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

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Abstract -Results from earlier laboratory and field experiments are 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. Labelled 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 substantial 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. OC close to mineral surfaces or within microaggregates is held most strongly. C sequestration may occur in subsoils with unsaturated mineral surfaces. However, incorporation of carbon into macroaggregates from enhanced plant growth might be most effective to remove excess carbon from the atmosphere, albeit over the short-term.

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32   INTRODUCTION

33   The earth's climate is undergoing change, and the consensus is that its principal cause is the

34   rise in the atmosphere of so-called "greenhouse gases" from anthropogenic activities. In particular,

35   carbon dioxide generated by the combustion of fossil forms of carbon (Le Quéré *et al*., 2009) and

36   also methane, often generated by agriculture (Smith *et al*., 2008), are major sources of these gases

37   in the atmosphere. These gaseous forms of carbon are also released into the atmosphere when

38   formerly frozen sources such as permafrost Arctic regions are warmed (Schuur *et al*., 2011).

39   Many authors in the scientific literature (see, e.g. Stockmann *et al*., 2013; Minasny *et al*.

40   2017) have proposed that soil organic matter (SOM) can be used as a "managed" sink for

41   atmospheric carbon gases and particularly carbon dioxide, through carbon sequestration. Politicians

42   and others in public life have seen carbon sequestration as a solution to the problems that rising

43   emissions of these gases cause to the climate. Hence there is a strong need to assess the viability of

44   the apparently useful role for SOM in halting or at least diminishing the advance of climate change.

45   The global stock of carbon in the soil as organic matter (SOM) has been estimated as ~ 700

46   Pg to a depth of 30 cm and ~1500 Pg to a depth of 1 m (Batjes, 1996). The SOM to 30 cm depth

47   represents about twice the amount of C in the atmosphere and 3 times that in above-ground

48   vegetation (Powlson *et al*., 2011). Carbon as soil organic carbon (SOC) is particularly labile.

49   Historically, the reservoir of C held in land has diminished drastically over decades, whereas that

50   held in oceans, which is also labile and of a comparable size, has changed only a little (Lal, 2014). The

51 loss of C from land is attributable to agriculture. Many (e.g. Lal (2014) have concluded that, because

52 C has been lost from their soils, managed agricultural soils have the capacity to replenish the losses

53 and hence sequester C from the atmosphere.

54   The clay fraction of soils, comprising clay minerals (including metal oxides, oxyhydroxides

55 and hydroxides) is their most reactive fraction for forming associations with organic matter

56 (Churchman, 2010, 2018; Sarkar *et al*., 2018; Singh *et al*., 2018).

57   Several approaches have been used to investigate the importance of clay minerals in the

58 uptake and retention, hence, potentially, the sequestration of carbon in soils (e.g. Churchman and

59 Velde, 2019). These include correlations of the contents of SOC with properties of soil clays,

60 including their contents and their cation exchange capacities (CECs). Where narrow ranges of soil

61 types have been studied, some good correlations have been obtained, but where the ranges are

62 wider, SOC contents and those of clays or their properties have been poorly correlated, if at all

63 (Churchman and Velde, 2019). In tropical Australia (Spain, 1990), such correlations were poor when

64 soils originated from basalt were included, and a set of 167 soils taken from throughout New

65 Zealand showed no correlation between SOC and clay fraction contents (Percival *et al.,* 2000). The

66 lack of a relationship between SOC and clay contents or properties was explained by the important

67 roles played by compounds of Fe (Spain, 1990; Percival *et al*., 2000) and Al (Percival *et al*., 2000),

68 particularly when these were poorly crystalline (Percival *et al*., 2000).

69   Another approach to the study of mineral-organic interactions in soils include the

70 fractionation of soils, either by particle density, selective chemical dissolutions or physical

71 disaggregation. These studies have confirmed the important roles played by Fe (Eusterhues *et al.,*

72 2003, 2005) in the stabilisation of SOC in many soils, and by Ca^{2+} in some (Oades, 1989). In particular,

73 leached, hence, generally, acid soils involve Fe and Al in the stabilisation of C by bridging while Ca^{2+} is

74 more involved in bridging with SOC in high base status soils (Oades, 1989; Rowley *et al.,* 2018).

75   Studies of incubations of soils have revealed that clay minerals with the highest surface area,

76   namely allophane and smectite in the soils they used, had the strongest effect on the suppression of

77   the decomposition of SOC (Saggar *et al.,* 1996), while Rasmussen *et al.* (2007) found that poorly

78   crystalline Fe oxyhydroxides strongly suppressed SOC decomposition.

79   These three types of approaches, together with others (e.g. Churchman and Velde, 2019),

80   have shown that clay minerals, including metal oxides, oxyhydroxides and hydroxides, are important

81   in the uptake and retention of SOC in soils. Even so, these studies do not provide an assessment of

82   the strength and duration of the binding of SOM by soil minerals. Strong and long-term binding of

83   SOM is required for the sequestration of carbon in soils. "Sequester" is defined as "to hold on to" or

84   "to keep separate" (Powlson *et al*, 2011). In the chemical or environmental context, sequestration

85   means "the trapping of a chemical in the atmosphere or environment and its isolation in a natural or

86   artificial storage area" (Dictionary.com, 2019). The sequestration of organic C in soils is generally

87   taken to mean the retention of SOC for a "stipulated duration timeframe (usually 100 years)"

88   (Stockmann *et al*., 2013). The most useful meaning for carbon sequestration for a decrease in

89   greenhouse gases in the atmosphere is given by a net gain of SOC. This represents "new"

90   sequestration of carbon.

91   Several recent experiments (Singh *et al*, 2016, 2017a; 2017b; 2019; Schapel *et al*., 2018)

92   have been carried out to help assess or improve the effectiveness of soils for the uptake and

93   retention of OC. Experiments were carried out in the laboratory and also in the field.

94   The laboratory experiments included determinations of the stabilisation of OC by clay

95   minerals as they occur in soils, in contrast to clay minerals from deposits, as determined by Saidy *et*

96   *al*. (2012). Clay minerals originating in soils can have quite different properties from "pure" clay

97   minerals from deposits (Churchman, 2010; Churchman *et al*., 2012; Churchman and Lowe, 2012;

98   Churchman and Velde, 2019).

99   The field experiments were based on a common agricultural practice in much of the States

100   of South Australia and Western Australia where sandy soils often become hydrophobic in summer in

101   the xeric moisture conditions prevailing in these areas. A practical solution to this problem has been

102   to add clay to the soils (McKissock *et al*., 1998; Cann, 2000; Churchman *et al*., 2014; Churchman and

103   Velde, 2019). Initially, clay-rich material was incorporated in the surface soils but, because most of

104   the soils concerned are texture-contrast types having sandy topsoils over clay-rich subsoils, the

105   common practice now is to obtain clay for incorporation in surface soils via mechanical deep ripping,

106   a process known as "delving" (Betti *et al*., 2015).

107   The results of these various experiments have enabled an assessment of the potential of

108   soils to uptake and retain added OC, especially in relation to their clay mineral composition,

109   Reference to the literature has also pointed to likely causes of limitations on carbon uptake and

110   retention in soils.

111   In this paper, some of the important results and conclusions of these various recent

112   experiments, particularly from Singh (2016), Singh *et al*. (2016, 2017a) and Schapel *et al*. (2018) are

113   highlighted and assessed together with results from earlier work, especially Churchman *et al*. (2014),

114   as indicators of the prospects for (new) carbon sequestration in soils.

115   It is hypothesized that clays, as the most reactive inorganic compounds in soils, ultimately

116   govern the prospects for sequestration of organic carbon in soils.

117   LABORATORY EXPERIMENTS AND RESULTS

118   Three soils were studied: a Calcic Haplosteralf, a Pellustert and a Thaptic Haploxerand,

119   according to Soil Taxonomy (Soil Survey Staff, 1992) (Singh *et al*., 2017b). Respectively, these were

120   dominated by kaolinite and illite (together), smectite and allophane (Singh et al., 2016).

121   The OC added to soils in these experiments was in liquid form, as dissolved organic carbon

122   (DOC), produced by dissolving ground wheat straw in water. Experiments carried out assessed the

123   capacities of three different soils to 1. adsorb DOC, 2. retain adsorbed DOC in the presence of water

124   (or "desorb DOC") (both Singh *et al*., 2016), and 3. mineralize added carbon and limit the

125   decomposition of adsorbed DOC to carbon dioxide by the "priming effect" (Singh *et al*., 2017a).

126   *Adsorption experiments*

127   Adsorption experiments were performed on clay (< 2 μm) fractions extracted from the soils

128   (at 5-20 cm depth) following prolonged shaking in Milli-Q water then gravity sedimentation. Hence

129   both minerals and organic matter in clay-sized material were preserved in the collected fractions.

130   The soils, all from South Australia, were characterised by their dominant clay minerals: (a) kaolinite

131   and illite together, (b) smectite, and (c) allophane (Singh *et al.*, 2016; 2017b). Adsorption was carried

132   out at pH 7 in solutions of calcium or sodium nitrate, either 0.1 or 0.01 M, for 24 h and DOC in

133   solution analysed after filtering. See Singh *et al*. (2016) for details.

134   The different clay minerals adsorbed DOC to various extents. All sorption isotherms, for

135   natural clay fractions, clay fractions after OC removal and clay fractions after iron removal following

136   OC removal followed the Langmuir model (Singh et al, 2016). Results of maximum OC adsorption by

137   the clay fraction of each soil are summarized in Table 1 for the following conditions: untreated, after

138   organic carbon removal, and after iron removal following organic carbon removal. These data are

139   from adsorption in 0.01M $Ca(NO_3)_{2.}$, a concentration likely to closely represent typical soil solutions

140   (Blakemore *et al.*, 1987). Analyses of total C and specific surface areas, before and after chemical

141   treatments, as well as Fe contents of the untreated clay fractions (from Singh, 2016) are also

142   included in Table 1. There are similar trends for the nitrate solutions differing in calcium or sodium

143   and with different concentrations (0.01 or 0.1M). The sorptive capacities of all clays were increased

144   when native OC was removed and were reduced when Fe was removed.

145   (Insert Table 1 about here)

146   *Desorption experiments*

147   Clay fraction samples taken from the adsorption experiments at various levels of equilibrium

148   concentrations of DOC were first washed with Milli-Q water to remove entrained DOC then

149   equilibrated for 24 h and supernatants were analysed for DOC after filtering. See Singh *et al.* (2016)

150   for details.

151   The percentages of adsorbed C that was desorbed in water from each clay fraction without

152   treatment, after OC removal and after iron removal following OC removal, in relation to the amounts

153   of DOC added in the adsorption experiments, are shown in Table 2. These data are from adsorption

154   in 0.01M $Ca(NO_3)_2$. There were similar trends for desorption for clay fractions following adsorption

155   from the nitrate solutions differing in calcium or sodium and with two different concentrations (0.01

156   or 0.1M) (Singh *et al.*, 2016).

157   (Insert Table 2 about here)

158   More than 30% of the C adsorbed in Ca nitrate and more than 50% of that adsorbed in Na

159   nitrate was released on simple desorption in water (Singh *et al.*, 2016). The proportion of adsorbed C

160   that was desorbed was greatest for the kaolinite-illite clay, less for the smectite clay and least for the

161   allophanic clay, but even in this latter case, ~ 20% of that adsorbed in Ca nitrate and ~30% of that

162   adsorbed in Na nitrate was lost on desorption in water. In each case, the proportion of adsorbed C

163   that was lost on desorption increased when DOC adsorption had been performed on clays from

164   which Fe-oxide was removed, and diminished when adsorption had occurred on clays from which

165   native C was removed.

166   *Effects of priming*

167   Samples of the whole soils that had been sieved to < 2 mm to remove coarse particles were

168   equilibrated with ^{14}C – labelled malic acid and also unamended in sterile Milli-Q water. CO_2 from

169   respiration was collected at different time periods in a solution of NaOH and the unconsumed alkali

170   was determined by titration with HCl. See Singh *et al*. (2017a) for details of the experiments and

171   calculations.

172   Results showed that more C was lost (as CO_2) from all soils after priming with malic acid

173   (Singh *et al*, 2017a). However, the extent of loss on priming depended upon the mineralogy of the

174   soils, with more C lost from the smectite soil than from the soil dominated by illite-kaolinite and the

175   allophanic soil. These two latter soils had similar losses on priming. Decomposition of native C

176   increased by 108% in the smectitic soil upon priming and by 37% in the kaolinitic-illitic soil and 42%

177   in the allophanic soil (Singh *et al*., 2017a).

178   FIELD EXPERIMENTS AND RESULTS

179   Soils in South Australia that were classified as Luvisols in the World Reference Base (Michéli

180   and Spaargaren, 2012) were studied at four sites where clay amendments had been carried out. All

181   soils were texture contrast. Farming systems in all sites were rotations of cereal and grazed pasture,

182   using minimum or no tillage and stubble retention. At each site, the soil had been amended by both

183   incorporation of clay-rich soils from subsoils within pits dug nearby and also by deep incorporation

184   from *in situ* using mechanical means. Trials were sampled at depth intervals to 50 cm after at least 3

185   years following treatments. See Schapel *et al*. (2018) for detailed descriptions of the sites and

186   processes used for clay amendment.

187   Soils were sampled during the non-growing phase as cores from various depths. They did not

188   contain gravel so were ground to pass a <2 mm sieve. Homogenised samples were analysed for OC

189   by the Walkley-Black wet digestion and bulk densities were also determined gravimetrically for

190   known volumes of soil. See Schapel *et al*. (2018) for details of methods.

191   Schapel *et al*. (2018) found that the stock (or reservoir) of OC was significantly and positively

192   correlated (R^2 = 0.47) with the stock (or reservoir) of clay when these values were adjusted to an

193   equivalent soil mass (ESM) from bulk density determinations.

194 Results showed that OC stock (or reservoir) in the surface (0-30 cm) of 14 clay-amended soils

195 increased on average by 5.5 Mg C ha^{-1} (range -1.6 to 14.2 Mg C ha^{-1}) from unamended sands, with

196 the increases largely brought about by increases in clay content. Clay and OC were concentrated at

197 the surface in clay-spread treatments and at depth in delved treatments (Schapel *et al*., 2018).

198   DISCUSSION

199 Organic carbon in solution is adsorbed by soils, and especially by their most reactive clay

200 fractions, to various extents, depending upon their clay mineral composition. The uptake of OC

201 correlates with the specific surface area of the soil clay fractions (Table 1). Uptake of OC was

202 increased by the presence of iron oxides, as also demonstrated by Kahle *et al*. (2003, 2004). Some

203 organic matter in natural soils is held particularly strongly, and, notwithstanding that a small fraction

204 was even resistant to peroxidation, the oxidation of OC enables further uptake. Others, e.g., Kaiser

205 and Guggenberger (2003), and Mikutta *et al*. (2005), have also found that some OC is held

206 particularly strongly in soils. The strongly-held portion may be located within small pores (McCarthy

207 *et al*., 2008).

208 Desorption shows that considerable organic matter was easily lost in water (Table 2). OC was

209 held more strongly, i.e., less was released on desorption, after removal of native OC had occurred

210 prior to its uptake. OC was held less strongly when Fe oxides were removed prior to its uptake.

211 Nonetheless, much adsorbed OC was quite labile. Kahle *et al*. (2004), Mikutta *et al*. (2007), and Saidy

212 *et al*. (2013) found that OC adsorbed on pure clay minerals included a substantial portion that was

213 lost easily on desorption.

214 The results of the priming experiments showed that, for all the soils, addition of extra OC led

215 to an enhanced release of CO_2 due to stimulation of microbial activity, hence respiration. Singh *et al*.

216 (2017a) attributed the greater effect of priming in the smectitic soil than in the allophanic soil or the

217 soil dominated by kaolinite and illite to the higher microbial activity which they measured for the

218 smectitic soil. Even so, priming, showing breakdown of SOC, occurred even in the allophanic soil,

219 where OC was held more strongly against desorption than in the other two soils studied. This

220 confirms the results of Finley *et al*. (2018), who found a high rate of decomposition of native OC in

221 soils comprising the short-range order minerals, allophane and ferrihydrite.

222 Field experiments (Schapel *et al*., 2018) demonstrated that both direct incorporation of

223 exogenous clay addition and 'delving' of *in-situ* clay addition resulted in an increase in SOC content.

224 Increases in SOC were also observed 8 years after additions of subsoil kaolinitic clay to sandy topsoils

225 by delving in Western Australia (Hall *et al*., 2010). The top 10 cm of soil contained only 1% clay,

226 which increased to 6% clay on delving. There was a resulting increase of 0.2% in SOC. In South

227 Australia, Bailey and Hughes (2012) found that delving soils in 11 sites increased the mean SOC

228 contents of their A2 horizons from 0.3% to 0.7%, Other clayey material can also enable increases in

229 SOC, and wastes from bauxite processing (85% silt, 11% clay and 4% sand) were added to sandy soils

230 in Western Australia (Harper *et al*., 2012; Churchman *et al*., 2014). Over a 19-20 year period,

231 addition of this waste led to increases in SOC in the top 30 cm of soil of between 0.1 to 0.65%,

232 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,

233 $P<0.001$) curvilinear correlation between clay content and SOC for the 0-5 cm layer (Churchman *et*

234 *al*., 2014). This amounts to an annual uptake of 1.9 Mg CO_2-eq. ha^{-1} year.

235 *Implications for carbon sequestration in soils*

236 Carbon is turned over - and lost from the soil system- through the biological processes

237 needed for soil functioning in agriculture (e.g. Janzen, 2006). Sequestration of C through long-term

238 storage and the use of soil for growing plants appear to be conflicting aims. For example, Bolan *et al*.

239 (2012) concluded that amending soils with biochar, which is more stable than composts, could

240 enhance soil carbon sequestration (long term carbon storage) but this carbon might not be useful for

241 an immediate improvement of soil health, such as for supplying food to soil microorganisms for

242 keeping the nutrient cycling operational. Following Jensen (2006), the most efficient way of

243 extracting extra carbon as CO_2 from the atmosphere may be by using it more rapidly for increasing

244 plant production, hence flow-through of SOM.

245   Increased adsorption which occurred when native C was first removed from all soils (Singh *et*

246 *al.*, 2016) shows that some C had occupied the most reactive mineral sites. The results from

247 desorption (Singh *et al.*, 2016) show that further C occupied less reactive sites in all soils and was

248 easily removed. The effect of priming (Singh *et al.*, 2017a) shows that simple addition of new C to

249 soils may result in the loss of C that is already present. Overall, these results show that simply adding

250 new C to soils that already contain C does not result in additional C that is held strongly, i.e.

251 sequestered.

252   However, the addition of clays to soils can enable the net uptake of C. Furthermore, the rate

253 of incubation of wheat residues added to a sandy soil was retarded by the addition of the clay

254 fractions used in the studies of sorption of DOC (Singh *et al.*, 2019). The addition of clay produces

255 new surfaces for holding C.

256   According to Churchman and Velde (2019, p. 152) "SOC can be associated with almost any

257 secondary (and also altered primary) minerals, but shows a preference for poorly crystalline oxides

258 and also silicates of Fe and Al". If these are rare, SOC binds to phyllosilicates according to their

259 relative surface reactivities, with smectites the most reactive of these. pH also plays a role in

260 governing reactivities of minerals for SOC. Low pHs favor Fe and Al compounds and higher pHs favor

261 phyllosilicates. The type, hence strength, of these associations also vary with pH. Associations

262 between SOC and minerals tend to be inner-sphere, hence stronger, at low pH and outer-sphere at

263 high pH (Kleber *et al.*, 2015).

264   Various functional groups in organic matter can be bound to minerals in layers. Proteins and

265 molecules containing carboxyl groups often occur adjacent to mineral surfaces while molecules

266 containing hydrophobic groups tend to occur in outer layers (e.g., Kleber *et al.,* 2007). The layering

267 of organic molecules around the clay minerals is onion-like. Functional groups with a strong

268   attraction to minerals are likely to form associations with them early in soil development that are

269   long-lasting. Examples are proteins, which are attracted to the negative charges that characterize

270   many clay minerals, especially 2:1 (Si:Al) phyllosilicates via electrostatic bonds through -NR_3^+ groups

271   (where R is H or CH_x and x= 1-3), and also carboxyl and O/N alkyl groups, which form covalent bonds

272   with Fe oxides that may be free or else associated with phyllosilicates (Schőning *et al.*, 2005).

273   Organic matter most intimately held on mineral surfaces would be held for longer times

274   than that beyond the surfaces. Even so, associations of organic matter with minerals in soils often

275   occur in 3-dimensional entities known as microaggregates. These are distinguished from

276   macroaggregates by size, although the demarcation between the two may be arbitrary and

277   pragmatic (Totsche *et al.*, 2018). In the literature, microaggregates are defined as being variously in

278   the < 250 µm (Totsche *et al.*, 2018), 53-250 µm (Beare *et al.*, 1994; Six *et al.*, 1999; Denef *et al.*,

279   2004) and/or 2-50 µm size ranges (Tisdall and Oades, 1982; Paradelo et al., 2016) while Liefeld and

280   Kőgel-Knabner (2003) measured their mean weight diameters in a range of soils as from 11.8 – 15.6

281   µm. Using transmission electron microscopy of thin slices of soil, Chenu and Plante (2006) and

282   Churchman *et al*. (2010) have found many microaggregates involving mineral and organic

283   associations in the size range of 1-5 µm.

284   In any case, microaggregates provide the basis of the structure of soils, stabilising them

285   against disruption by agricultural practices and erosion. In particular, SOC is stabilised in

286   microaggregates. In microaggregates, organic matter, often occurs within "shells" of the minerals

287   (Chenu and Plante, 2006; McCarthy *et al*., 2008; Churchman *et al*., 2010).

288   Organic matter turnover in microaggregates has been estimated variously in at least four

289   different studies as from ~100 – 1000 years (Churchman and Velde, 2019). Studies of

290   chronosequences (Totsche *et al.*, 2018) have shown that the accretion of newly formed soil

291   components such as microbial residues or hydrous Fe oxides into microaggregates appears to take

292   place within ~ 200 years. Turnover time is slow even in larger, silt-size aggregates (Virto *et al*., 2010).

293   In truth, gases such as carbon dioxide are not removed directly from the atmosphere by soils

294   or SOM. Generally, they are taken up by plants for photosynthesis leading to their growth and

295   release into the soils. This occurs during the growth of plants, e.g., through root exudates or after

296   their death, by their decomposition. The extra OC added to soils when clay was added to overcome

297   non-wetting (Churchman *et al*., 2014; Schapel *et al*., 2018) came about because addition of clays

298   encouraged plant growth, mainly by holding water on their large hydrophilic surfaces for later

299   release to plant roots. In other experiments, additions of clays to light-textured (sandy) soils have

300   been shown to increase plant production. In the laboratory, Churchman and co-workers (unpub.

301   results, 2001) found that addition of 12.5% by weight of foundry waste containing 35% bentonite to

302   a non-wetting sandy soil from South Australia not only overcame its hydrophobicity but trebled dry

303   matter production. In the field, addition of similar foundry waste to a sandy soil in Thailand (without

304   non-wetting problems) also led to increases of up to three times in the dry matter yield of maize

305   (Soda *et al*., 2006). Pot trials adding 40 t ha^{-1} to a degraded Oxisol and a sandy Ultisol from northern

306   Australia showed increases in the biomass production of forage sorghum of 3 and 8 times

307   respectively (Noble *et al*. 2001). C contents were not measured in these various experiments, but the

308   increased plant growth in each case would have led to substantial increase in SOC. Wherever excess

309   clay is available locally, increased retention, if not new sequestration of C can occur in sandy soils

310   where sparse plant growth is the norm.

311   Limited sources of clays occur as industrial wastes, with, e.g. ~ one million tonnes of

312   "bleaching earths", which are acid-activated bentonites being released as wastes from cooking oil

313   manufacture world-wide each year (Crossley, 2001), as well as some from foundries. However, huge

314   areas of sandy soils are found world-wide (> 900 million hectares, according to FAO/UNESCO, 1995)

315   and their augmentation by clays from these sources offers prospects for only limited overall

316   sequestration of carbon.

317   The prospects for the (new) sequestration of C are constrained by 1) the availability of

318   reactive surfaces, and 2) the possible formation of microaggregates. Most surfaces in soils are

319   mineral rather than organic (Mayer and Xing, 2001), with microorganisms and organic matter

320   occupying only a very small fraction (<1%, according to Kleber *et al.*, 2015) of soil surfaces. Selective

321   spots, variously described as "organo-mineral clusters with rough surfaces" (Vogel et. al., 2014, p. 5)

322   appear to occur for the uptake of OC in soils. Etch pits, micropores and cracks on mineral surfaces

323   are likely to constitute such spots (Churchman and Velde, 2019), which are probably related to those

324   for microorganisms, and include the rhizospheres of plants (Hinsinger *et al.*, 2009). Hence the

325   opportunities for uptake, and, especially, for strong uptake, i.e., sequestration, of C are quite limited.

326   C sequestration takes place in microaggregates but takes a long time, so that their formation

327   does not provide an immediate solution to the removal of newly released greenhouse gases from

328   the atmosphere. Nonetheless, formation of microaggregates takes place within macroaggregates

329   (Oades, 1984; Golchin *et al.*, Six *et al.,* 1999; Balesdent *et al.*, 2000) and the formation of these is

330   favoured by vigorous plant growth (Six, 2004). Although strong plant growth may not sequester C in

331   the long term, its promotion could remove some C from the atmosphere. The removal of C by

332   isolation in larger, macroaggregates is transitory (Balesdent, 1996; Puget *et al.*, 2000; Six *et al.*,

333   2002), but continues as long as the strong plant growth is maintained. The process "buys time" while

334   possible new technologies may become available, as Minasny *et al.* (2017) claimed for the "4 per

335   mille" initiative for increasing soil C world-wide. The C isolated in macroaggregates may be

336   transferred into microaggregates and hence truly sequestered, but only in the very long-term.

337   Soil management has often been proposed as the key to increasing the sequestration of C

338   (Lal, 2004, 2014; Minasny *et al.*, 2017). West and Six (2007) suggest step-wise increases in the

339   capacity of soils to sequester C with distinct changes in soil management. The introduction of no-till

340   farming (NT) is a common management strategy, for example, but considerable evidence suggests

341   that NT may only change the distribution of C within the soil profile (Luo *et al.,* 2010), generally

342   towards the surface of profiles.

343   Even so, the experiments reported here, as well as those cited in discussion, involve surface

344   soils. Studies of organic matter in subsoils, e.g. Lorenz and Lal (2005), Chabbi *et al*. (2009) and

345   Salomé *et al*. (2010) have found several characteristics of organic matter in subsoils that suggest that

346   its functioning and stabilisation differs from that in topsoils. For example, (some) subsoil SOC may be

347   very old (several thousands of years old) (Chabbi *et al*., 2009) and strongly bound to minerals

348   (Chabbi *et al*. 2009), including in structural units (Salomé *et al*., 2010). Subsoil SOC appears to have

349   high spatial heterogeneity (Chabbi *et al*., 2009; Salomé *et al*., 2010) and may not be subject to a

350   priming effect (Salome *et al*., 2010). Sequestration of C in subsoils may be brought about by the use

351   of plants/cultivars with deep and thick root systems (Lorenz and Lal, 2005). Nonetheless, new C

352   sequestration in subsoils is also subject to considerations of the degree of saturation of mineral

353   surfaces. If fully saturated, they are not good candidates for net sequestration. Certainly, the

354   subsoils in the texture contrast soils studied by Schapel *et al*. (2018) and also others discussed by

355   Churchman *et al*. (2014) proved to be useful for net uptake of C, hence good candidates for C

356   sequestration.

357   Soils have a limited capacity for OC (Hassink, 1997; Stewart et al., 2008). The limits for C

358   sequestration, rather than for overall, maybe partly transitory, uptake of C, should reflect the

359   capacity of reactive mineral surfaces for carbon. Such limits are likely to be somewhat less that the

360   total capacity of soil for C. Following analyses of several results from field trials of the addition of C

361   to soils, Stewart *et al.* (2007) proposed an "effective stabilization capacity" which defines the

362   "maximum sequestration possible with increasing C input level under a particular management

363   scenario". In this work, we confirm the validity of Stewart *et al.* (2007)'s "effective stabilization

364   capacity" concept, but through the use of laboratory experiments and those of additions of clays to

365 soils in the field. If, or when, the adsorption capacity of its reactive mineral surfaces is reached, there

366 is little – or no- prospect of new sequestration of C from the atmosphere into a soil.

367 CONCLUSIONS

368 The results of recent laboratory experiments on the interaction of DOC with various southern

369 Australian soil clays and of field experiments on the effects on carbon of additions of clays to a

370 Southern Australian soil, together with the literature, have been interpreted in the context of

371 prospects for the sequestration of carbon in soils. .

372 It has been found that the amount of organic carbon (OC) that can be adsorbed by soils depends on

373 their clay minerals, including Fe oxides. However, much of the OC that can be adsorbed by soils can

374 also be lost easily and substantial OC in soils can be lost when more is added (by priming).

375 Nonetheless, some (native) OC is held strongly in soils. OC close to mineral surfaces or within

376 microaggregates is held most strongly. Even so, only very limited areas of mineral surfaces allow the

377 uptake of OC, and when reactive surfaces are occupied, new C will not be held strongly.

378 It was found that addition of clay provides new surfaces for the uptake and retention of C.

379 Overall, it can be concluded that net new sequestration of C in soils cannot be achieved by simply

380 adding C to unamended (top) soils, although net C sequestration may occur in subsoils. On the other

381 hand, increasing the isolation of OC within macroaggregates by enhancing plant growth, although

382 transitory, may provide a more effective method of decreasing atmospheric C than by its

383 sequestration.

384

385 CONFLICTS OF INTEREST

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

387

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598

599   LIST OF TABLES

600   Table 1. Maximum amounts (mg g^{-1}) of DOC adsorbed in 0.01 Ca(NO$_3$)$_2$ by the clay fractions of soils

601   with various dominant minerals in relation to their contents of C and Fe and their specific surface

602   areas (SSAs) calculated using the BET equation for adsorption by N$_2$ gas (data from Singh, 2016)

603

604   Table 2. Percent desorption of DOC in water after its adsorption in 0.01 Ca(NO$_3$)$_2$ at various loadings

605   from the clay fractions of soils with different dominant minerals sequentially treated to remove

606   native C and Fe (data from Singh, 2016)

607

608 **Table 1. Maximum amounts (mg g^{-1}) of DOC adsorbed in 0.01 Ca(NO$_3$)$_2$ by the clay fractions**

609 **of soils with various dominant minerals in relation to their contents of C and Fe and their specific**

610 **surface areas (SSAs) calculated using the BET equation for adsorption by N$_2$ gas (data from Singh,**

611 **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

612   * Not determined

613

614 **Table 2. Percent desorption of DOC in water after its adsorption in 0.01 Ca(NO₃)₂ at**

615 **various loadings from the clay fractions of soils with different dominant minerals sequentially**

616 **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

617