

Research Article

The Role of Sorption on Mineralization of Carbon in Soils

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Submitted: 27 August 2013

Accepted: 30 September 2013

Published: 02 October, 2013

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Abstract

There is a general consensus that soil organic carbon (SOC) stabilization and destabilization processes are mainly controlled by three major mechanisms: recalcitrance of C inputs, physical protection and chemical protection. However, integration of these mechanistic processes for accurate simulation of SOC-climate feedbacks is still in infancy, partly due to the lack of process-level experimental data. We conducted 8 hour sorption experiments and 1 year decomposition experiments in order to understand the linkages between sorptive chemical protection and C stabilization. We eliminated physical protection by using the fine (silt- and clay-sized) fraction of soils. Four uniformly-labeled ^{14}C substrates (glucose, cinnamic acid, starch and stearic acid) were added to a temperate Mollisol and a sub-arctic Andisol. The maximum sorption capacity (Q_{\max}) followed the order: glucose < cinnamic acid < starch < stearic acid. After 1 year of incubation, the cumulative mineralization of added C was inversely related to the Q_{\max} (stearic acid < starch < cinnamic acid < glucose). We found evidence for a link between C stabilization and chemical sorption, but we could not eliminate the role of chemical recalcitrance. By conducting the experiment on the fine fraction, we ruled out the possibility of physical protection to promote C stabilization in our soils. This study highlights the absence of data in the literature that can be used to predict the stabilization of organic compounds in SOC.

Keywords

- Soil organic carbon
- Decomposition
- Stabilization
- Sorption
- Fine fraction
- Glucose
- Cinnamonic acid
- Starch
- Stearic acid

INTRODUCTION

Soil is the largest terrestrial carbon (C) pool, which consists of 2500 Pg of organic carbon (OC) to 1-m depth [1]. As the size of soil OC (SOC) pool is large, even a small change in biotic and/or abiotic controls on C decomposition could cause dramatic impacts on the concentration of CO_2 in the atmosphere and alter the potential for global warming. The rate of SOC decomposition is controlled by three key mechanisms: (i) recalcitrance, i.e. selective preservation of OC compounds which are structurally resistant to decomposition, (ii) physical protection, i.e. inclusion of OC in aggregates which become spatially inaccessible to microbial activity, and (iii) chemical protection, i.e. specific sorption reactions of OC with reactive soil minerals which reduces their bioavailability [2-4].

Chemical protection through sorption is considered to be one of the major mechanisms of SOC stabilization and it occurs through various chemical bonds between organic functional groups and charged mineral surfaces and/or with other organic functional groups already sorbed onto the mineral surfaces. The extent of sorption depends on the properties of both sorbents and sorbates. Strong correlations were reported between Fe

and Al oxyhydroxides and C sorption capacity of soils [5,6]. Initial C content of soils was also positively correlated to the subsequent sorption of additional C [7]. Mayes et al. [8] analyzed 213 representative subsoil samples from three major soil orders (Mollisols, Ultisols and Alfisols) of US for their sorption capacities to a natural dissolved organic matter (DOM) solution and reported that sorption capacity of Ultisols and Alfisols was correlated strongly with clay and Fe content, and sorption capacity of Mollisol was correlated strongly with OC content. Properties of sorbate compounds also control the extent of sorption. Hydrophobic compounds in general exhibit higher sorption than hydrophilic compounds [9-11]. Nonetheless, most past studies used natural, complex DOM as the sorbate. Only a few studies specifically focused on understanding the interaction of individual sorbate functional groups on mineral surface and those studies concluded that the properties of C sorbates are equally important as the properties of soil sorbents in controlling sorption reactions [12-15].

The chemistry of sorbate compounds imparts a profound influence on the extent of sorption, but we don't know how differential sorption affects the extent of bioavailability. Past studies provided some evidence that sorption processes are

responsible for reducing the microbial degradation of DOM [16,17]. Since those studies used natural heterogeneous DOM as sorbate, the type of C functional groups that resisted or responded slowly to biodegradation can't be discerned. This information is very important as new generation ecosystem models are beginning to consider parameters specific to individual classes of C compounds [18,19]. In this study, our objective was to understand the relationship between the sorptive protection and microbial decomposition of several C compounds predominant in natural DOM. We hypothesized that the bioavailability of OC compounds is inversely related to their ability to sorb onto soil minerals.

MATERIALS AND METHODS

Soils and fractionation

Two soils were used for this study, a Mollisol from Illinois, USA and an Andisol from Reykjanes, Iceland. Soils from top 15 cm were collected, air-dried and sieved to < 2 mm. Since OC is primarily adsorbed to the silt and clay-sized fine fraction (<53 μm) of soils, we conducted the sorption and decomposition experiments in the fine fractions isolated from the soils. Further, the separation process likely destroyed soil aggregates and thereby eliminated protection against microbial decomposition via aggregate protection. The fine fraction was isolated from <2 mm soil following a size-based fractionation protocol modified from [20]. 25 g soil was taken in a 250 mL polyethylene bottle, mixed with 125 mL deionized water and 25 glass beads of 4 mm diameter, and shaken on a reciprocal shaker for 16 hours. The fine fraction (silt+clay-sized) was separated from the coarse fraction (sand and plant residues) by wet sieving the soil suspension through a 53 μm sieve, and oven drying at 60 $^{\circ}\text{C}$.

Carbon compounds

Four uniformly-labeled synthetic compounds were used in this study: ^{14}C -glucose, ^{14}C -starch, ^{14}C -cinnamic acid and ^{14}C -stearic acid. These compounds are considered as biochemical markers for simple sugars, polysaccharides, phenolic compounds and fatty acids, respectively, present in soil organic matter (SOM). ^{14}C -glucose, ^{14}C -starch and ^{14}C -stearic acid were purchased from PerkinElmer and ^{14}C -cinnamic acid was purchased from ARC, Inc.

Sorption experiments

A range of concentrations (1 to 100 mg L^{-1}) of OC solutions were prepared using unlabeled glucose, starch, cinnamic acid and stearic acid, and these solutions were spiked with 4440 disintegration per minute mL^{-1} of corresponding ^{14}C labeled compounds. Batch experiments were conducted for 8 hours using 0.5 g fine fraction and 30 mL of OC solutions, and the supernatants were collected after centrifuging the mixtures. Shaking time of 8 hours was chosen because preliminary kinetic tests ranging from 1 to 24 hours revealed that the equilibrium sorption was reached after 8 h of shaking for all the compounds tested. Five mL of the supernatant were mixed with 10 mL of scintillation cocktail (Ultima Gold XR, PerkinElmer) and the ^{14}C activity in the soil solution was measured with a Packard Tri-Carb liquid scintillation counter. Based on ^{14}C measurements, the amount of OC sorbed onto the soil solids was calculated and sorption isotherms were generated. Maximum sorption capacity,

Q_{max} (mg C kg^{-1}) and binding coefficient k (L mg^{-1}) were calculated by fitting the isotherms to Langmuir equation [8,14,21]. The results are summarized in Jagadamma et al. [15].

Decomposition experiments

Three replicates of 25 g fine fractions from each soil type were placed in specimen cups, pre-wetted for 1 week at 40 % water holding capacity and added with 0.4 mg C g^{-1} fraction of each unlabeled C compounds (glucose, starch, cinnamic acid, stearic acid) and 296 Bq g^{-1} fraction of corresponding ^{14}C -labeled compound. These specimen cups were placed in 1L glass jars along with a glass tube containing 17 mL of 0.5N NaOH solution to trap the CO_2 respired from the samples. The jars were tightly closed and incubated in the dark at 20 $^{\circ}\text{C}$ at 50 % water holding capacity for one year. The CO_2 trapped NaOH solution was collected 15 times at periodic time intervals within one year of the experiment to determine $^{14}\text{CO}_2$ respiration. At each time point, 5 mL of the NaOH solution was mixed with 10 mL of scintillation cocktail and the ^{14}C activity was counted to determine the respiration of the added ^{14}C . Because the ^{14}C is a tracer for stable C, respiration and sorption will be referred to as C rather than ^{14}C .

Statistical analysis

Statistical analyses were conducted using SAS software from SAS Institute Inc. The analysis of variance (ANOVA) was conducted to test the difference in cumulative respiration and in sorption across the different substrates using the PROC GLM procedure (fixed effects model). Statistical significance was evaluated at $P \leq 0.05$.

RESULTS AND DISCUSSION

There was a significant effect of substrate type on the mineralization of added C of both soils ($P \leq 0.05$) with the respiration following glucose addition being the greatest and that following stearic acid being the lowest (Figure 1A, B). Respiration following cinnamic acid and starch were in between that of glucose and stearic acid. Across the substrate types, 37-69 % of added substrate was respired from Mollisol and 40-72 % was respired from Andisol within one year of incubation. During the initial days of experiment, the respiration rate was highly variable among substrates (Figure 1A inset, 1B inset). Within the first day, 17-28 % of C present in glucose and starch was mineralized; however the respiration of C from cinnamic acid was only 3-6 %. We observed a delay of several days to initiate the respiration of C from stearic acid. The respiration rate following glucose addition was consistent with previous studies [22-24]. Literature on the respiration of substrates other than sugars is limited. Orwin *et al.* [25] found that CO_2 efflux from sugars was greater than that from fatty acids and tannin.

A recent study of us demonstrated significant differences in the maximum sorption capacity, Q_{max} of two soils for the different compounds with Q_{max} follows the order: glucose < cinnamic acid < starch < stearic acid, where stearic acid is one or two orders of magnitude higher than the other compounds (STable 1) [15]. Stearic acid is a C-18 fatty acid with a hydrophobic methyl tail and hydrophilic carboxylic head, and its octanol-water coefficient (K_{ow}), a common measurement of the propensity to partition into a hydrophobic organic solvent over hydrophilic water, is much

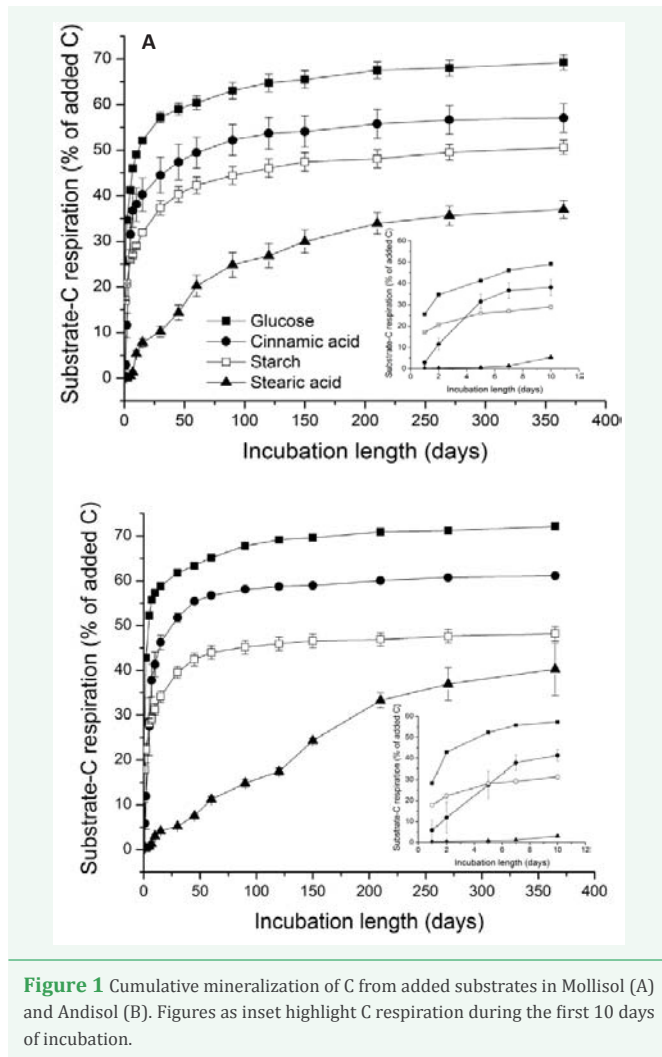


Figure 1 Cumulative mineralization of C from added substrates in Mollisol (A) and Andisol (B). Figures as inset highlight C respiration during the first 10 days of incubation.

higher than that of cinnamic acid and glucose. The $\log K_{ow}$ of stearic acid is 8.23, cinnamic acid is 2.25 [26], and glucose is -3.33 [27], which suggests that stearic acid will be more likely to partition into SOM than cinnamic acid, and cinnamic acid in turn is more likely to partition than glucose. Cinnamic acid is an aromatic compound with an extended carboxylic acid functional group, glucose is a simple monosaccharide, and starch is composed of glucose units linked by glycosidic bonds. The observed Q_{max} values are in agreement with the general understanding that the extent of sorption on mineral surface is greater for hydrophobic than hydrophilic compounds [10,11].

Q_{max} was inversely related to the cumulative mineralization after one year (Figure 2A, B). Glucose, which exhibited the lowest Q_{max} , was mineralized the most and stearic acid, which exhibited the highest Q_{max} , was mineralized the least. These results suggested that the extent of chemical binding of C compounds on the soil mineral phase imparts a negative control on biodegradation. By conducting sorption and mineralization experiments on the fine fraction instead of bulk soils, we eliminated the role of physical protection and aggregate formation on the rate of mineralization. To the best of our knowledge, no previous studies explored the linkages between the chemical sorption

and biodegradation of specific C compounds present in SOM. Though we found evidence for chemical protection mechanism of SOC stabilization, the possibility of biological recalcitrance, i.e., thermodynamic resistance to decomposition, of the compounds in our experiments cannot be ruled out. Glucose is more easily biodegradable than other compounds because it doesn't require enzymatic depolymerization before uptake by microbes [28], which might explain its susceptibility to decomposition in our experiments. Among enzymatically-depolymerized compounds there is a large range in the energy required to break bonds and produce a depolymerized compound for microbial uptake [29]. Thus, the differences observed here for stearic acid, cinnamic acid, and starch may involve both different degrees of sorptive protection and differences in thermodynamic resistance to depolymerization. More soil C models are emerging with novel approaches to incorporate mechanistic C stabilization processes for accurate simulation of feedbacks between soil C and climate [30-32]. The roles of sorptive protection and chemical stability will be important to distinguish in order to adequately predict C stabilization over a variety of time frames. Clearly, these efforts for model refinement will benefit from more experimental data on mineralization parameters specific to distinct stabilization mechanisms.

CONCLUSION

We found an inverse qualitative correlation between sorption

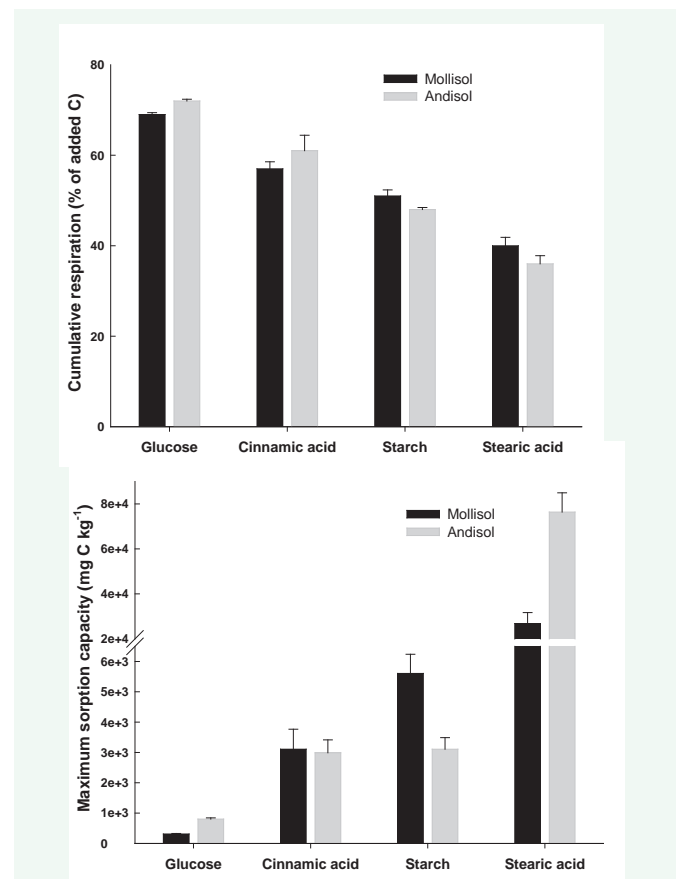


Figure 2 Comparison of one year cumulative mineralization of C from added substrates (A) and the maximum sorption capacity of fine fractions (B).

and mineralization for four different substrates. The confounded effect of physical aggregation on C protection was eliminated in this study by using the silt and clay-sized fine fraction as the sorbent, but we could not separate the role of chemical recalcitrance from sorptive protection. Future studies could focus on understanding the extent of chemical recalcitrance of the C substrates by inoculating the dissolved form of the substrates with a microbial culture extracted from the same soil and quantifying the $^{14}\text{CO}_2$ evolution from the substrates alone (without contacting with sorbents) over time.

ACKNOWLEDGMENTS

This research was funded in part by the Laboratory Directed Research and Development (LDRD) Program of the Oak Ridge National Laboratory (ORNL) and by the U.S. Department of Energy Biological and Environmental Research program. ORNL is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725. We thank Julie Jastrow and Guðrún Gísladóttir for providing soil samples, and Chad Covert and Jennifer Dabbs for help with laboratory analyses.

This manuscript has been authored by UT-Battelle, LLC, under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

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Cite this article

Jagadamma S, Mayes MA (2013) The Role of Sorption on Mineralization of Carbon in Soils. *JSM Environ Sci Ecol* 1(1): 1005.