate storage on gravels may be prohibitive, we hope this work will provide a framework to calibrate soil carbonate studies that do not include the gravel fraction with studies that do include gravels.

Our study expands the understanding of SIC storage through examination of both the carbonate coatings on gravel clasts and pedon-scale variability in SIC. We sample soil pits throughout the Reynolds Creek Experimental Watershed (RCEW) in southwestern Idaho to collect data on soils with a wide range of gravel content (Fig. 1). We quantify the pedon-scale variability by comparing multiple profiles from the same soil pits throughout the watershed. By processing replicates of both field samples and known standards, we determine the precision of our methods and the natural heterogeneity present in soils. We hypothesize that the gravel SIC coatings will constitute a significant portion of the total inorganic carbon pool in the soils, and that the differences in SIC concentration within a pit will be significant. The results of this work will highlight pedon-scale variability in SIC, and the importance of SIC stored in the gravel fraction of soils in this semi-arid ecosystem.

1.1. Background

1.1.1. Inorganic carbon formation

The precipitation of secondary carbonate minerals ($CaCO_3$ and $MgCO_3$) stores soil inorganic carbon within calcic soils. These minerals are commonly found in arid and semi-arid soils, where evaporative processes concentrate the dissolved species (Ca^{2+}, Mg^{2+}, and carbonate (CO_3^{2-}) ions) within the soil pore water, promoting precipitation of carbonate minerals (Birkeland, 1999). Although the amount of dissolved CO_2 is one of the largest controls on SIC precipitation (McFadden et al., 1998; McFadden, 2013; Zamanian et al., 2016), adequate amounts of water can ultimately prevent carbonate from forming (Jenny, 1941; Arkley, 1963; Birkeland, 1999). When precipitation is sufficiently high and soil water evaporation is limited, infiltrating water flushes the ionic components of carbonate formation from the profile. A high pH (above ~8.2) goes hand-in-hand with the presence of calcic soil horizons and the formation of carbonates (Birkeland, 1999). The relatively low pH of rainwater, as well as mineral and organic acids forming in soils may inhibit the precipitation of these minerals. The presence of carbonate-bearing parent material (e.g. limestone or marble) will dramatically increase the potential of forming secondary calcic horizons within the associated soils.

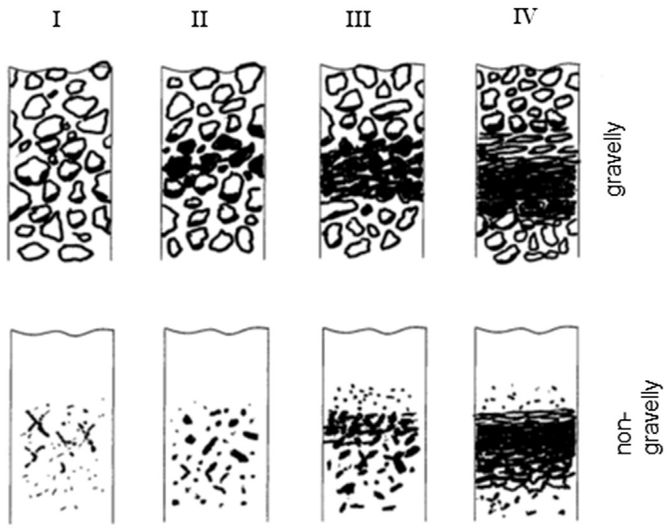

Fig. 2. Conceptual sketch of the diagnostic morphology of the stages of carbonate development in gravelly and non-gravelly parent materials (modified from Gile et al., 1966). This sketch highlights the differences in SIC accumulation between gravelly and non-gravelly soils. The highest level of carbonate development from this study was stage III.

As calcic soils accumulate carbonate over time, they go through a series of stages of development that are dependent upon the gravel content of the soil (Fig. 2). Importantly for this study, carbonate accumulates differently in gravelly vs. non-gravelly soils. In gravelly soils, carbonates precipitate preferentially on the bottoms of clasts as surface tension holds the water to clasts and allows it to evaporate from the underside (Gile et al., 1966). Soil progresses through the initial four stages as carbonate covers soil particles (stages I-II) and then interstitial pore space is filled (stages III-IV). Studies from the southwestern US show gravelly soils reach stage IV more quickly than non-gravelly soils (Gile et al., 1966). Since the carbonate coatings preferentially form on clasts, studies of gravelly soils with stage I-II development are disproportionally affected by the exclusion of > 2 mm material. As carbonate precipitates over a greater portion of the soil material and fills pore space, the relative importance of gravel SIC diminishes slightly.

1.1.2. Gravel SIC in previous studies

In a survey of 4353 soil profiles from the World Inventory of Soil Emission Potentials (WISE) database, Batjes (1996) found that 79% of sampled profiles had no gravel data collected. Some previous studies measure the SIC content of the combined fine and gravel fractions (Schlesinger, 1985; Reheis et al., 1992; Grinand et al., 2012) and do ultimately account for the amount of carbonate stored on gravels. Other studies, however, do not measure the gravel SIC concentration (Sobecki and Wilding, 1983; Vincent et al., 1994; Treadwell-Steitz and McFadden, 2000; Rasmussen, 2006; Kunkel et al., 2011; Ramnarine et al., 2012; Washbourne et al., 2012; Austreng, 2012) and may be under-estimating soil carbonate storage. One study (Hirmas et al., 2010) measured both the fine and gravel SIC fractions and combined the measurements into a single value with no separate examination of the different pools. Other studies did not specify their methods used to process and quantify SIC on gravel (Drees and Nordt, 2001). A number of studies have addressed the amount of SIC on gravels through other methods. Vincent et al. (1994) measured clast coatings to develop a soil chronosequence. Treadwell-Steitz and McFadden (2000) measured the