CLAY MINERALS AS THE KEY TO THE SEQUESTRATION OF CARBON IN SOILS

Gordon Jock Churchman[1] *, Mandeep Singh[2], Amanda Schapel[1,3], Binoy Sarkar[4], and Nanthi Bolan[5]

[1]School of Agriculture, Food and Wine, University of Adelaide, Adelaide, SA 5005, Australia
[2]Future Industries Institute, University of South Australia, Mawson Lakes, SA 5095, Australia
[3]Primary Industries and Regions South Australia, Rural Solutions SA, SA 5000, Australia
[4]Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK
[5]Global Centre for Environmental Remediation, University of Newcastle, Callaghan, NSW 2308, Australia

Abstract—Results from earlier laboratory and field experiments were interrogated for the possibilities of sequestration, or long-term accumulation, of carbon from excess greenhouse gases in the atmosphere. In the laboratory study, samples of three (top) soils dominated by kaolinite and illite (together), smectite, and allophane were examined for the adsorption and desorption of dissolved organic carbon (DOC). Adsorption and desorption of DOC were carried out on clay fractions extracted physically and after first native organic matter and then iron oxides were removed chemically. Labeled organic material was added to the soils to assess the priming effect of organic carbon (OC). In the field, changes in OC were measured in sandy soils that had been amended by additions of clay for between 3 and 17 years, both through incorporation of exogenous clay and delving of in situ clay. The laboratory experiments demonstrated that a portion of DOC was held strongly in all soils. The amount of DOC adsorbed depended on clay mineral types, including Fe oxides. Much adsorbed DOC was lost by desorption in water and a substantial amount of native OC was lost on priming with new OC. Addition of clay to soils led to increased OC. Therefore, addition of clay to soil may enhance net sequestration of C. Organic carbon close to mineral surfaces or within microaggregates is held most strongly. Carbon sequestration may occur in subsoils with unsaturated mineral surfaces. However, incorporation of carbon into macroaggregates from enhanced plant growth might be most effective in removing excess carbon from the atmosphere, albeit over the short-term.

Keywords—Adsorption · Clay amendment · Desorption · Delving · Dissolved organic carbon · Priming

INTRODUCTION

The Earth's climate is undergoing change, and the consensus is that the principal cause is the increase in the atmosphere of so-called 'greenhouse gases' from anthropogenic activities. In particular, carbon dioxide generated by the combustion of fossil forms of carbon (Le Quéré et al. 2009) and also methane, often generated by agriculture (Smith et al. 2008), are major sources of these gases in the atmosphere. These gaseous forms of carbon are also released into the atmosphere when formerly frozen sources such as Arctic permafrost regions are warmed (Schuur and Abbott 2011).

Many authors in the scientific literature (e.g. Stockmann et al. 2013; Minasny et al. 2017) have proposed that soil organic matter (SOM) can be used as a "managed" sink for atmospheric carbon gases and particularly carbon dioxide, through carbon sequestration. Politicians and others in public life have seen carbon sequestration as a solution to the problems that increasing emissions of these gases cause for the climate. A strong need exists, therefore, to assess the viability of the apparently useful role of SOM in halting or at least diminishing the advance of climate change.

The global stock of carbon in the soil as organic matter has been estimated as ~700 Pg to a depth of 30 cm and ~1500 Pg to

a depth of 1 m (Batjes 1996). The SOM to 30 cm depth represents about twice the amount of C in the atmosphere and three times that in above-ground vegetation (Powlson et al. 2011). Carbon as soil organic carbon (SOC) is particularly labile. Historically, the reservoir of C held in land has diminished drastically over decades, whereas that held in oceans, which is also labile and of a comparable size, has changed only a little (Lal 2014). The loss of C from land is attributable to agriculture. Many (e.g. Lal 2014) have concluded that, because C has been lost from their soils, managed agricultural soils have the capacity to replenish the losses and hence sequester C from the atmosphere.

The clay fraction of soils, comprising clay minerals (including metal oxides, oxyhydroxides, and hydroxides) is their most reactive fraction for forming associations with organic matter (Churchman 2010, 2018; Sarkar et al. 2018; Singh et al. 2018).

Several approaches have been used to investigate the importance of clay minerals in the uptake and retention, hence, potentially, the sequestration of carbon in soils (e.g. Churchman and Velde 2019). These include correlations of the contents of SOC with properties of soil clays, including their contents and their cation exchange capacities (CECs). Where narrow ranges of soil types have been studied, some good correlations have been obtained, but where the ranges are wider, Soil organic carbon contents and those of clays or their properties have been poorly correlated, if at all (Churchman

and Velde 2019). In tropical Australia (Spain 1990), such correlations were poor when soils originating from basalt were included, and a set of 167 soils taken from throughout New Zealand showed no correlation between SOC and clay fraction contents (Percival et al. 2000). The lack of a relationship between SOC and clay contents or properties was explained by the important roles played by compounds of Fe (Spain 1990; Percival et al. 2000) and Al (Percival et al. 2000), particularly when these were poorly crystalline (Percival et al. 2000).

Another approach to the study of mineral–organic interactions in soils is the fractionation of soils, either by particle density, selective chemical dissolutions, or physical disaggregation. These studies have confirmed the important roles played by Fe (Eusterhues et al. 2003, 2005) in the stabilization of SOC in many soils, and by Ca^{2+} in some (Oades 1989). In particular, leached, hence, generally acid, soils involve Fe and Al in the stabilization of C by bridging while Ca^{2+} is more involved in bridging with SOC in high base status soils (Oades 1989; Rowley et al. 2018).

Studies of incubations of soils revealed that clay minerals with the largest surface area, namely allophane and smectite, in the soils used had the strongest effect on the suppression of the decomposition of SOC (Saggar et al. 1996), while Rasmussen et al. (2007) found that poorly crystalline Fe oxyhydroxides strongly suppressed SOC decomposition.

These three approaches, together with others (e.g. Churchman and Velde 2019), have shown that clay minerals, including metal oxides, oxyhydroxides, and hydroxides, are important in the uptake and retention of SOC in soils. Even so, these studies do not provide an assessment of the strength and duration of the binding of SOM by soil minerals. Strong and long-term binding of SOM is required for the sequestration of carbon in soils.

"Sequester" is defined as "to hold on to" or "to keep separate" (Powlson et al. 2011). In the chemical or environmental context, sequestration means "the trapping of a chemical in the atmosphere or environment and its isolation in a natural or artificial storage area" (Dictionary.com 2019). The sequestration of organic C in soils is generally taken to mean the retention of SOC for a "stipulated duration timeframe (usually 100 years)" (Stockmann et al. 2013). The most useful meaning for carbon sequestration for a decrease in greenhouse gases in the atmosphere is given by a net gain of SOC. This represents "new" sequestration of carbon.

Several recent experiments (Singh et al. 2016, 2017a, 2017b, 2019; Schapel et al. 2018) were carried out to help assess or improve the effectiveness of soils for the uptake and retention of OC. Experiments were carried out in the laboratory and also in the field.

The laboratory experiments included determinations of the stabilization of OC by clay minerals as they occur in soils, in contrast to clay minerals from deposits, as determined by Saidy et al. (2012). Clay minerals originating in soils can have quite different properties from "pure" clay minerals from deposits (Churchman 2010; Churchman et al. 2012; Churchman and Lowe 2012; Churchman and Velde 2019).

The field experiments were based on a common agricultural practice in much of the States of South Australia and Western Australia where sandy soils often become hydrophobic in summer in the xeric moisture conditions prevailing in these areas. A practical solution to this problem has been to add clay to the soils (McKissock et al. 1998; Cann 2000; Churchman et al. 2014; Churchman and Velde 2019). Initially, clay-rich material was incorporated in the surface soils but, because most of the soils concerned are texture-contrast types having sandy topsoils over clay-rich subsoils, the common practice now is to obtain clay for incorporation in surface soils via mechanical deep ripping, a process known as "delving" (Betti et al. 2015).

The results of these various experiments have enabled an assessment of the potential of soils to take up and retain added OC, especially in relation to their clay mineral composition. Reference to the literature has also pointed to likely causes of limitations on carbon uptake and retention in soils.

In this paper, some of the important results and conclusions of these various recent experiments, particularly from Singh (2016), Singh et al. (2016, 2017a), and Schapel et al. (2018), are highlighted and assessed together with results from earlier work, especially Churchman et al. (2014), as indicators of the prospects for (new) carbon sequestration in soils.

The hypothesis is that clays, as the most reactive inorganic compounds in soils, ultimately govern the prospects for sequestration of organic carbon in soils.

LABORATORY EXPERIMENTS AND RESULTS

Three soils were studied: a Calcic Haplosteralf, a Pellustert, and a Thaptic Haploxerand, according to Soil Taxonomy (Soil Survey Staff 1975) (Singh et al. 2017b). Respectively, these were dominated by kaolinite and illite (together), smectite, and allophane (Singh et al. 2016). The OC added to soils in these experiments was in liquid form, as dissolved organic carbon (DOC), produced by dissolving ground wheat straw in water. Experiments were performed to assess the capacities of three different soils to: (1) adsorb DOC, (2) retain adsorbed DOC in the presence of water (or "desorb DOC") (Singh 2016, Singh et al. 2016), and (3) mineralize added carbon and limit the decomposition of adsorbed DOC to carbon dioxide by the "priming effect" (Singh et al. 2017a).

Adsorption Experiments

Adsorption experiments were performed on clay (<2 μm) fractions extracted from the soils (at 5–20 cm depth) following prolonged shaking in Milli-Q water then gravity sedimentation. Hence, both minerals and organic matter in clay-sized material were preserved in the collected fractions. The soils, all from South Australia, were characterized by their dominant clay minerals: (a) kaolinite and illite together, (b) smectite, and (c) allophane (Singh et al. 2016, 2017b). Adsorption was carried out at pH 7 in solutions of Ca or Na nitrate, either 0.1 or 0.01 M, for 24 h, and DOC in solution was analyzed after filtering. See Singh et al. (2016) for details.

The various clay minerals adsorbed DOC to various extents. All sorption isotherms (for natural clay fractions, clay

fractions after OC removal, and clay fractions after iron removal following OC removal) followed the Langmuir model (Singh et al. 2016). Results of maximum OC adsorption by the clay fraction of each soil are summarized in Table 1 for the following conditions: untreated, after organic carbon removal, and after iron removal following organic carbon removal. These data are from adsorption in 0.01 M $Ca(NO_3)_2$, a concentration likely to represent closely typical soil solutions (Blakemore et al. 1987). Analyses of total C and specific surface areas, before and after chemical treatments, as well as Fe contents of the untreated clay fractions (from Singh 2016) are also included in Table 1. Similar trends were observed for the nitrate solutions differing in terms of Ca or Na content and with different concentrations (0.01 or 0.1 M). The sorptive capacities of all clays were increased when native OC was removed and were reduced when Fe was removed.

Desorption Experiments

Clay fraction samples taken from the adsorption experiments at various levels of equilibrium concentrations of DOC were first washed with Milli-Q water to remove entrained DOC, then equilibrated for 24 h, and supernatants were analyzed for DOC after filtering. See Singh et al. (2016) for details.

The percentages of adsorbed C that were desorbed in water from each clay fraction (i.e. without treatment, after OC removal, and after iron removal following OC removal) in relation to the amounts of DOC added in the adsorption experiments are shown in Table 2. These data are from adsorption in 0.01 M $Ca(NO_3)_2$. Similar trends were observed for desorption from clay fractions following adsorption from either Ca or Na nitrate solution regardless of concentration (0.01 or 0.1 M) (Singh et al. 2016).

More than 30% of the C adsorbed in Ca nitrate and more than 50% of that adsorbed in Na nitrate was released on simple desorption in water (Singh et al. 2016). The proportion of adsorbed C that was desorbed was greatest for the kaolinite-illite clay, less for the smectite clay, and least for the allophanic clay, but even in this last case, ~20% of that adsorbed in Ca nitrate and ~30% of that adsorbed in Na nitrate was lost on desorption in water. In each case, the proportion of adsorbed C that was lost on desorption increased when DOC adsorption had been performed on clays from which Fe oxide was removed and diminished when adsorption had occurred on clays from which native C was removed.

Effects of Priming

Samples of the whole soils that had been sieved to <2 mm to remove coarse particles were equilibrated with ^{14}C-labeled malic acid and also unamended in sterile Milli-Q water. CO_2 from respiration was collected at different time periods in a solution of NaOH and the unconsumed alkali was determined by titration with HCl. See Singh et al. (2017a) for details of the experiments and calculations.

The results showed that more C was lost (as CO_2) from all soils after priming with malic acid (Singh et al. 2017a). However, the extent of loss on priming depended on the mineralogy of the soils, with more C lost from the smectite soil than from the soil dominated by illite-kaolinite and the allophanic soil. These two latter soils had similar losses on priming. Decomposition of native C increased by 108% in the smectitic soil upon priming and by 37% in the kaolinitic-illitic soil and 42% in the allophanic soil (Singh et al. 2017a).

FIELD EXPERIMENTS AND RESULTS

Soils in South Australia that were classified as Luvisols in the World Reference Base (Michéli and Spaargaren 2012) were studied at four sites where clay amendments had been carried out. All soils were texture-contrast types. Farming systems in all sites were rotations of cereal and grazed pasture, using minimum or no tillage and stubble retention. At each site, the soil had been amended by both incorporation of clay-rich soils from subsoils within pits dug nearby and also by deep incorporation in situ using mechanical means. Trials were sampled at depth intervals to 50 cm after at least 3 years following treatments. See Schapel et al. (2018) for detailed descriptions of the sites and processes used for clay amendment.

Soils were sampled during the non-growing phase as cores from various depths. They did not contain gravel so were ground to pass a <2 mm sieve. Homogenized samples were analyzed for OC by Walkley-Black wet digestion and bulk densities were determined gravimetrically for known volumes of soil. See Schapel et al. (2018) for details of the methods.

Schapel et al. (2018) found that the stock (or reservoir) of OC was significantly and positively correlated ($R^2 = 0.47$) with the stock (or reservoir) of clay when these values were adjusted to an equivalent soil mass (ESM) from bulk density determinations.

The results showed that OC stock (or reservoir) in the surface (0–30 cm) of 14 clay-amended soils increased on average by 5.5 Mg C ha^{-1} (range –1.6 to 14.2 Mg C ha^{-1}) from unamended sands, with the increases brought about largely by increases in clay content. Clay and OC were concentrated at the surface in clay-spread treatments and at depth in delved treatments (Schapel et al. 2018).

DISCUSSION

Organic carbon in solution is adsorbed by soils to various extents, and especially by their most reactive clay fractions and depending on their clay mineral composition. The uptake of OC correlates with the specific surface area of the soil clay fractions (Table 1). Uptake of OC was increased by the presence of iron oxides, as also demonstrated by Kahle et al. (2003, 2004). Some organic matter in natural soils is held particularly strongly, and, notwithstanding that a small fraction was even resistant to peroxidation, the oxidation of OC enables further uptake. Other workers, e.g. Kaiser and Guggenberger (2003) and Mikutta et al. (2005), have also found that some OC is held particularly strongly in soils. The strongly held portion may be located within small pores (McCarthy et al. 2008).

Desorption shows that considerable organic matter was easily lost in water (Table 2). OC was held more strongly, i.e.

Table 1. Maximum amounts (mg g^{-1}) of DOC adsorbed in 0.01 Ca (NO$_3$)$_2$ by the clay fractions of soils with various dominant minerals in relation to their contents of C and Fe and their specific surface areas (SSAs) calculated using the BET equation for adsorption by N$_2$ gas (data from Singh 2016).

Dominant clay type	Treatment	C (mg kg^{-1})	Total Fe	SSA (m^2 g^{-1})	Max. adsorbed (mg g^{-1})
Kaolinite + Illite	None	15	1.6	55	22.0
"	Removal of C	4	–*	69	29.2
"	Removal of C + Fe	2	–*	39	16.9
Smectite	None	23	1.2	74	50.2
	Removal of C	3	–*	93	77.5
	Removal of C + Fe	1.2	–*	60	36.9
Allophane	None	130	7.5	119	101
	Removal of C	32	–*	140	123.5
	Removal of C + Fe	15	–*	90	71

*Not determined

less was released on desorption, after removal of native OC had occurred prior to its uptake. OC was held less strongly when Fe oxides were removed prior to its uptake. Nonetheless, much adsorbed OC was quite labile. Kahle et al. (2004), Mikutta et al. (2007), and Saidy et al. (2013) found that OC adsorbed on pure clay minerals included a substantial portion that was lost easily on desorption.

The results of the priming experiments showed that, for all the soils, addition of extra OC led to an enhanced release of CO$_2$ due to stimulation of microbial activity, hence respiration. Singh et al. (2017a) attributed the greater effect of priming in the smectitic soil than in the allophanic soil or the soil dominated by kaolinite and illite to the higher microbial activity which they measured for the smectitic soil. Even so, priming, showing breakdown of SOC, occurred even in the allophanic soil, where OC was held more strongly against desorption than in the other two soils studied. This confirms the results of Finley et al. (2018), who found a high rate of decomposition of native OC in soils comprising the short-range order minerals, allophane and ferrihydrite.

Field experiments (Schapel et al. 2018) demonstrated that both direct incorporation of added exogenous clay and 'delving' of in situ clay resulted in an increase in SOC content. Increases in SOC were also observed in Western Australia 8 years after additions of subsoil kaolinitic clay to sandy topsoils by delving (Hall et al. 2010). The top 10 cm of soil contained only 1% clay, which increased to 6% clay on delving. The increase in SOC was 0.2%. In South Australia, Bailey and Hughes (2012) found that delving soils in 11 sites increased the mean SOC contents of their A2 horizons from 0.3% to 0.7%, Other clayey material can also enable increases in SOC, and wastes from bauxite processing (85% silt, 11% clay, and 4% sand) were added to sandy soils in Western Australia (Harper et al. 2012; Churchman et al. 2014). Over a 19–20 year period, addition of this waste led to increases in SOC in the top 30 cm of soil of between 0.1 to 0.65%, resulting in a significant ($P<0.01$) increase of 11.6 Mg C ha^{-1} across the sites with a strong ($r^2 = 0.93$, $P<0.001$) curvi-linear correlation between clay content and SOC for the 0–5 cm layer (Churchman et al. 2014). This amounts to an annual uptake of 1.9 Mg CO$_2$-eq. ha^{-1} year^{-1}.

Table 2. Percent desorption of DOC in water after its adsorption in 0.01 Ca (NO$_3$)$_2$ at various loadings from the clay fractions of soils with various dominant minerals sequentially treated to remove native C and Fe (data from Singh 2016).

Dominant clay type	Treatment	Loading of DOC for adsorption (mg g^{-1})					
		25	50	75	100	150	200
		Percentage of adsorbed C that was desorbed in water					
Kaolinite + Illite	None	16	16	20	29	34	34
"	Removal of C	12	14	17	23	28	28
"	Removal of C + Fe	18	17	23	32	40	40
Smectite	None	6	12	17	23	28	28
	Removal of C	10	10	12	17	23	23
	Removal of C + Fe	12	12	15	22	31	31
Allophane	None	7	11	14	16	24	24
	Removal of C	6	7	7	12	15	15
	Removal of C + Fe	12	12	15	20	27	27

Implications for Carbon Sequestration in Soils

Carbon is turned over – and lost from the soil system – through the biological processes needed for soil functioning in agriculture (e.g. Janzen 2006). Sequestration of C through long-term storage and the use of soil for growing plants appear to have conflicting aims. For example, Bolan et al. (2012) concluded that amending soils with biochar, which is more stable than composts, could enhance soil carbon sequestration (long-term carbon storage) but this carbon might not be useful for an immediate improvement of soil health, such as for supplying food to soil microorganisms for keeping the nutrient cycling operational. Following Janzen (2006), the most efficient way of extracting extra carbon as CO_2 from the atmosphere may be by using it more rapidly for increasing plant production, hence flow-through of SOM.

Increased adsorption which occurred when native C was first removed from all soils (Singh et al. 2016) shows that some C had occupied the most reactive sites. The results from desorption (Singh et al. 2016) show that further C occupied less reactive sites in all soils and was easily removed. The effect of priming (Singh et al. 2017a) shows that simple addition of new C to soils may result in the loss of C that is already present. Overall, these results show that simply adding new C to soils that already contain C does not result in additional C that is held strongly, i.e. sequestered.

However, the addition of clays to soils can enable the net uptake of C. Furthermore, the rate of incubation of wheat residues added to a sandy soil was retarded by the addition of the clay fractions used in the studies of sorption of DOC (Singh et al. 2019). The addition of clay produces new surfaces for holding C.

According to Churchman and Velde (2019, p. 152), "SOC can be associated with almost any secondary (and also altered primary) minerals, but shows a preference for poorly crystalline oxides and also silicates of Fe and Al." If these are rare, SOC binds to phyllosilicates according to their relative surface reactivities, with smectites being the most reactive of these. pH also plays a role in governing reactivities of minerals for SOC. Low pH favors Fe and Al compounds and higher pH favors phyllosilicates. The type, hence strength, of these associations also varies with pH. Associations between SOC and minerals tend to be inner-sphere, hence stronger, at low pH and outer-sphere at high pH (Kleber et al. 2015).

Various functional groups in organic matter can be bound to minerals in layers. Proteins and molecules containing carboxyl groups occur commonly adjacent to mineral surfaces while molecules containing hydrophobic groups tend to occur in outer layers (e.g. Kleber et al. 2007). The layering of organic molecules around the clay minerals is onion-like. Functional groups with a strong attraction to minerals are likely to form long-lasting associations with them early in soil development. Proteins provide an example in which they are attracted to the negative charges that characterize many clay minerals, especially 2:1 (Si:Al) phyllosilicates via electrostatic bonds through $-NR_3^+$ groups (where R is H or CH_x with $x = 1–3$). The same applies to carboxyl and O/N alkyl groups, which form covalent bonds with Fe oxides that may be free or else associated with phyllosilicates (Schöning et al. 2005).

Organic matter most intimately held on mineral surfaces would be held for longer times than that beyond the surfaces. Even so, associations of organic matter with minerals in soils often occur in 3-dimensional entities known as microaggregates. These are distinguished from macroaggregates by size, although the demarcation between the two may be arbitrary and empirical (Totsche et al. 2018). In the literature, microaggregates are defined as being, variously, in the <250 μm (Totsche et al. 2018), 53–250 μm (Beare et al. 1994; Six et al. 1999; Denef et al. 2004), and/or 2–50 μm size ranges (Tisdall and Oades 1982; Paradelo et al. 2016), while Liefeld and Kőgel-Knabner (2003) measured their mean weight diameters in a range of soils as being 11.8–15.6 μm. Using transmission electron microscopy of thin slices of soil, Chenu and Plante (2006) and Churchman et al. (2010) found many microaggregates involving mineral and organic associations in the size range of 1–5 μm.

In any case, microaggregates provide the basis of the structure of soils, stabilizing them against disruption by agricultural practices and erosion. In particular, SOC is stabilized in microaggregates. In microaggregates, organic matter often occurs within "shells" of the minerals (Chenu and Plante 2006; McCarthy et al. 2008; Churchman et al. 2010).

Organic matter turnover in microaggregates has been estimated variously in at least four different studies as from ~100–1000 years (Churchman and Velde 2019). Studies of chronosequences (Totsche et al. 2018) have shown that the accretion of newly formed soil components such as microbial residues or hydrous Fe oxides into microaggregates appears to take place within ~200 y. Turnover time is slow even in larger, silt-size aggregates (Virto et al. 2010).

In truth, gases such as carbon dioxide are not removed directly from the atmosphere by soils or SOM. Generally, they are taken up by plants for photosynthesis leading to their growth and release into the soils. This occurs during the growth of plants, e.g. through root exudates or after their death, by their decomposition. The extra OC added to soils when clay was added to overcome non-wetting (Churchman et al. 2014; Schapel et al. 2018) came about because addition of clays encouraged plant growth, mainly by holding water on their large hydrophilic surfaces for later release to plant roots. In other experiments, additions of clays to light-textured (sandy) soils have been shown to increase plant production. In the laboratory, Churchman and co-workers (unpub. results 2001) found that addition of 12.5% by weight of foundry waste containing 35% bentonite to a non-wetting sandy soil from South Australia not only overcame its hydrophobicity but trebled dry matter production. In the field, addition of similar foundry waste to a sandy soil in Thailand (without non-wetting problems) also led to increases of up to three times in the dry matter yield of maize (Soda et al. 2006). Pot trials adding 40 t ha^{-1} to a degraded Oxisol and a sandy Ultisol from northern Australia showed increases in the biomass production of forage sorghum of three and eight times, respectively (Noble et al. 2001). Carbon contents were not measured in these various experiments, but the increased plant growth in each case would have led to substantial increase in SOC. Wherever excess clay is available locally, increased retention, if not new sequestration, of

C can occur in sandy soils where sparse plant growth is the norm.

Limited sources of clays occur as industrial wastes, with, for example, ~ one million tons of "bleaching earths," which are acid-activated bentonites, being released as wastes from cooking oil manufacture world-wide each year (Crossley 2001), as well as from some foundries. However, huge areas of sandy soils are found world-wide (>900 million hectares, according to FAO/UNESCO 1995) and their augmentation by clays from these sources offers prospects for only limited overall sequestration of carbon.

The prospects for the (new) sequestration of C are constrained by (1) the availability of reactive surfaces, and (2) the possible formation of microaggregates. Most surfaces in soils are mineral rather than organic (Mayer and Xing 2001), with microorganisms and organic matter occupying only a very small fraction (<<1%, according to Kleber et al. 2015) of soil surfaces. Selective spots, variously described as "organo-mineral clusters with rough surfaces" (Vogel et al. 2014, p. 5), appear to occur for the uptake of OC in soils. Etch pits, micropores, and cracks on mineral surfaces are likely to constitute such spots (Churchman and Velde 2019), which are probably related to those for microorganisms, and include the rhizospheres of plants (Hinsinger et al. 2009). Hence, the opportunities for uptake and especially for strong uptake, i.e. sequestration, of C are quite limited.

Carbon sequestration takes place in microaggregates but takes a long time, so that the formation of microaggregates does not provide an immediate solution to the removal of newly released greenhouse gases from the atmosphere. Nonetheless, formation of microaggregates takes place within macroaggregates (Oades 1984; Golchin et al. 1994; Six et al. 1999; Balesdent et al. 2000) and macroaggregate formation is favored by vigorous plant growth (Six et al. 2004). Although strong plant growth may not sequester C in the long term, its promotion could remove some C from the atmosphere. The removal of C by isolation in larger macroaggregates is transitory (Balesdent 1996; Puget et al. 2000; Six et al. 2002), but continues as long as the strong plant growth is maintained. The process "buys time" while possible new technologies may become available, as Minasny et al. (2017) claimed for the "4 per mille" initiative for increasing soil C worldwide. The C isolated in macroaggregates may be transferred into microaggregates and, hence, truly sequestered, but only in the very long-term.

Soil management has often been proposed as the key to increasing the sequestration of C (Lal 2004, 2014; Minasny et al. 2017). West and Six (2007) postulated that step-wise increases in the capacity of soils to sequester C with distinct changes occur in soil management. The introduction of no-till farming (NT) is a common management strategy, for example, but considerable evidence suggests that NT may only change the distribution of C within the soil profile (Luo et al. 2010), generally toward the surface of profiles.

Even so, the experiments reported here, as well as those cited in discussion, involve surface soils. Studies of organic matter in subsoils, e.g. Lorenz and Lal (2005), Chabbi et al.

(2009), and Salomé et al. (2010), have found several characteristics of organic matter in subsoils that suggest that its functioning and stabilization differs from that in topsoils. For example, (some) subsoil SOC may be very old (several thousands of years old) (Chabbi et al. 2009) and strongly bound to minerals (Chabbi et al. 2009), including in structural units (Salomé et al. 2010). Subsoil SOC appears to have high spatial heterogeneity (Chabbi et al. 2009; Salomé et al. 2010) and may not be subject to a priming effect (Salomé et al. 2010). Sequestration of C in subsoils may be brought about by the use of plants/cultivars with deep and thick root systems (Lorenz and Lal 2005). Nonetheless, new C sequestration in subsoils is also subject to consideration of the degree of saturation of mineral surfaces. If fully saturated, they are not good candidates for net sequestration. Certainly the subsoils in the texture-contrast soils studied by Schapel et al. (2018) and also others discussed by Churchman et al. (2014) proved to be useful for net uptake of C; hence, good candidates for C sequestration.

Soils have a limited capacity for OC (Hassink 1997; Stewart et al. 2008). The limits for C sequestration, rather than for overall, may be partly transitory, uptake of C should reflect the capacity of reactive mineral surfaces for carbon. Such limits are likely to be somewhat less than the total capacity of soil for C. Following analyses of several results from field trials of the addition of C to soils, Stewart et al. (2007) proposed an "effective stabilization capacity" which defines the "maximum sequestration possible with increasing C input level under a particular management scenario." Discussion in the present work confirms the validity of the Stewart et al. (2007) "effective stabilization capacity" concept, but through the use of laboratory experiments and field experiments in which clays were added to soils. If, or when, the adsorption capacity of its reactive mineral surfaces is reached, little or no prospect exists for new sequestration of C from the atmosphere into a soil.

CONCLUSIONS

The results of recent laboratory experiments on the interaction of DOC with various southern Australian soil clays and of field experiments on the effects on carbon of additions of clays to a southern Australian soil, together with the literature, have been interpreted in the context of prospects for the sequestration of carbon in soils. The amount of organic carbon (OC) that can be adsorbed by soils depends on their clay minerals, including Fe oxides. However, much of the OC that can be adsorbed by soils can also be lost easily, and substantial OC in soils can be lost when more is added (by priming). Nonetheless, some (native) OC is held strongly in soils. OC close to mineral surfaces or within microaggregates is held most strongly. Even so, only very limited areas of mineral surfaces allow the uptake of OC, and when reactive surfaces are occupied, new C will not be held strongly. The addition of clay provides new surfaces for the uptake and retention of C.

Overall, one can conclude that net new sequestration of C in soils cannot be achieved by simply adding C to unamended (top) soils, although net C sequestration may occur in subsoils.

On the other hand, increasing the isolation of OC within macroaggregates by enhancing plant growth, although transitory, may provide a more effective method of decreasing atmospheric C than by its sequestration.

CONFLICTS OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

REFERENCES

Bailey, G. & Hughes, B. (2012). An observational study of clay delving and its impact on the A2 horizon in sand over clay soils. Pp 201–210 in: *Proceedings of the 5th joint Australia and New Zealand soil science conference*, *Hobart*. (L.L. Burkitt and L.A. Sparrow, editors). Australian Society of Soil Science Inc.

Balesdent, J. (1996). The significance of organic separates to carbon dynamics and its modelling in some cultivated soils. *European Journal of Soil Science, 47*, 485–493.

Balesdent, J., Chenu, C., & Balabane, M. (2000). Relationship of soil organic matter dynamics to physical protection and tillage. *Soil & Tillage Research, 53*, 215–230.

Batjes, N. H. (1996). Total carbon and nitrogen in the soils of the world. *European Journal of Soil Science, 47*, 151–163.

Beare, M. H., Hendrix, P. F., & Coleman, D. C. (1994). Water-stable aggregates and organic matter fractions in conventional and no-tillage soils. *Soil Science Society of America Journal, 58*, 777–786.

Betti, G., Grant, C., Churchman, G., & Murray, R. (2015). Increased profile wettability in texture-contrast soils from clay delving: case studies in South Australia. *Soil Research, 53*, 125–136.

Blakemore, L.C., Searle, P.L., & Daly, B.K. (1987). Methods for chemical analysis of soils. *N.Z. Soil Bureau Scientific Report 80*.

Bolan, N. S., Kunhikrishnan, A., Choppala, G. K., Thangarajan, R., & Chung, J. W. (2012). Stabilization of carbon in composts and biochars in relation to carbon sequestration and soil fertility. *Science of the Total Environment, 424*, 264–270.

Cann, M. A. (2000). Clay spreading on water repellent sands in the south east of South Australia–promoting sustainable agriculture. *Journal of Hydrology, 231–232*, 333–341.

Chabbi, A., Kögel-Knabner, I., & Rumpel, C. (2009). Stabilised carbon in subsoil horizons is located in spatially distinct parts of the soil profile. *Soil Biology and Biochemistry, 41*, 256–261.

Chenu, C., & Plante, A. F. (2006). Clay-sized organo-mineral complexes in a cultivation chronosequence: revisiting the concept of the 'primary organo-mineral complex'. *European Journal of Soil Science, 57*, 596–607.

Churchman, G. J. (2010). Is the geological concept of clay minerals appropriate for soil science? A literature–based and philosophical analysis. *Physics and Chemistry of the Earth, 35*, 927–940.

Churchman, G.J. (2018). Game changer in soil science. functional role of clay minerals in soil. *Journal of Plant Nutrition and Soil Science, 181*, 99–103.

Churchman, G.J. & Lowe, D.J. (2012). Alteration, formation and occurrence of minerals in soils. Pp. 1–20 in: *Handbook of Soil Sciences. Properties and Processes*, 2nd edition. (P.M. Huang, Y. Li, and M.E. Sumner, editors). CRC Press, Boca Raton, Florida, USA.

Churchman, G. J., & Velde, B. (2019). *Soil Clays, Linking Geology, Biology, Agriculture, and the Environment*. Boca Raton, Florida, USA: CRC Press.

Churchman, G. J., Foster, R. C., D'Acqui, L. P., Janik, L. J., Skjemstad, J. O., Merry, R. H., & Weissmann, D. A. (2010). Effect of land-use history on the potential for carbon sequestration in an Alfisol. *Soil & Tillage Research, 109*, 23–35.

Churchman, J., Hesterberg, D., & Singh, B. (2012). Soil clays (Editorial). *Applied Clay Science, 64*, 1–3.

Churchman, G. J., Noble, A., Bailey, G., Chittleborough, D., & Harper, R. (2014). Clay addition and redistribution to enhance carbon

sequestration in soils. In A. E. Hartemink & K. McSweeney (Eds.), *Soil Carbon*, *Progress in Soil Science* (pp. 327–335). Switzerland: Springer.

Crossley, P. (2001). Clear opportunities for bleaching and clarifying clays. *Industrial Minerals, 2001*, 69–75.

Denef, K., Six, J., Merckx, R., & Paustian, K. (2004). Carbon sequestration in microaggregates of no-tillage soils with different clay mineralogy. *Soil Science Society of America Journal, 68*, 1935–1944.

Dictionary.com (2019). – accessed 12 August 2019

Eusterhues, K., Rumpel, C., Kleber, M., & Kőgel-Knabner, I. (2003). Stabilisation of organic matter by interactions with minerals as revealed by mineral dissolution and oxidative degradation. *Organic Geochemistry, 34*, 1591–1600.

Eusterhues, K., Rumpel, C., & Kőgel-Knabner, I. (2005). Stabilization of soil organic matter isolated via oxidative degradation. *Organic Geochemistry, 36*, 1567–1575.

FAO/UNESCO. (1995). *Digital soil map of the world and derived properties*. Italy: Rome.

Finley, B. K., Dijkstra, P., Rasmussen, C., Schwartz, E., Mau, R. L., Liu, X.-J. A., van Gestel, N., & Hungate, B. A. (2018). Soil mineral assemblage and substrate quality effects on microbial priming. *Geoderma, 322*, 38–47.

Golchin, A., Oades, J. M., Skjemstad, J. O., & Clarke, P. (1994). Soil structure and carbon cycling. *Australian Journal of Soil Research, 32*, 1043–1068.

Hall, D. J., Jones, H. R., Crabtree, W. L., & Daniels, T. L. (2010). Claying and deep ripping can increase crop yields and profits on water repellent sands with marginal fertility in southern Western Australia. *Australian Journal of Soil Research, 48*, 178–187.

Harper, R.J., Sochacki, S.J., Bell, R.W., & 7 others (2012). Increasing soil carbon storage in sandy soils with clay amendments. P. 75 in: The CCRSPI (Climate Change Research Strategy for the Primary Industries) conference, Melbourne, 27–29 Nov., 2012

Hassink, J. (1997). The capacity of soils to preserve organic C and N by their association with clay and silt particles. *Plant and Soil, 191*, 77–87.

Hinsinger, P., Bengouh, A. G., Vetterlin, D., & Young, I. M. (2009). Rhizosphere: biophysics, biogeochemistry and ecological relevance. *Plant and Soil, 321*, 117–152.

Janzen, H. H. (2006). The soil carbon dilemma: Shall we hoard it or use it? *Soil Biology and Biochemistry, 38*, 419–424.

Kahle, M., Kleber, M., & Jahn, R. (2003). Retention of dissolved organic matter by illitic soils and clay fractions: influence of mineral phase properties. *Journal of Plant Nutrition and Soil Science, 166*, 737–741.

Kahle, M., Kleber, M., & Jahn, R. (2004). Retention of dissolved organic matter by phyllosilicate and soil clay fractions in relation to mineral properties. *Organic Geochemistry, 35*, 269–276.

Kaiser, K., & Guggenberger, G. (2003). Mineral surfaces and soil organic matter. *European Journal of Soil Science, 54*, 219–236.

Kleber, M., Sollins, P., & Sutton, R. (2007). A conceptual model of organo-mineral interactions in soils: self-assembly of organic molecular fragments into zonal structures on mineral surfaces. *Biogeochemistry, 85*, 9–24.

Kleber, M., Eusterhues, K., Keiluweit, M., Mikutta, C., Mikutta, R., & Nico, P. S. (2015). Mineral-organic associations: formation, properties, and relevance in soil environments. *Advances in Agronomy, 130*, 1–140.

Lal, R. (2004). Soil carbon sequestration impacts on global climate change and food security. *Science, 304*, 1623–1627.

Lal, R. (2014). Soil carbon management and climate change. In A. E. Hartemink & K. McSweeney (Eds.), *Soil Carbon*, *Progress in Soil Science* (pp. 339–361). Switzerland: Springer.

Le Quéré, C., Raupach, M. R., Canadell, J. G., et al. (2009). Trends in the sources and sinks of carbon dioxide. *Nature Geoscience, 2*, 831–836.

Liefeld, J., & Kögel-Knabner, I. (2003). Microaggregates in agricultural soils and their size distribution determined by X-ray attenuation. *European Journal of Soil Science, 54*, 167–174.

Lorenz, K., & Lal, R. (2005). The depth distribution of soil organic carbon in relation to land use and management and the potential of carbon sequestration in subsoil horizons. *Advances in Agronomy, 88*, 35–66.

Luo, Z., Wang, E., & Sun, O. J. (2010). Can no-tillage stimulate carbon sequestration in agricultural soils? A meta-analysis of paired experiments. *Agriculture, Ecosystems and Environment, 139*, 224–231.

Mayer, L. M., & Xing, B. (2001). Organic matter-surface area relationships in acid soils. *Soil Science Society of America Journal, 65*, 250–258.

McCarthy, J. F., Ilavsky, J., Jastrow, J. D., Mayer, L. M., Perfect, E., & Zhuang, J. (2008). Protection of organic carbon in soil microaggregates via restructuring of aggregate porosity and filling of pores with accumulating organic matter. *Geochimica et Cosmochimica Acta, 72*, 4725–4744.

McKissock, I., Gilkes, R. J., & Walker, E. L. (1998). The reduction of water repellency by added clay is influenced by clay and soil properties. *Applied Clay Science, 20*, 225–239.

Michéli, E. & Spaargaren, O.C. (2012). Other systems of soil classification. Pp. 32–1–32-34 in: *Handbook of Soil Sciences. Properties and Processes, 2nd edition* (P.M. Huang, Y. Li and M.E. Sumner, editors). CRC Press, Boca Raton, Florida.

Mikutta, R., Kleber, M., & Jahn, R. (2005). Poorly crystalline minerals protect organic carbon in clay subfractions from acid subsoil horizons. *Geoderma, 128*, 106–115.

Mikutta, R., Mikutta, C., Kalbitz, K., Scheel, T., Kaiser, K., & Jahn, R. (2007). Biodegradation of forest floor organic matter bound to minerals via different binding mechanisms. *Geochimica et Cosmochimica Acta, 71*, 2569–2590.

Minasny, B., Malone, B. P., McBratney, A. B., et al. (2017). Soil carbon 4 per mille. *Geoderma, 292*, 59–86.

Noble, A. D., Gillman, G. P., Nath, S., & Srivastava, R. J. (2001). Changes in the surface charge characteristics of degraded soils in the wet tropics through the addition of beneficiated bentonite. *Australian Journal of Soil Research, 39*, 991–1001.

Oades, J. M. (1984). Soil organic matter and structural stability: mechanisms and implications for management. *Plant and Soil, 76*, 319–337.

Oades, J.M. (1989). Introduction to organic matter in mineral soils. Pp. 89–159 in: *Minerals in Soil Environments* (J.B. Dixon and S.B. Weed, editors). 2nd edition, Soil Science Society of America Inc., Madison, Wisconsin, USA.

Paradelo, R., van Oort, F., Barré, P., Billiou, D., & Chenu, C. (2016). Soil organic matter stabilization at the pluri-decadal scale: Insight from bare fallow soils with contrasting physicochemical properties and macrostructures. *Geoderma, 275*, 48–54.

Percival, H. J., Parfitt, R. L., & Scott, N. A. (2000). Factors controlling soil carbon levels in New Zealand grasslands: Is clay content important? *Soil Science Society of America Journal, 64*, 1623–1630.

Powlson, D. S., Whitmore, A. P., & Goulding, K. W. T. (2011). Soil carbon sequestration to mitigate climate change: a critical re-examination to identify the true and the false. *European Journal of Soil Science, 62*, 42–55.

Puget, P., Chenu, C., & Balesdent, J. (2000). Dynamics of soil organic matter associated with particle-size fractions of water-stable aggregates. *European Journal of Soil Science, 51*, 595–605.

Rasmussen, C., Matsuyama, N., Dahlgren, R. A., Southard, R. J., & Brauer, N. (2007). Soil genesis and mineral transformation across and environmental gradient on andesitic lahar. *Soil Science Society of America Journal, 71*, 225–237.

Rowley, M. C., Grand, S., & Verrecchia, E. P. (2018). Calcium-mediated stabilization of soil organic carbon. *Biogeochemistry, 137*, 27–49.

Saggar, S., Parshotam, A., Sparling, G. P., Feltham, C. W., & Hart, P. B. S. (1996). ^{14}C-labelled ryegrass turnover and residence times in soils varying in clay content and mineralogy. *Soil Biology and Biochemistry, 28*, 1677–1686.

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

Saidy, A. R., Smernik, R. J., Baldock, J. A., Kaiser, K., & Sanderman, J. (2013). The sorption of organic carbon onto differing clay minerals in the presence and absence of hydrous iron oxide. *Geoderma, 209*, 15–21.

Salomé, C., Nunan, N., Pouteau, V., Lerch, T. Z., & Chenu, C. (2010). Carbon dynamics in topsoil and in subsoil may be controlled by different regulatory mechanisms. *Global Change Biology, 16*, 416–426.

Sarkar, B., Singh, M., Mandal, S., Churchman, G.J., & Bolan, N.S. (2018). Clay minerals—organic matter interactions in relation to carbon stabilization in soils. Pp. 71–86 in: *The Future of Soil Carbon: Its Conservation and Formation* (C. Garcia, P. Nannipieri, and T. Hernandez, editors). New York: Academic Press.

Schapel, A., Marschner, P., & Churchman, J. (2018). Clay amount and distribution influence organic carbon content in sand with subsoil clay addition. *Soil & Tillage Research, 184*, 253–260.

Schöning, I., Knicker, H., & Kőgel-Knabner, I. (2005). Intimate association between O/N-alkyl carbon and iron oxides in clay fractions of forest soils. *Organic Geochemistry, 36*, 1378–1390.

Schuur, E. A. G., & Abbott, B. W. (2011). High risk of permafrost thaw. *Nature, 480*, 32–33.

Singh, M. (2016). Role of clay minerals in carbon stabilisation in soils. Unpublished PhD Thesis, University of South Australia.

Singh, M., Sarkar, B., Biswas, B., Churchman, J., & Bolan, N. S. (2016). Adsorption-desorption behavior of dissolved organic carbon by soil clay fractions of varying mineralogy. *Geoderma, 280*, 47–56.

Singh, M., Sarkar, B., Biswas, B., Bolan, N. S., & Churchman, G. J. (2017a). Relationship between soil clay mineralogy and carbon protection capacity as influenced by temperature and moisture. *Soil Biology and Biochemistry, 109*, 95–106.

Singh, M., Sarkar, B., Hussain, S., Ok, Y. S., Bolan, N. S., & Churchman, G. J. (2017b). Influence of physico-chemical properties of soil clay fractions on the retention of dissolved organic carbon. *Environmental Geochemistry and Health, 39*, 1335–1350.

Singh, M., Sarkar, B., Sarkar, S., Churchman, J., Bolan, N., Mandal, S., Menon, M., Purakayastha, T. J., & Beerling, D. J. (2018). Stabilization of soil organic carbon as influenced by clay mineralogy. *Advances in Agronomy, 148*, 33–84.

Singh, M., Sarkar, B., Bolan, N. S., Ok, Y. S., & Churchman, G. J. (2019). Decomposition of soil organic matter as affected by clay types, pedogenic oxides and plant residue addition rates. *Journal of Hazardous Materials, 374*, 11–19.

Six, J., Elliott, E. T., & Paustian, K. (1999). Aggregate and soil organic dynamics under conventional and no-tillage systems. *Soil Science Society of America Journal, 63*, 1350–1359.

Six, J., Conant, R. T., Paul, E. A., & Paustian, K. (2002). Stabilization mechanisms of soil organic matter: implications for C-saturation of soils. *Plant and Soil, 241*, 155–176.

Six, J., Bossuyt, H., Degryze, S., & Denef, K. (2004). A history of research on the link between (micro)aggregates, soil biota, and soil organic matter dynamics. *Soil & Tillage Research, 79*, 7–31.

Smith, P., Martino, D., Cai, Z., et al. (2008). Greenhouse gas mitigation in agriculture. *Philosophical Transactions of the Royal Society B, 363*, 789–813.

Soda, W., Noble, A. D., Suzuki, S., Simmons, R., Sindhusen, L., & Bhuthornharaj, S. (2006). Composting of acid waste bentonites and their effects on soil properties and crop biomass. *Journal of Environmental Quality, 35*, 2293–2301.

Soil Survey Staff (1975). Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. U.S. Dept. of Agriculture Soil Conservation Service, Washington, D.C.

Spain, A. V. (1990). Influence of environmental conditions and some soil chemical properties on the carbon and nitrogen contents of some typical Australian rainforest soils. *Australian Journal of Soil Research, 28*, 825–839.

Stewart, C. E., Paustian, K., Conant, R. T., Plante, A. F., & Six, J. (2007). Soil carbon saturation: concept, evidence and evaluation. *Biogeochemistry, 86*, 19–31.

Stewart, C. E., Plante, A. F., Paustian, K., Conant, R. T., & Six, J. (2008). Soil carbon saturation: linking concept and measurable carbon pools. *Soil Science Society of America Journal, 72*, 379–392.

Stockmann, U., Adams, M. A., Crawford, J. W., et al. (2013). The knowns, known unknowns and unknowns of sequestration of soil organic carbon. *Agriculture, Ecosystems and Environment, 164*, 80–99.

Tisdall, J. M., & Oades, J. M. (1982). Organic matter and water-stable aggregates in soils. *Journal of Soil Science, 33*, 141–163.

Totsche, K. U., Amelung, W., Gerzabeck, M. H., et al. (2018). Microaggregates in soils. *Journal of Plant Nutrition and Soil Science, 181*, 104–136.

Virto, I., Moni, C., Swanston, C., & Chenu, C. (2010). Turnover of intra- and extra-aggregates organic matter at the silt scale. *Geoderma, 156*, 1–10.

Vogel, C., Mueller, C. W., Hőschen, C., et al. (2014). Submicron structures provide preferential spots for carbon and nitrogen sequestration in soils. *Nature Communications, 5*, 2947.

West, T. O., & Six, J. (2007). Considering the influence of sequestration duration and carbon saturation on estimates of soil carbon capacity. *Climatic Change, 80*, 25–41.