Investigating carbonate formation in urban soils as a method for capture and storage of atmospheric carbon

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ABSTRACT

This paper investigates the potential for engineered urban soils to capture and store atmospheric carbon (C). Calcium (Ca) and magnesium (Mg) bearing waste silicate minerals within the soil environment can capture and store atmospheric C through the process of weathering and secondary carbonate mineral precipitation. Anthropogenic soils, known to contain substantial quantities of Ca and Mg-rich minerals derived from demolition activity (particularly cement and concrete), were systematically sampled at the surface across a 10 ha brownfield site, Science Central, located in the urban centre of Newcastle upon Tyne, U.K. Subsequent analysis yielded average carbonate contents of $21.8 \pm 4.7\%$ wt $CaCO_3$. Isotopic analysis demonstrated $\delta^{18}O$ values between $-9.4\permil$ and $-13.3\permil$ and $\delta^{13}C$ values between $-7.4\permil$ and $-13.6\permil$ (relative to Pee Dee Belemnite), suggesting that up to $39.4 \pm 8.8\%$ of the carbonate C has been captured from the atmosphere through hydroxylation of dissolved CO_2 in high pH solutions. The remaining carbonate C is derived from lithogenic sources. 37.4 kg of atmospheric CO_2 has already been captured and stored as carbonate per Mg of soil across the site, representing a carbon dioxide (CO_2) removal rate of 12.5 $kgCO_2\ Mg^{-1}\ yr^{-1}$. There is the potential for capture and storage of a further 27.3 $kgCO_2\ Mg^{-1}$ in residual reactive materials, which may be exploited through increased residence time (additional in situ weathering). Overall, the Science Central site has the potential to capture and store a total of 64,800 Mg CO_2 as carbonate minerals. This study illustrates the potential for managing urban soils as tools of C capture and storage, an important ecosystem service, and demonstrates the importance of studying C storage in engineering urban anthropogenic soils.

1. Introduction

Carbon capture and storage as a consequence of soil processes is a form of carbon sequestration, removing CO_2 from the atmosphere and storing it as organic (soil organic matter) and inorganic (pedogenic carbonates) forms of carbon (C). During silicate weathering, calcium (Ca) and magnesium (Mg) silicate minerals naturally react with dissolved carbon dioxide (CO_2) to form carbonates (Berner et al., 1983), effectively capturing and fixing atmospheric C. Weathering involves leaching and transport of Ca^{2+} and Mg^{2+} in solution, some of which reacts with carbonate anions (depending on pH, as H_2CO_3, HCO_3^- and CO_3^{2-}) formed by CO_2 dissolution in soil pore waters, or in the surface ocean, to precipitate pedogenic (soil-formed) and marine carbonates. This process contributes to the stabilisation of

atmospheric CO_2 concentrations over geological timescales (Berner et al., 1983; Berner and Lasaga, 1989) and forms pedogenic carbonates in both natural (Nettleton, 1991) and artificial soils (Renforth and Manning, 2011). A simplified version of the carbonation reaction for artificial calcium silicates is given in Reaction 1.

$$CaSiO_3 + CO_2 + 2H_2O \rightarrow CaCO_3 + H_4SiO_4. \tag{1}$$

By this reaction, C is captured and stored. It has been proposed that through addition of Ca and Mg-rich silicates to soils it may be possible to promote the accelerated draw-down and storage of CO_2 from the atmosphere as relatively stable carbonate minerals (Schuiling and Krijgsman, 2006; Manning, 2008). Recent research has found that this process occurs in urban brownfield soils where Ca-rich demolition waste derived from cement mortar is mixed into the soil profile (Renforth et al., 2009). Isotopic analysis of carbonate C and oxygen (O) shows that pedogenic carbonates in urban soils have similar isotopic compositions to carbonates from natural soils in which photosynthesis contributed to their formation (Cerling, 1984), and confirms that a significant proportion of the C has been captured from the atmosphere (Wilson et al., 2009; Renforth et al., 2009). This may be a characteristic phenomenon of urban brownfield

sites and other anthropogenic soils, as construction activities in urban soils usually involve addition of Ca/Mg-rich substrates. If added to such soils, construction and demolition (C&D) waste, fly ashes, iron and steel slag etc. may enhance C capture and storage in the urban environment (Renforth et al., 2009, 2011a, 2011b; Morales-Flórez et al., 2011), thus the value of materials which may otherwise be regarded as 'wastes' is increased. In principle, carbonation of these materials could be used to offset the C emissions associated with their production. There is potential for C capture and storage to become a routine design consideration in the engineering of anthropogenic soils, with minimal additional energy input, little change in current management practise and minimal translocation of materials.

1.1. Mineral carbonation for carbon capture and storage

The use of Ca/Mg-rich wastes for C sequestration (especially capture) has been extensively considered (e.g. Huijgen et al., 2005; Rawlins et al., 2008; Huntzinger et al., 2009; Gunning et al., 2010). This work has largely focused on carbonation in batch reactors, where elevated pressure and/or temperature is applied to accelerate dissolution/corrosion of a Ca/Mg silicate or oxide, leading to carbonate precipitation (Lackner et al., 1995; Huijgen and Comans, 2006). This may also involve pre-treatment of the material (grinding, heat treatment etc.) to accelerate dissolution. The efficacy of the carbonation reaction has been demonstrated (Huijgen et al., 2007), but pilot scale studies have yet to be implemented. Acceleration of capture and storage by wastes in passive in situ settings, soils and open-air stockpiles, is an alternative low energy process (Renforth et al., 2009; Wilson et al., 2009). At present there is insufficient available information concerning material fluxes to permit comprehensive quantitative assessment of global C capture and storage potential. An estimate of slag, construction and demolition waste, pulverised fuel ash and quarry fines production since the 18th century is provided in Renforth et al. (2011b); overall these materials have the potential to collectively capture 190–332 Tg C yr^{-1}. Globally 7–17 Pg of waste silicates suitable for this purpose are produced each year, and so there appears to be a considerable incentive to develop and assess procedures that harness this potential. Further understanding of the settings in which the natural carbonation reaction is promoted must be developed through an understanding of soil C storage processes.

1.2. Carbon storage in soils

The potential of soils to store C has long been recognised (IPCC, 1996; Lal, 2004), however, the magnitude and significance of this store have only recently been quantitatively estimated (Smith et al., 1997; Smith, 2004). In a global context, soils are now recognised as an important potential tool for mitigation of rising atmospheric CO_2 concentrations. The 1997 Kyoto Protocol highlighted soils as a 'major carbon store' and recognised that processes underlying soil function should be considered in CO_2 emissions accounting. In the UK, DEFRA's Soil Strategy documents (2009) highlighted a pressing need to 'develop a better understanding of steps that can be taken to protect or enhance levels of soil carbon'.

Total carbon content in soil is a combination of organic compounds and inorganic carbonate minerals, which are consumed, produced and mobilised by biotic and abiotic processes. While total carbon content usually refers to that contained in solid matter, there is a substantial proportion that is turned over rapidly through the soil solution (organic acids, dissolved carbonate species) ultimately becoming CO_2 in the gaseous phase (Manning, 2008). Organic carbon in soils is functionally differentiated into labile (rapid turnover) and recalcitrant (slow turnover) pools, with differing chemical reactivity and residence times, ultimately derived from photosynthesis (Sohi et al., 2001). Inorganic carbon storage in soils is dominated by Ca- and (to a lesser extent) Mg-carbonates (Schlesinger, 1982).

There is a wide acceptance that the preservation of soil organic matter (SOM) is critical in maintaining soil carbon stores, which may be increased through effective management (Kyoto Protocol 1997; EU Soil Framework Directive 2006), especially in agricultural soils, many of which are net C sources to the atmosphere. Research on the potential impact of preserving or increasing the inorganic C pool has been limited by the scarcity of data relating to the formation of soil carbonate in temperate climates (Rawlins et al., 2011). The significance of soil inorganic C storage may have been historically underestimated due to the belief that pedogenic carbonates, formed by mineral carbonation, were not widespread phenomena, tending to be a feature of arid soils (Jenny, 1980). However, recent work has identified pedogenic carbonates in temperate regions (Boguckyj et al., 2006; Łącka et al., 2008). In both natural and anthropogenic soil, carbonates appear to form readily in the presence of Ca/Mg source materials.

1.3. The importance of urban soils

Extensive urban areas are now a global phenomenon, with the world's urban population projected to increase by 1.76% yr^{-1} between 2009 and 2025 (UN, 2009), reaching 6.3 billion people by 2050, and then representing ~69% of the world's population. As urban areas grow in magnitude and complexity, an understanding of the environment which supports them becomes critical to ensuring sustainable growth and maintenance of ecosystem services, benefits provided by the natural environment. Urban soils are the basal component of built and green infrastructure within cities and are a critical element of the urban ecosystem. As noted by Lehmann and Stahr (2007), they can be seen as a fundamental ecological asset for land-use planning and are critical in urban landscaping. Physical and chemical development of urban soils often differs from their rural counterparts and may include extensive excavation, emplacement, compaction or translocation (Rosenbaum et al., 2003). It may also include the addition of anthropogenic or technogenic materials, some of which may be considered contaminants or pollutants (Lorenz and Lal, 2009). Urban soils, however, are also subject to the same pedogenic influences as 'natural' soils (e.g. climatic, hydrological). Soil forming processes in urban soils may occur at different rates and be mediated by agents within the urban environment which are not present in natural settings, e.g. translocation by pedestrian footfall rather than excavation by natural fauna (Effland and Pouyat, 1997). Soil scientists generally accept that these complex formation histories create 'manipulated' soils which function differently from soils in the 'natural' landscape (Craul, 1992). Although they are frequently grouped with natural soils (Lehmann and Stahr, 2007), agricultural soils can also be regarded as a class of non-urban anthropogenic soils, with complex histories of human intervention where organic C content is considered a particularly significant managed factor.

Urban soils provide an opportunity for in situ manipulation and monitoring of properties over well constrained, easily observable geographic areas. Much research on urban and anthropogenic soils has been 'comparative', focussing upon disparities in physical properties and the respective enhancement or depletion of nutrient cycling when compared to 'natural' counterparts (Yaalon and Yaron, 1966). The preparation and management of urban soils can have a detrimental effect on nutrient availability and organic C content (Scharenbroch et al., 2005). Pouyat et al. (2006) demonstrated the potential for soil organic carbon (SOC) to be significantly depleted through soil degradation in temperate urban settings, though it is proposed that urban soils under effective management regimes (with water and nutrient supplies) may actually act as effective C stores, possessing higher SOC than natural analogues (Kaye et al., 2005). Few studies have focussed on the potential for inorganic C capture and storage by mineral carbonation in urban settings (Manning, 2008; Renforth et al., 2009).