

Effect of Coating Phyllosilicate Clays with Hydrrous Oxides on Organic Carbon Stabilisation

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the degree of Doctor of Philosophy

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Abstract

Phyllosilicate clays and hydrous oxides are recognised as important minerals in soils for organic carbon (OC) stabilisation. Most studies on the influence that hydrous oxides have on OC stabilisation have been carried out using different soils that contain different amounts of Fe or Al oxides or in experiments where OC stabilisation was measured separately on phyllosilicate clays and oxides. Consequently, the interactive effect of different types of phyllosilicate clays and hydrous oxides on OC stabilisation remains poorly understood. In this work, a series of experiments was carried out to obtain a better understanding of the effect of different phyllosilicate clays on OC stabilisation in the presence and absence of different hydrous oxides.

In the first set of experiments, stabilisation of plant-derived OC by three different phyllosilicate clays (kaolinite, illite, smectite) with and without goethite coating and illitic clay coated with different oxides (goethite, haematite, ferrihydrite, imogolite) was quantified by measuring mineralisation of added OC to these clays or clay-oxide associations in a model system consisting of sand mixed with clay. The amount of OC added to mineral was the same for all treatments (5 mg C g^{-1} sand-clay mixture). These conditions correspond to a relatively high OC loading, such as may be experienced in top soils in highly productive systems (i.e. lots of vegetation). Experiments were carried out under moist soil conditions of $\sim 70\%$ water-filled pore space; under these conditions OC mineralisation should not be limited by availability of water or oxygen. For uncoated clays, OC stabilisation increased in order kaolinite < illite < smectite. It was found that the stabilisation of OC for kaolinite increased with goethite coating; this effect was not observed for illite- and smectite-oxide associations. For illite coated with different oxides, only ferrihydrite increased OC stabilisation over the illitic clay alone. Increasing OC stabilisation for these oxide-coated clays was related closely with increasing specific surface area (SSA). These results demonstrate that there is a clear effect of oxide coating on OC stabilisation that varies with the mineralogy of phyllosilicate clays and type of hydrous oxides and that

under the conditions of this set of experiments, mineral surface area is the dominant factor.

In these experiments the progress of mineralisation over time was closely monitored. Fitting cumulative C mineralisation data to a two-pool C mineralisation model revealed that where the OC stabilisation increased in the presence of oxide-hydroxides, there were reductions in the size of both slowly and rapidly mineralisable C pools. This demonstrates that OC stabilisation was brought about by an increase in the size of undecomposable pool rather than changes in the rates of decomposition of either pool.

It has been suggested that the interactive effect of phyllosilicate clays and oxides on OC stabilisation is controlled by the capacity of clay-oxide associations to sorb dissolved OC. Therefore, a second set of experiments was carried out to assess the effect clay-oxide associations on the sorption of plant derived-OC. The sorption capacity of clays increased in the order kaolinite < illite < smectite on a mass basis or illite < smectite < kaolinite on a surface area basis. Goethite coating on kaolinite increased the sorption of dissolved OC while the sorption capacity of illitic and smectitic clays was not influenced by goethite coating. For illitic clay coated with three different hydrous iron oxides (goethite, haematite, ferrihydrite), an increase in the sorption capacity of dissolved OC was observed only for illite-ferrihydrite associations. Increases in the sorption capacity of dissolved OC were most evident for clay-oxide associations involving either a low-charge clay or high surface area oxide. Desorption experiments showed that only 6-14% of the initially sorbed OC by mineral associations was released by a single extraction step. Coating phyllosilicate clays with hydrous iron oxides reduced desorption of clays, but the effect was most evident for the kaolinite-goethite and illite-ferrihydrite associations. It is likely that the net charge of oxide-coated clays, which is influenced by the balance between the negative charge of phyllosilicate clays and the positive charge of hydrous iron oxides, was crucial for performance of clay-oxide associations in the sorption and desorption of dissolved OC. These experiments showed that differences in OC stabilisation observed in the first set

of experiments were closely related to the sorption capacity of the clays and oxide-coated clays. However, these experiments also showed that the strength of sorption of OC to the minerals, as reflected in the amount of DOC that could be desorbed in a single extraction, varied in a different order among the mineral assemblages and appeared to be related to surface charge rather than specific surface area. This suggests that the degree of OC stabilisation afforded by the assemblages may be quite different at low OC loadings than at high OC loadings.

A third set of experiments was conducted to investigate OC stabilisation at low OC loadings, such as may be experienced in many sub-soils. In these experiments, OC was pre-sorbed onto clays and oxide-coated clays under batch sorption conditions of equal initial solution OC concentration. This resulted in systems with different OC loading on a mass basis, but loadings that were approximately proportional to the sorption capacity of mineral assemblages. In these experiments, incubations were performed “wet”, with 0.5 – 1.g solid in 20 mL nutrient solution; treatments were kept oxic though intermittent shaking. Goethite coating increased the stability of OC sorbed to kaolinite and smectite against microbial decomposition, while the stability of OC sorbed to illite did not change with goethite coating. Among the three hydrous iron oxides tested, only ferrihydrite coating increased the stability of illite-associated OC against microbial degradation. These result showed that under these conditions of low OC loading, the biological stability of OC sorbed to clay-oxide associations again varied with the mineralogy of phyllosilicate clays and the different hydrous iron oxides. In this case, however, the bioavailability of mineral-associated OC was significantly correlated with the reversibility of OC sorption and with the affinity of dissolved OC for clay-oxide associations, as measured in the batch sorption experiments of the second set of experiments on these systems. This suggests the degree of OC stabilisation at low OC loading is controlled by the strength of mineral-organo associations rather the surface area of the minerals.

Under conditions of low OC availability, microbial activity can be limited by energy availability to microorganisms. Under such conditions, the addition of a small amount

of readily available organic matter can increase the decomposition of the pre-existing but less available OC. This is known as a priming effect. In a fourth set of experiments, the stability of OC sorbed onto minerals against microbial degradation was determined in the presence of glucose at C levels equivalent to 1% and 10% of sorbed OC over a 120-day incubation. It was found that the total amount of C mineralised from clay–OC associations for all phyllosilicate clays increased with glucose addition. However, the net amount of C mineralised from clay–associated OC with glucose, which was determined by subtracting the amount of CO₂ produced in the corresponding glucose-only treatment, was not significantly different from that mineralised from clay–associated OC without glucose addition. This result suggests the absence of a priming effect of easily decomposable C source on the mineralisation of OC sorbed to phyllosilicate clays. Therefore, it can be concluded that mechanisms other than energy availability control the stability of OC sorbed to phyllosilicate clays against microbial decomposition.

Declaration

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Publications Arising from this Thesis

Saidy, A.R., Smernik, R.J., Baldock, J.A., Kaiser, K., Sanderman, J. and Macdonald, L.M. 2012. Effect of clay mineralogy and hydrous iron oxides on labile organic carbon stabilisation. *Geoderma* 173-174, 104-110.

Saidy, A.R., Smernik, R.J., Baldock, J.A., Kaiser, K., Sanderman, J. 2012. The sorption of organic carbon onto differing clay minerals in the presence and absence of hydrous iron oxide. Submitted.

Structure of this Thesis

This thesis is presented as a combination of papers that have been published, submitted for publication and chapters that have not been submitted for publication.

Chapter 1 provides an overview of the literature on the stabilisation of soil organic carbon (OC), the importance of clays and oxides for chemical OC stabilisation and the stability of sorbed OC against biodegradation. This chapter also includes the proposed objectives of this study.

Chapter 2 consists of a paper published in *Geoderma* (Saidy, A.R., Smernik, R.J., Baldock, J.A., Kaiser, K., Sanderman, J. and Macdonald, L.M. (2012) Effect of clay mineralogy and hydrous iron oxides on labile organic carbon stabilisation. *Geoderma*, 173-174, 104-110). It describes an incubation experiment used to determine OC stabilisation at a relatively high OC loading, such as may be experienced in top soils, by different phyllosilicate clays with and without oxide coatings.

Chapter 3 describes a second experiment that follows on from the incubation experiment described in Chapter 2. It describes the effects of coating clay mineral with hydrous iron oxides on the sorption of dissolved OC. These results have been submitted to *Geoderma*.

Chapter 4 describes experiments to determine the effects of the presence of hydrous iron oxides on the mineralisation of OC sorbed to phyllosilicate clays. It provides approach to investigate the stabilisation of OC at low OC loading, such as may be found in many sub-soils. These results have been prepared but not yet submitted for publication.

Chapter 5 comprises an incubation experiment used to provide additional explanation of relatively low C mineralisation of sorbed OC found in Chapter 4. It describes the mineralisation of OC sorbed to clay minerals in the presence and absence of easily decomposable C source. These results have been prepared but not yet submitted for publication.

Chapter 2, 3, 4 and 5 were prepared as standalone for publication. Therefore, this style of presentation results in some areas of repetition, particularly in the introductions, methods and reference lists.

Chapter 6 provides a summary of the findings contained in this thesis and includes recommendations for future work.