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1     **Sustainable soil improvement and water use in agriculture: CCU**  
2             **enabling technologies afford an innovative approach**

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5     **Working title: CCU and soil improvement**

6

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21     **List of abbreviations:** C; carbon, CCm; denoted product name, CCS; carbon capture and  
22     storage, CCU; carbon capture and utilisation, FC; field capacity, JI; John Innes no.2  
23     trademark compost, M3; Levington's trademark compost, OC; organic carbon, PWP;  
24     permanent wilt point,  $\Psi$ ; soil matric potential (kPa)

25

## 26 **Abstract**

27 With industrial CO<sub>2</sub>-emission reduction the heart of carbon capture enabling technologies, we  
28 report on a solution engineered to potentially redress the issues of soil improvement and  
29 sustainable use of fresh water for food production. In a laboratory-scale pilot study, we  
30 demonstrate the capabilities of an innovative and novel product utilising carbon-capture to  
31 restore soil properties critical for crop production. In the first study of its kind, the carbon-  
32 initiated mode-of-action resulted in changes to soil physical and chemical properties. Soil  
33 water retention in a range of soil types was significantly increased by up to 62%; soil pH  
34 increased by 0.7 to 1.1 units: soil microbial colonisation increased by ~20% over the short  
35 term and crop biomass was enhanced by up to 38%. These results give impetus for  
36 developing CCU technologies to address environmental issues.

37 Key words: carbon capture, CCU, soil, sustainable agricultural water use, sustainability,  
38 climate change

39

## 40 **1. Introduction**

41 Climate change and environmental degradation currently present humanity with an enormous  
42 and varied array of challenges. CO<sub>2</sub> emission reduction has progressed over recent years with  
43 respect to changes in energy use. In the UK a reduction of coal fired power stations has led to  
44 an average annual emission reduction of 16% between 2012 and 2016, however, other sectors  
45 (industry, transport, buildings and agriculture) have contributed only 1% over the same time  
46 period [1]. It is recognised that innovative state-of-the-art technologies have the potential to  
47 improve emission reductions, but also to act synergistically with other priorities [1]. Two key  
48 priority environmental challenges are becoming increasingly urgent. The first is soil  
49 degradation with associated impacts on agricultural production and global food security. The  
50 second is access to fresh water resources and the competing factors that impose a constraint  
51 on food production [2-4]. Furthermore, these challenges have relevance over a range of  
52 spatial scales from the individual small-holder/gardener, medium to large-sized horticultural  
53 enterprises producing food under glass, to industrial scale agricultural production.

54 Soils have undergone substantial changes over the last 50 years due to intensified use and  
55 mechanised practices, industrial pollution and contamination [3, 5-7]. The result is  
56 accumulated damage to the content and structure of soils with the subsequent loss of  
57 beneficial characteristics defined as soil ecosystem services. Soil structure is comprised of a  
58 complex arrangement of particles and pore spaces which underpin the ability of soils to retain  
59 water, provide a substrate for plant, fungal and microbial growth, facilitating the constant  
60 cycling of minerals and maintenance of fertility. Organic matter (essentially organic carbon;  
61 OC) is argued to be the most important indicator of soil health [8] as it structurally supports  
62 ecosystem services including vital physico-chemical properties for agriculture; water holding  
63 capacity, nutrient retention, chemical buffering [3] and efficient crop growth. OC is  
64 recognised to significantly improve available soil water [9] with recent assessments of critical  
65 thresholds of sustainability strongly linking retention of OC to the successful maintenance of  
66 fertile soils [8] and therefore, the ability to achieve sustainable food production.

67 The second challenge is the availability of fresh water resources required to facilitate the use  
68 of land across all spatial scales for food production while competing with demands from  
69 other economic sectors; industry [4], energy [10] and increasing urban water demand [11].  
70 Water availability and accessibility are the largest constraining factors on crop production,

71 with strong relationships between these and output capacity [4]. While it is known that  
72 productivity can be improved with irrigation even in humid climates, for example, the UK  
73 where wheat yield could be increased by an average of 25% [12], the failure to reach full  
74 potential yield is a consequence of deteriorating soils [3] rather than a lack of water.

75 Clearly, novel and innovative solutions are required to rapidly address present and future  
76 losses to agricultural capacity providing a sustainable approach to the management of soil.  
77 We have developed an engineering process which can directly fix CO<sub>2</sub> at source to procure a  
78 compound that has the potential to manipulate soil physico-chemical properties and  
79 substantially contribute to re-establishment of soil ecosystem services while also adopting  
80 Climate-Smart Agricultural practices to reduce greenhouse gases [13].

81 It has been recognised that carbon capture and sequestration (CCS), as a readily available  
82 source of carbon, has potential for crop productivity improvement via CO<sub>2</sub> storage materials  
83 (CO<sub>2</sub>SMs) as demonstrated for glasshouse crops [14]. Soil improvement can be achieved by  
84 the crop sequestration of CO<sub>2</sub> and subsequent reincorporation of crop residues into soil [15].  
85 This however, requires that land be left for residues to be naturally broken down over time.  
86 Carbon capture and utilisation (CCU) technologies have been engineered to efficiently  
87 capture industrial CO<sub>2</sub> and safely convert it into materials with the potential to restore and  
88 enhance the ability of soils to resist degradation via soil OC amendment. Using this  
89 technology we have engineered a novel CCU product comprising of a matrix derived from  
90 cellulosic waste feedstock (e.g. straw/paper pulp/digestate) that is coated in a nitrogenous  
91 material which facilitates capture of industrial CO<sub>2</sub> at source (see section 1.2.1). The matrix is  
92 then stabilised as a carbonate which has potential to re-introduce an OC-element to degraded  
93 soils. The product (denoted CCm hereafter) can be tailored to specific chemical compositions  
94 i.e. carbon to nitrogen ratio and/or the form it takes, powder, pellet or granular. It can also be  
95 produced to replicate commercial fertilizers with the addition of waste or recycled materials;  
96 nitrogen and potassium (from anaerobic digestate) and phosphate (from slaughterhouse  
97 waste), giving outputs greater sustainable credibility. The production of each tonne of CCm  
98 generates up to 6.5 tonnes less CO<sub>2</sub> than a typical conventional fossil-fuel based fertiliser  
99 supply route i.e. the Haber-Bosch process, which can contribute as much as 40% of C-  
100 emissions in the production of bread [16]. There is, therefore, potential to provide  
101 remediation of both soil OC status, structural integrity and associated water retentive  
102 capabilities over significant (catchment wide) areas, while the use of recycling waste streams  
103 results in more sustainable supply chains.

## 104 **2. Materials and methods**

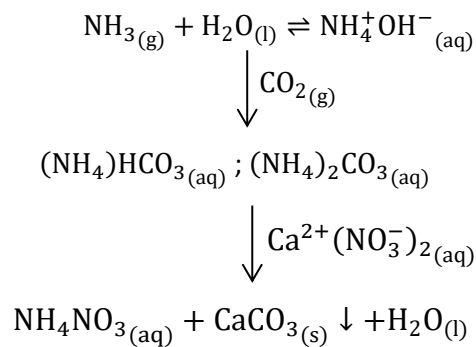
### 105 **2.1. The engineered process**

106 The process for procurement of CCm has been developed to utilise recycled materials as far  
107 as possible and is shown schematically in Figure 1. A cellulose based waste material is fed to  
108 the mixer; at the same time a solution of aqueous ammonia is fed to the reactor together with  
109 industrially sourced CO<sub>2</sub> entrained within flue gas. Potential contaminants in the industrial  
110 gas stream include NO<sub>x</sub> and SO<sub>y</sub>, however, measured concentrations of both in flue gas are  
111 below 500 ppm in the analysed systems and are therefore, negligible. Furthermore, due to the  
112 presence of ammonia in the capture reaction, any NO<sub>x</sub> and SO<sub>y</sub> present are converted to  
113 ammonium nitrate and ammonium sulphate, which are well established fertiliser materials.  
114

115 The gas reacts with the ammonia. A solution of aqueous calcium nitrate is fed to the reactor  
116 where it forms a suspension of calcium carbonate in the ammonium nitrate solution. This

117 reaction is highly exothermic and importantly, the heat produced can be recovered for  
 118 ancillary processes, reducing energy needs. The suspension is injected into the mixer to be  
 119 absorbed by the cellulosic matrix. Further CO<sub>2</sub> may be fed to the mixer in order to complete  
 120 the reaction process. Plant nutrients may be subsequently added to the mixer during the  
 121 completion phase prior to pelletisation.

122 Equation 1 shows the reaction pathway between ammonia-calcium nitrate solution and  
 123 gaseous CO<sub>2</sub>. The concentration of CO<sub>2</sub> at the inlet is approximately 10% on average.  
 124 A portion of the flue gas emitted is fed through the system, where it is circulated until the  
 125 CO<sub>2</sub> concentration drops below 1%. The amount of CO<sub>2</sub> captured as a proportion of the  
 126 reactants is about 13%. however, products of the reaction (ammonium nitrate and calcium  
 127 carbonate), and therefore the amount of CO<sub>2</sub> captured, are dependent on the concentration of  
 128 reagents and the reaction conditions, particularly gas injection rate and bubble size, agitation  
 129 speed, temperature, pressure and residence time, all of which can be manipulated.



130

131

132 Ca(NO<sub>3</sub>)<sub>2</sub> is used as NH<sub>4</sub>HCO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> are not stable long-term and readily revert to  
 133 ammonia and CO<sub>2</sub>, which is unsuitable and unsafe to be sold as a fertiliser product, and is  
 134 sourced from fertiliser materials suppliers. CO<sub>2</sub> is converted to CaCO<sub>3</sub>, which acts as both a  
 135 binder for the pellets, as well as nutrients for plants. The stability of stored CO<sub>2</sub> and residence  
 136 time in soil is beyond the scope of this pump-priming study and will require long-term  
 137 experiments, inclusive of soil biota, to be measured.

138

139 With sustainability at the heart of CCU technologies, a completely new approach to  
 140 simultaneously address key environmental issues highlighted above has been engineered and  
 141 developed with the aim of improving soil capabilities. Here we report on a pump-priming  
 142 investigation into the potential of CCm to improve soil characteristics relevant to food  
 143 production, and in particular soil water retention. As a completely novel product, the research  
 144 objective was to provide initial quantification of effects on soil physical, chemical and  
 145 biological components of the CCU-derived product, other than as a base-line fertiliser. With a  
 146 specific emphasis on soil water retention and availability, carbon input, pH, crop growth and  
 147 microbial numbers and provide impetus for further development of the technology.

148 All experiments were conducted under controlled laboratory or growth conditions to  
 149 maximise throughput due to the inherent nature of soil to respond slowly to changes in  
 150 physical properties.

## 151 2.2. Experiments

### 152 2.2.1. Standardised soil

153 Two types of compost were used as standardised soil, an organic peat-based compost,  
154 Levington's M3 and an open-structured mineral soil, John Innes no. 2 (JI) (East Riding  
155 Horticulture Ltd., UK) both widely used in the horticultural sector. For each experiment  
156 compost from the same bag or batch number was used to minimise soil heterogeneity. Wet  
157 soil bulk density when taken from the bag was measured as  $0.48 \text{ g cm}^{-3}$  (M3) and  $0.53 \text{ g cm}^{-3}$   
158 (JI) [17]. For M3 this corresponds to a peat-based compost comprising ~60% sphagnum moss  
159 [18].

### 160 **2.2.2. Physico-chemical properties with addition of CCm**

161 A preliminary pot experiment was set up using M3 in a 1L pot size. 5 Replicates each of M3  
162 and M3 plus CCm ( $25 \text{ g L}^{-1}$ ). Pots were weighed prior to start to ensure the same weight per  
163 pot. In controlled constant conditions ( $23.5 \pm 0.7 \text{ }^\circ\text{C}$  temperature,  $33 \pm 2\%$  relative humidity),  
164 the pots were watered to saturation with 400 mL (standing water in pot trays) and then  
165 measured daily for water loss both gravimetrically (weighing each pot) and by theta probe  
166 (ML3 theta probe and HH2 data meter, Delta-T Devices, Cambridge, UK) for 16 days.  
167 Temperature in the centre of each pot was measured via thermocouples (K-type, RS  
168 components, UK) inserted to the centre of each pot and coupled to a continual logging system  
169 (TC-08, PicoTechnology, UK). This experiment was repeated using JI in 400 mL pots with a  
170 reduced application rate of CCm of  $2.3 \text{ g L}^{-1}$ .

171 A dose-dependent study to measure the potential for added carbon to influence soil water  
172 retention (the water/carbon relationship) was investigated by correlation using horticultural  
173 sand (400 mL volume) with addition of CCm at 0, 0.5, 1.0, 2.0, 4.0, and 8.0 g CCm. Pots  
174 were watered to saturation and allowed to dry over 10 days.

175 % total carbon: 3g samples of CCm (raw product), M3 and M3 plus CCm were dried for 7  
176 days at  $70^\circ\text{C}$ , ground in an agate pestle and mortar. Measurements were made on 0.1 mg sub-  
177 samples by combustion in a Sercon (PDZ Europa) ANCA-GSL Elemental Analyser (EA)  
178 coupled to a 20-20 continuous-flow mass spectrometer using an ANCA GSL preparation  
179 module, coupled to a 20–20 stable isotope analyser. 3 replicates each. Sand was treated in the  
180 same way.

181 Soil pH: 3g samples of soil were added to 50 mL water, shaken for 30 mins, allowed to settle  
182 for 1 hour, shaken and measured (Jenway 3520 pH meter, SLS Laboratory Supplies, UK).

183 Leachate pH: after watering to saturation, soil was allowed to dry out for 5 days, re-watered  
184 until water collected in pot saucers. 25 mL of the leachate was collected using a syringe,  
185 placed in universal tubes and measured as above.

### 186 **2.2.3. Soil water retention in different substrates**

187 The same controlled conditions were used to trial CCm in different substrates; sand, a  
188 degraded agricultural mid-field soil (degraded, subjected to mechanised agricultural  
189 practices), agricultural margin soil (not currently under mechanised practises and recovering)  
190 (samples collected from East Anglia, UK), M3 and JI. Agricultural soils are different to  
191 standardised soils in both structure and uniformity. These were included to verify the  
192 responses seen in standardised soils. Wet bulk density [19] of agricultural margin and mid-  
193 field soils were measured as  $1.15$  and  $1.05 \text{ g cm}^{-3}$  respectively, both having >25%  
194 gravel/stone content and poorly graded.  $25 \text{ g L}^{-1}$  of CCm was added to 400 mL pots (9 cm)  
195 pots, soaked to saturation (200mL water) and measured against controls (no CCm) for water  
196 retention using the theta probe over 35 days with re-wetting on day18 with 50 mL water. 3  
197 replicates per substrate per treatment.

#### 198 **2.2.4. Soil matric potential**

199 Soil matric potential was measured over time in 5 L pots using sensors (Decagon MPS-6  
200 matric potential/soil temperature sensors coupled to an Em50 data logger; Labcell Ltd, Alton,  
201 UK). 2 separate experiments were run using JI and M3. Pots included controls (no CCm),  
202 CCm at 2.3g L<sup>-1</sup>. One of each treatment had sensors (limited availability) but all replicates (3  
203 per treatment) were measured daily for soil water content via theta probe to confirm results of  
204 the sensors. Wheat (*Triticum aestivum* cv. Skyfall) was included in both experiments to exert  
205 plant root hydraulic pressure (4 plants per pot). Experiments were carried out in a controlled  
206 environment greenhouse (conditions set as 20/15 °C day/night, day length of 16 hrs with  
207 supplementary lighting ( Philips master colour cdm-tp mw 315w/942, Philips Lighting UK)  
208 of 180 μmol m<sup>-2</sup> s<sup>-1</sup> at bench height, total of 240 μmol m<sup>-2</sup> s<sup>-1</sup> ± 50 μmol m<sup>-2</sup> s<sup>-1</sup> ( Licor light  
209 meter, Licor Inc., USA). Relative humidity was not controlled but measured as 36 ± 5%.

#### 210 **2.2.5. Plant interactions**

211 A dose-dependent experiment was set up to investigate plant interactions with CCm at  
212 increasing concentration. Wheat (*Triticum aestivum* cv. Skyfall) was sown 5 per pot (400 mL  
213 vol) using JI and CCm at concentrations of 0, 0.42, 1.67, 3.33, 6.67 g L<sup>-1</sup>, grown in the  
214 controlled greenhouse (conditions as before) for 29 days. Pots were watered on days 1, 3, 6,  
215 14 (50 mL), and 19 (100 mL) to allow plant establishment and growth. Gravimetric  
216 measurements were made throughout. Water loss from pots was calculated as start weight  
217 minus final weight (g). Plant biomass was measured as all leaf material per pot, fresh weight  
218 on harvest then dried to constant weight at 55 °C. % water lost from leaves was calculated as  
219 fresh minus dry weight (g). Carbon and nitrogen content: plant and soil samples (0.1mg of  
220 leaf and roots per plant; 10g soil material per pot) were dried for one week at 50° C and  
221 ground in an agate pestle and mortar. Five plants per pots per treatment were analysed.  
222 Analyses were performed by combustion in a Sercon (PDZ Europa) ANCA-GSL Elemental  
223 Analyser (EA) coupled to a 20-20 continuous-flow mass spectrometer. (n= 5).

#### 224 **2.2.6. Microbial interactions**

225 JI was autoclaved twice (with 3 days between) to reduce microbial content to a baseline level  
226 and allow re-colonisation under experimental conditions. A test of effectiveness of  
227 autoclaving was carried out. 5g samples of freshly autoclaved and non-autoclaved (control)  
228 soil were weighed into centrifuge tubes. 20 mL sterile buffer (10mM MgSO<sub>4</sub> + 0.01% Tween  
229 40 [20]) was added to the tube and vortexed for 1 min. Serial dilutions from 200 μL to x7  
230 dilution were plated onto bacterial agar (VWR Chemicals, BDH, UK) sterile petri-dishes and  
231 incubated over 7 days at 28 °C (LMS cooled incubator). Daily counts of colonies were  
232 recorded. This gave suitable dilutions for the end of the experiment as 50 and 25 μL per  
233 plate.

234 Autoclaved soil (JI, and JI plus CCm at 30 g L<sup>-1</sup>) were placed in the greenhouse (conditions  
235 as before) and left for 25 days (replication of 3 pots per treatment) to allow for microbial re-  
236 colonisation. 3g of soil was sampled from each pot and diluted to 50 and 25μL per plate.  
237 Buffer, plating, incubation and counting followed the same procedure as above.

#### 238 **Statistics**

239 Time point and biological analyses utilised Student's t-tests, Pearson's correlation co-  
240 efficient and significance and one-way ANOVAs performed using Minitab V 13.

#### 241 **3. Results**

### 242 **3.1. Soil water retention in standardised soil**

243 Preliminary data of soil water volume using M3 and M3 + CCm applied at a rate of 25 g L<sup>-1</sup>  
244 over time are shown in Figure 2a. Addition of CCm produces statistically higher soil  
245 moisture content than controls throughout (Table 1). % volume measurements via theta probe  
246 were verified with additional daily measurements of gravimetric water content, each pot  
247 having started at the same weight. There was a highly significant correlation between both  
248 measures (Figure 2a insert). The mean % increase in soil moisture with CCm from controls  
249 (Figure 2b) gives an average over the experimental time frame of 36% with a maximum  
250 increase of >60% on day 12.

### 251 **3.2. Soil water retention in different substrates**

252 Soil water measurements were made on a set of different substrates, including sand (inert,  
253 very open structure), agricultural mid-field soil and agricultural field margin together with  
254 both standardised soils (JI and M3). Figure 3a - e show % water volume for each substrate  
255 measured daily over 35 days with and without the addition of CCm. Table 2 gives the mean  
256 % water content after 35 days, with the maximum % difference from controls occurring on  
257 specific days. Substrates were re-watered with half the initial amount of water on day 18.  
258 Mean increases above controls over the experimental time show a range of between 20 and  
259 62% (Figure 3f).

### 260 **3.3. Soil matric potential in standardised soil and the effect of plants**

261 Figure 4 shows  $\Psi$  logged over time from experiments using both M3 (Figure 4a) and JI  
262 (Figure 4b) with CCm at an application rate of 2.3g L<sup>-1</sup> (one tenth of previous experiments).  
263 M3 (control) was tested separately with CCm and with the addition of a crop plant, wheat  
264 (*Triticum aestivum* cv. Skyfall). JI had wheat in both control (soil) and CCm addition.  
265 Watering was carried out on days 20, 24 and 26 to allow sufficient root growth of wheat to  
266 exert an effect on  $\Psi$ . **Table 3** shows the effect of both CCm and plants on  $\Psi$  over time,  
267 together with the stage (day number) that each treatment took to breach both the field  
268 capacity (FC) and permanent wilt point (PWP). Prior to watering on day 20, FC is breached  
269 in both soil types with the addition of wheat on day 6, however with the addition of CCm this  
270 occurs on days 16 (M3) and 18 (JI). PWP is not reached in M3 without plants, however, with  
271 plants this occurs on days 28 (M3) and 29 (JI) without CCm. At the end of the experiment  
272 (day 35), the addition of CCm affords 88% and 99% difference in  $\Psi$  in the presence of plants  
273 (Table 3).

### 274 **3.4. CCm effect on physico-chemical properties of standardised soil**

275 Standardised soils (M3 and JI) were used for measurements on physico-chemical properties  
276 relevant to cultivation. Figure 5a shows mean carbon (C) content at the end of the preliminary  
277 experiment (shown in Figure 2) measured in CCm (raw product), M3 control and M3 plus  
278 CCm as 15.3, 9.5 and 22.5% respectively (Table 4). Figure 5b shows both the response of  
279 water retention to addition rates of 0, 0.5, 1, 2, 4 and 8 g CCm in 400mL sand and the  
280 response of water retention to the % carbon input from the product. Soil temperature of the  
281 M3 experiment was logged over 16 days (Figure 5c, Table 4) with a slight initial increase  
282 from day 2 to 4 of ~0.5° C. Figure 5d (Table 4) shows the effect of CCm on pH of M3 as an  
283 increase of 0.7 and JI of 1.1 pH units. Additional pH measurements of both soil and soil  
284 leachate were carried out using JI after 16 days. A dose-dependent study for leachate pH was  
285 performed using M3 to verify the action of CCm on pH (Figure S1).

### 286 **3.5. Plant and microbe interactions**



287 Figure 6a shows the linear relationship of a dose dependent study on gravimetrically  
288 measured water retention in M3 with wheat. Figure 6b and c show the mean biomass of all  
289 harvested wheat leaves and the % water loss on drying (the difference between fresh weight  
290 and dry weight (Figure 6b) after 29 days. Figure 6c shows the % nitrogen content of leaves,  
291 roots and soil after harvest.

292 Figure 7 shows results of microbial numbers in response to addition of CCm against controls  
293 using JI. Initial autoclaving results in a 50% reduction in microbial numbers (Figure 7a).  
294 Figure 7b shows a significant increase in microbial numbers with addition of CCm following  
295 an incubation period of 25 days.

## 296 **4. Discussion**

### 297 **4.1. Soil water retention in standardised soils and different growing substrates**

298 Initial quantification of soil water retentive properties of CCm was carried out using an  
299 organic peat-based compost, Levington's M3 (M3). This followed standard experimental  
300 protocol to minimise heterogeneity for measurement of physical properties. Daily  
301 measurements over 16 days show that the addition of CCm produces statistically higher soil  
302 moisture content than controls throughout (Figure 2a, Table 1) indicating a capability to  
303 significantly increase water retention with immediate effect. Theta probe measurements were  
304 tested against daily gravimetric determination of water loss producing a highly significant  
305 correlation, verifying the accuracy of the spot measurements of % volume. The % increase in  
306 soil moisture with CCm from controls (Figure 2b) over the experimental time frame results in  
307 30% better water retention compared to a widely used horticultural product, vermiculite,  
308 tested using the same system (Supplementary Table S1). Furthermore, water retention is  
309 enhanced as soil dries over time suggesting a prolonged impact on water retentive properties.

310 To test whether this capability is evident in a range of growing media and rapidly assess the  
311 potential for future research focus by comparison with real agricultural growing media, soil  
312 water measurements were made on a set of widely different substrates, including agricultural  
313 mid-field and field margin soils together with both standardised soils (JI and M3) and  
314 horticultural sand. Addition of CCm (again at an application rate of  $25\text{g L}^{-1}$ ) to different  
315 substrates shows the potential to increase water retention across a range of soil types and  
316 structures including sand, therefore water retention is afforded by CCm itself. Substrates  
317 were re-watered with half the initial amount of water on day 18 to test whether water  
318 retentive properties are maintained. Re-wetting demonstrates no loss of this capability.  
319 Profiles of soil moisture show that different substrates behave differently with respect to  
320 water retention. This was not unexpected as variation in soil characteristics and properties are  
321 well known.

322 The day of maximum difference from controls also differs between substrates (Table 2), and  
323 surprisingly, there is a larger effect in both degraded (mid-field) and marginal agricultural  
324 soils. Both soils hold ~28 and ~18% less water than standardised composts (M3 and JI)  
325 respectively when dry (days 17 and 37), indicative of degradation as mechanically degraded  
326 soils have a higher bulk density which can severely impact on water retentive properties [20].  
327 This was measured in the mid-field soil as  $1.15\text{g cm}^{-3}$  and the marginal soil as  $1.05\text{g cm}^{-3}$ .  
328 The mid-field soil shows correspondingly lower water content and demonstrates the link  
329 between bulk density and water retention [19]. Both M3 and JI have bulk densities of  $0.48\text{g cm}^{-3}$   
330 ( $0.48\text{g cm}^{-3}$  (M3) and  $0.53\text{g cm}^{-3}$ , again with correspondingly higher water content than  
331 agriculturally damaged soils. Mean increases above controls over the experimental time show  
332 a range of between 20 and 62% (Figure 3f) with both agricultural soils showing better

333 improvement in water retention over time with CCm addition than either of the standardised  
334 soils (M3 and JI). In comparable laboratory pot experiments, recent studies using the nearest  
335 equivalent soil improvement additive, biochar, in natural soils have reported increased  
336 available water of between 21 and 38% [21], water volume increases of ~11% [22] or no  
337 effects on soil moisture [23]. This demonstrates that soil variability, as well as climatic  
338 differences can affect the remediation of soil carbon. A more direct comparison is afforded  
339 by a study using biochar in sand at three doses which does give comparable increases in  
340 water retention of between 44 and 68% [24], however production of biochar involves  
341 feedstock materials, such as miscanthus or wood chips, which are slow-burned (pyrolysed)  
342 producing non-condensable gases, including CO<sub>2</sub> [25], whereas CCm technology involves  
343 direct capture of CO<sub>2</sub>.

#### 344 **4.2. Soil matric potential in standardised soil and the effect of plants**

345 Although measurements of soil water volume on a daily basis using the theta probe shows  
346 clear advantages of CCm, these measurements are not continuous and do not reflect water  
347 movement within the pot, e.g. vertically movement as evaporative demand occurs at the soil  
348 surface [26]. As such, there may be higher or static measurements as water migrates rather  
349 than a measure of total soil moisture within the pot. Soil matric potential ( $\Psi$ ) differs from %  
350 water volume as the base component (soil) of a continuous hydraulic pressure gradient from  
351 soil to atmosphere, whereby high  $\Psi$  (less negative) equates to greater water content and low  
352  $\Psi$  (more negative) to a drier environment. This is a more useful measurement for soil-plant  
353 interactions as plants utilise this gradient to passively take up water and nutrients via their  
354 roots, allowing water to escape from the leaf surface via evapotranspiration.  $\Psi$  is therefore a  
355 more accurate measure of water availability and depletion by crops. Field capacity (FC) is  
356 defined as the amount of water held by soil following natural drainage, and is equal to  
357 available soil water, and the permanent wilt point (PWP) is reached when there is insufficient  
358 water to sustain crop integrity. Unlike % water volume and gravimetric measurement,  $\Psi$   
359 initially remains constant at less than -11kPa in all treatments (equating to FC; [27]). This is  
360 because the magnitude of  $\Psi$  is dependent on soil water, pore spaces, surface properties of  
361 soil particles and the surface tension of soil water and is more usefully described by [28] as  
362 the 'water release characteristic'. As the matric potential becomes more negative, water  
363 drainage ceases and the matric potential state is tension saturated. Further drying of the soil  
364 allows air into the pore spaces which initiates the change in potential, becoming increasingly  
365 more negative.

366 FC was breached in all treatments within 18 days. In pots containing wheat, this occurred 5 to  
367 12 days earlier than with the addition of CCm with wheat. Interestingly, in M3 control and  
368 M3 with CCm but without wheat, this occurred earlier than treatments with wheat plus CCm.  
369 It is thought that the uncovered soil surface (no plant cover) allowed a greater loss of water  
370 initially and that root development was insufficient to exert an effect on  $\Psi$ . Watering was  
371 carried out, therefore, on days 20, 24 and 26 to allow sufficient root growth. This is  
372 manifested as slight increases (less negative) in  $\Psi$  in Figure 4a (shorter time and smaller scale  
373 for detail). PWP is not breached in pots containing no plants over the experimental time  
374 frame, however, PWP is breached in all pots containing wheat demonstrating the rapid  
375 depletion of available water through plant uptake. Addition of CCm affords a delay in PWP  
376 of 9 (M3) and 5 (JI) days with a difference of 99% and 88% in  $\Psi$  respectively, in the  
377 presence of plants (Table 3) by day 37 (Figure 4b, Table 3). These results also demonstrate  
378 the effect of soil type and structure with respect to  $\Psi$ . M3, an organic soil with a high content  
379 of large particulates (decayed plant material) and pore spaces, held water more readily  
380 initially but at the end of 37 days had a final  $\Psi$  of ~-85,000 kPa in the presence of wheat. By

381 contrast, JI, a mineral based soil with much smaller particles and pores, including a clay/silt  
382 component, held water more steadily over time, reaching a final  $\Psi$  of  $\sim$ 12,000 kPa. The  
383 addition of CCm acts to make both of these soils more uniform with respect to  $\Psi$  (Figure 4).  
384 No direct comparisons for this experiment were found in the literature, however, the delay  
385 afforded by CCm to reach the PWP may prove decisively beneficial at critical growth stages  
386 when crops become more sensitive to water deficit e.g. cereal grain filling or root crop tuber  
387 initiation [29].

### 388 **4.3. CCm effect on physico-chemical properties of standardised soil**

389 Mean % carbon (C) content at the end of the preliminary experiment ( shown in Figure 2)  
390 was measured in CCm (raw product), M3 control and M3 plus CCm as 15.3, 9.5 and 22.5%  
391 respectively (Figure 5a, Table 4) showing that  $\sim$ 90% of the C content of CCm was retained in  
392 soil over the experimental period of 16 days. However, there was a loss of  $\sim$ 10% suggesting a  
393 possible stimulation of soil respiration via microbial activity under controlled conditions  
394 (investigated below). The slight raise in temperature in the initial phase of the experiment  
395 provided further anecdotal evidence of an increase in soil activity (Figure 5c).

396 The relationship between water retention and % C input via the product was further  
397 investigated using horticultural sand. Figure 5b shows the response of water retention  
398 following addition rates of 0, 0.5, 1, 2, 4 and 8 g CCm to 400mL sand. Water content (% vol)  
399 is highly significantly correlated to the application rate of CCm. There is also a significant  
400 correlation between % C and water retention, however this is at lower values of % water  
401 volume, suggesting that the carbon input is a significant, but not exclusive, contribution to the  
402 mode-of-action of CCm. It is also less linear than the correlation with CCm added. This is  
403 likely to be due to the variation of small soil samples taken for C analysis (3g) of which only  
404 a fraction (0.1 mg) is used for mass spectrometry analysis. The correlation does provide  
405 evidence of a C input mode-of-action on water retention, in agreement with other studies [9].

406 Soil acidification is a major cause of soil degradation as a result of natural processes over  
407 time, but importantly, also by application of nitrogen fertilizers [6]. Results of soil pH  
408 measurements are to consistently increase pH by  $\sim$ 1 unit. This is a substantial increase,  
409 although it recognised that this increase may not be fully realised in an open system, as  
410 leachate also increases. However, as a novel fertiliser which doesn't reduce pH, there are  
411 advantages as increasing pH has beneficial effects on soil ecosystem services, particularly in  
412 respect of water quality, as previously described for land traditionally treated with lime [6].  
413 Such increases in soil pH may also be beneficial on degraded or even contaminated soils. It  
414 remains unclear how pH affects the OC content of different soils, with reports of both net  
415 losses and gains [30], therefore, further research in this area is required.

### 416 **4.4. Plant and microbe interactions**

417 As CCm substantially maintains  $\Psi$  at beneficial levels in both soil types M3 and JI (Figure  
418 4), this raised the question of whether the additional water retained was freely available to  
419 plants or held within the CCm/soil matrix. To address this question wheat was grown in a  
420 dose-dependent study over 29 days. At the end of the experiment gravimetric soil water loss  
421 revealed that soil water loss decreased with application rate, therefore water retention  
422 increased linearly (Figure 6a). Mean biomass (fresh and dry weight) of wheat leaves shows a  
423 dose dependent response up to a  $3.34\text{g L}^{-1}$  level of applied CCm (Figure 6b) and that  
424 harvested leaves contained more water (Figure 6c), both statistically significant as a function  
425 of CCm application rate (Table 4). This demonstrates that the product does not retain

426 available water at the expense of crop needs, despite the plants having no water for the last 10  
427 days of the experiment.

428 An incremental increase in biomass is consistent with an increasing addition of nitrogen (the  
429 product has a high concentration of ammonium as a consequence of specific production  
430 inputs) which stimulates growth and reaches to >40% at 3.34g L<sup>-1</sup> compared to control. This  
431 is confirmed by analysis of % total nitrogen in leaves, roots and soil, again increasing linearly  
432 with application rate (Figure 6d, Table 4). Biomass was noted to decline at the highest  
433 concentration (6.67 g L<sup>-1</sup>) observed (not measured) as consistent with symptoms of  
434 ammonium toxicity including leaf chlorosis [31], stunted leaf and root growth [32]. This was  
435 not unexpected as it represents a very high application rate for compounds containing ~15%  
436 total N (6.67 g L<sup>-1</sup> contains 1g L<sup>-1</sup>, equivalent 1mol L<sup>-1</sup>). Although ammonium toxicity is  
437 species specific with domesticated species generally showing more tolerance [32], symptoms  
438 have been reported at levels between 0.1 to 10 mmol L<sup>-1</sup> [32]. The result has informed on  
439 high N application rates for this product formula and future manipulation of formulae  
440 specifically for optimising water retention, OC input and plant growth.

441 The loss of soil carbon (Figure 5a) and slight increase in soil temperature recorded in the  
442 preliminary experiment (Figure 5c) suggested that soil respiration may be more active, which  
443 in turn suggests increased heterotrophic microbial activity [33]. To test this hypothesis  
444 microbial colonisation was measured with and without addition of CCm. JI was initially  
445 autoclaved to significantly reduce microbial content by ~50% but still provide a baseline for  
446 rapid microbial re-colonisation (Figure 7a). Autoclaved soil was then incubated for 25 days  
447 with and without (control) addition of CCm (30 g L<sup>-1</sup>). A significant increase in colony  
448 numbers (microbial classes were not examined) occurred compared to controls (Figure 7b).  
449 This provides evidence that CCm promotes re-colonization and microbial growth. As  
450 microbial growth and mobility are limited by available C and water respectively [34], CCm  
451 has the potential to deliver both a readily available C source and improve water availability.  
452 This may increase not only numbers, but soil microbial diversity. It is acknowledged that this  
453 requires further study but healthy soil requires a balance of microbes [35] and fungi [36] to  
454 successfully perform and maintain the essential ecosystem services of decomposition,  
455 nutrient cycling and fertility [35, 36].

## 456 **5. Conclusions**

457 We have clearly demonstrated the capabilities of a novel and innovative product to  
458 significantly improve soil physical, chemical and biological components. Key findings  
459 include an increase in soil water holding capacity of up to 60%, acting with immediate and  
460 prolonged effect which correlates significantly with soil carbon, providing evidence that  
461 carbon input is a constituent of the mechanism-of-action for water retention. Enhanced water  
462 retention occurs across a range of soil types. Crop plant water status is improved  
463 demonstrating that the water retained is available for plant growth, and both increased water  
464 content and carbon input facilitate an increase in microbial colonisation. A significant  
465 increase in soil pH of ~1.0 gives the product an added benefit as a general-use fertiliser. All  
466 of these properties have potential to impact on food production across a range of scales.

467 We recognise that trials conducted in this preliminary study utilise small-scale closed  
468 laboratory systems under controlled environment conditions, and it is fully acknowledged  
469 that mechanisms linking OC, soil water retention and interactions with living components in  
470 real-world soil systems are not simple (Minasny and McBratney 2018), however, results  
471 presented here provide impetus to further investigate mechanisms that produce and maintain

472 soil beneficial properties for development of the product to maximise effects over a full range  
473 of scales within horticultural/agricultural settings.

474 Furthermore, the engineered technology for efficient capture of otherwise ‘lost-to-  
475 atmosphere’ industrial CO<sub>2</sub>, gives a strong greenhouse gas reduction impetus which can be  
476 incorporated into methods for increasing sustainable use of finite resources and in particular  
477 to move toward a more sustainable approach to agricultural production.

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#### 481 **Author contribution**

482 JL conceived, designed and carried out all experiments. PK, PH and FM developed,  
483 engineered and supplied the products. All authors contributed to the manuscript.

#### 484 **Competing interests**

485 PK, PH and FM were employed by CCm Technologies Ltd. All authors declare no competing  
486 interests.

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614 **Table 1.** Statistical analysis of mean soil moisture retention (Fig 2a) and mean soil  
 615 temperature (Fig. 5c) [Time point Student's t-test, significance p value from control, n = 5,  
 616 DF = 5].

day number	% Soil water content	Soil temperature
1	0.008	0.273
2	0.012	0.016
3	0.041	0.073
4	0.099	0.089
5	0.01	0.185
6	0.002	0.187
7	0.001	0.21
8	<0.000	0.214
9	<0.000	
11	0.002	
12	<0.000	
13	<0.000	
14	0.015	
15	<0.000	
16	0.001	
17	<0.000	

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634 **Table 2.** Water volume measured in different substrates 35 days. Soils were saturated at the  
 635 start, and re-watered on day 18. (n=3 per substrate with CCm, n = 3 per substrate without  
 636 CCm)

<b>Soil type</b>	<b>sand</b>	<b>agricultural margin (soil)</b>	<b>agricultural mid-field (soil)</b>	<b>Levington's M3 compost</b>	<b>Jl no. 2 compost</b>
mean water content (%)	63.7	59.5	50.9	37.4	23.0
maximum increase from control (%)	96.7	95.6	75.0	61.0	51.7
Day of maximum increase (%)	18	32	13	35	32

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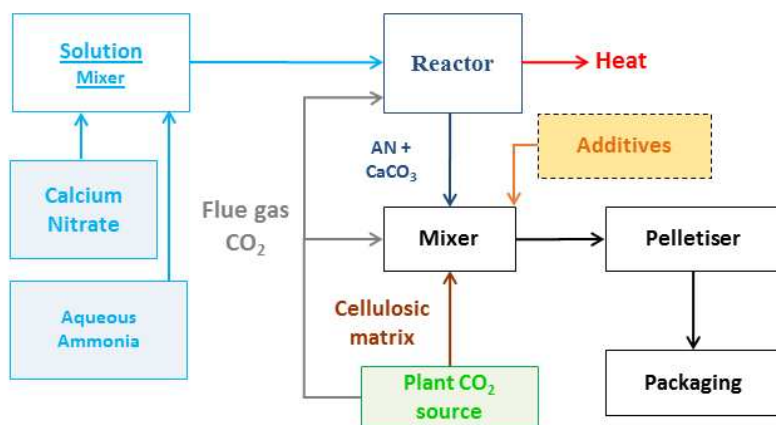
658 **Table 3.** Effect of CCm and wheat plants on soil matric potential ( $\Psi$ ) after 29 and 37 days for  
 659 M3 and JI and as a percentage difference in  $\Psi$  from controls. Day number to breach field  
 660 capacity (FC) and permanent wilt point (PWP) in each treatment.

treatment	$\Psi$ (kPa)		% difference with CCm (day 37) from controls	day number	
	Day 29	Day 37		FC	PWP
<b>M3</b>	-111	-175		11	Not breached
<b>M3 + CCm</b>	-117	-130	26%	11	Not breached
<b>M3 + wheat</b>	-1,750	-85,139		6	28
<b>M3 + CCm + wheat</b>	-389	-1,160	99%	16	37
<b>JI + wheat</b>	-236	-12,272		6	29
<b>JI + wheat + CCm</b>	-212	-2,732	88%	18	34

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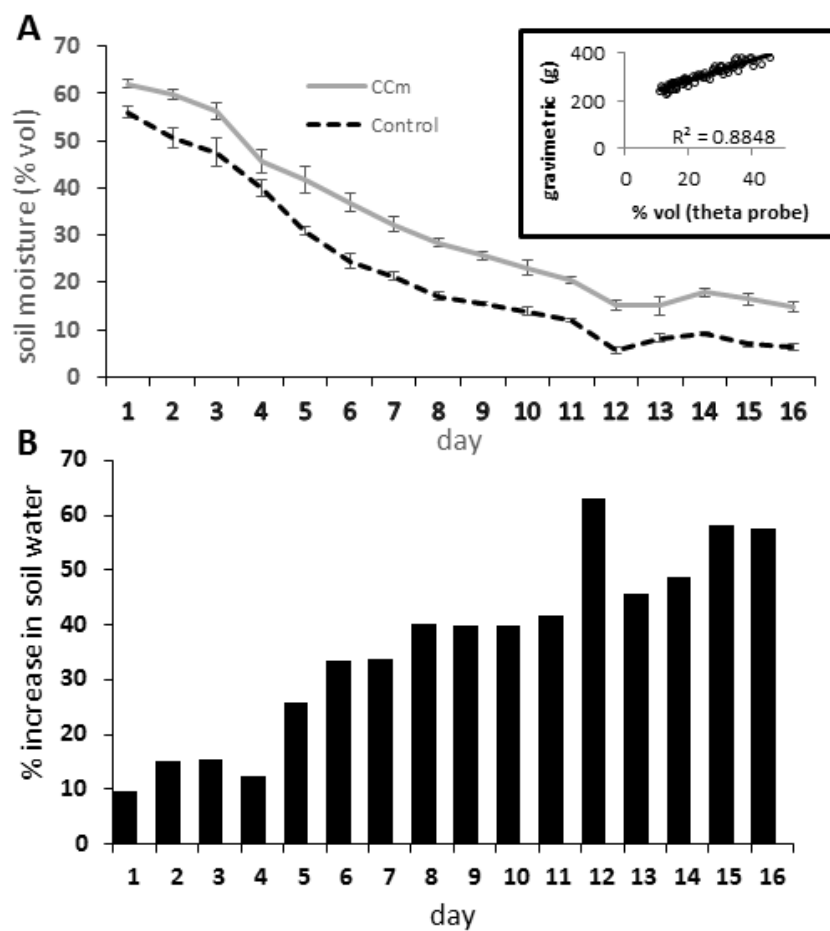
680 **Table 4.** One way ANOVA test for plant biomass (fresh weight, dry weight) ; % water loss  
 681 from leaves; % nitrogen in leaves, roots and soil and leachate pH all as a function of CCm  
 682 application rate.

factor	One way ANOVA				
	DF	SS	MS	F	P value
pH	4	0.757	0.189	18.38	<0.0001
Biomass (fr wt)	4	15.267	3.817	22.25	<0.0001
Biomass (dry wt)	4	0.3022	0.0756	13.5	<0.0001
% water loss (leaf)	4	10.47	2.618	3.98	0.035
% nitrogen/leaf	4	32.34	8.08	42.41	<0.0001
% nitrogen/root	4	17.35	4.33	40.16	<0.0001
% nitrogen/soil	4	1.662	0.416	50.1	<0.0001

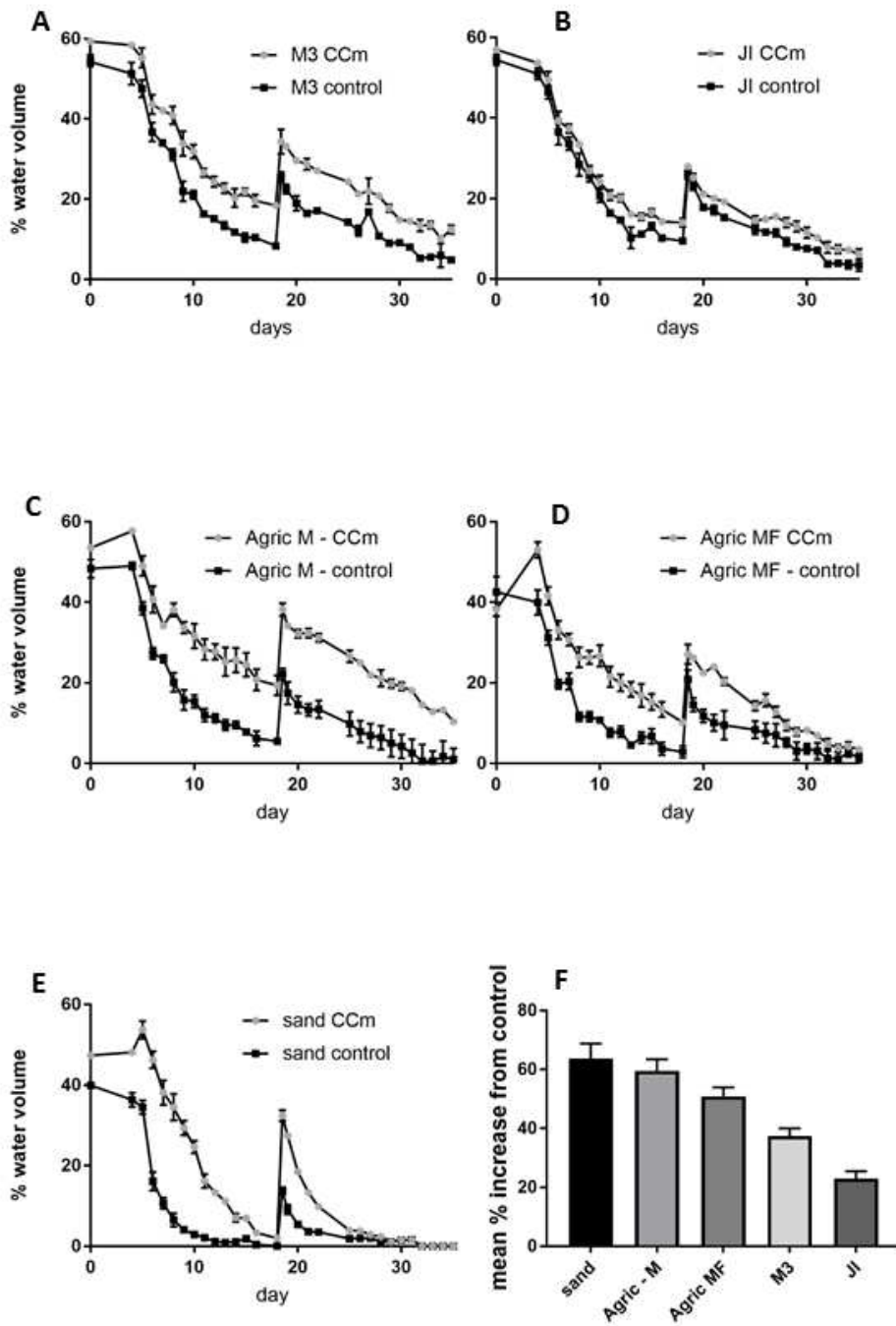


**Figure 1.** Schematic of the process of CO<sub>2</sub> capture and conversion into CCm pellets. AN = ammonium nitrate, additives are specified plant nutrients (nitrogen, potassium, phosphate) as required and do not affect the CO<sub>2</sub> capture process.

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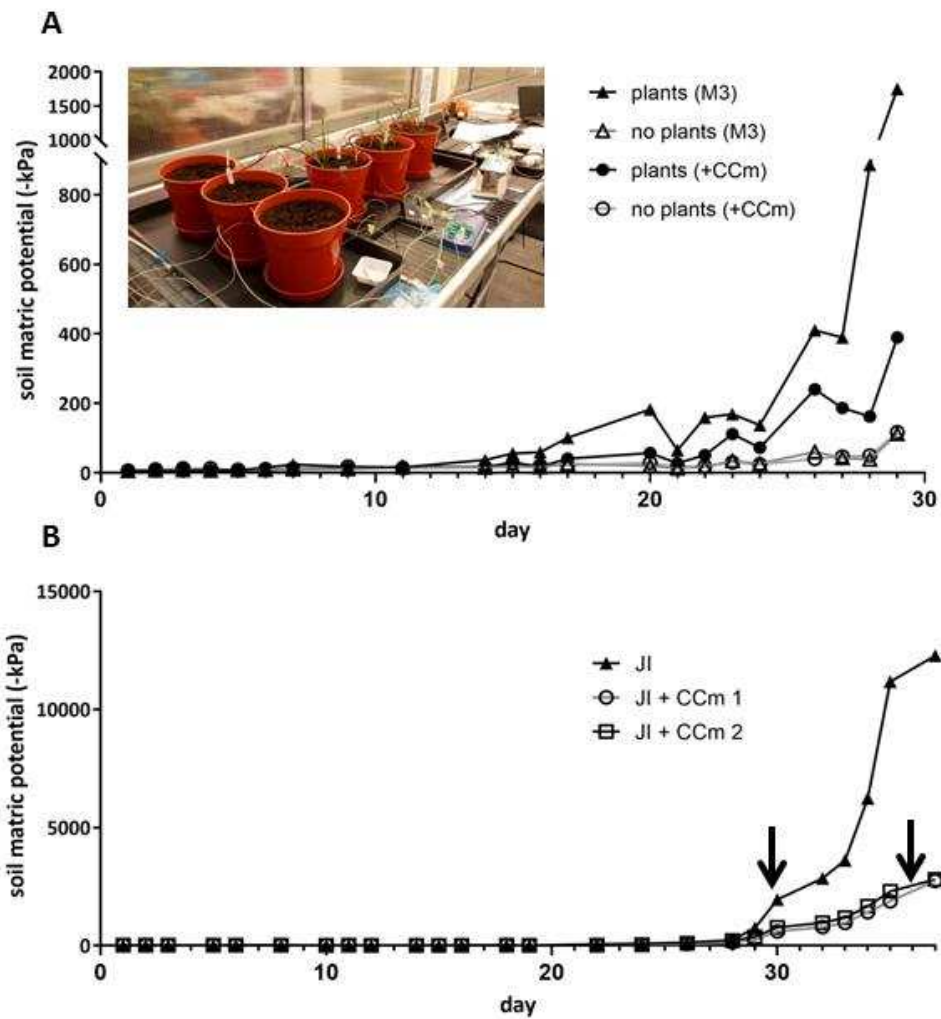
**Figure 2.** Water retention of M3 under controlled conditions with addition of CCm over 16 days drought. A) mean soil moisture (% vol water) measured by theta probe. (insert: gravimetric water content correlation with theta probe measurements; regression analysis  $R^2 = 0.866$ , Pearson's correlation co-efficient = 0.93,  $p < 0.0001$ ); B) mean % increase in soil moisture from control values [ $n=5$ , bars = SEmean]



**Figure 3.** A – E) % water volume of different substrates over 35 days (Agric M is marginal soil, Agric MF is mid-field soil) F) mean % increase from controls over the same period.[n = 3, bar = SEmean]

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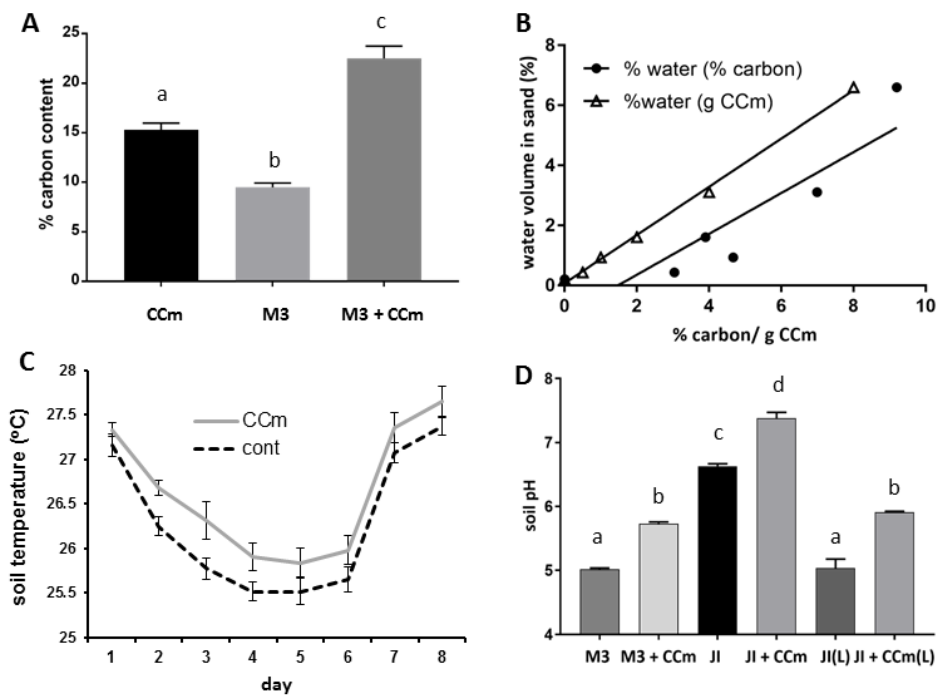
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**Figure 4.** A) Soil matric potential ( $\Psi$ ) logged over 29 days using M3 incorporating CCm and wheat. B) Effect of wheat on soil matric potential over 37 days in a repeated experiment using JI (JI + CCm 1 & 2 are replicates; arrow denotes permanent wilt point at -1,500 kPa)

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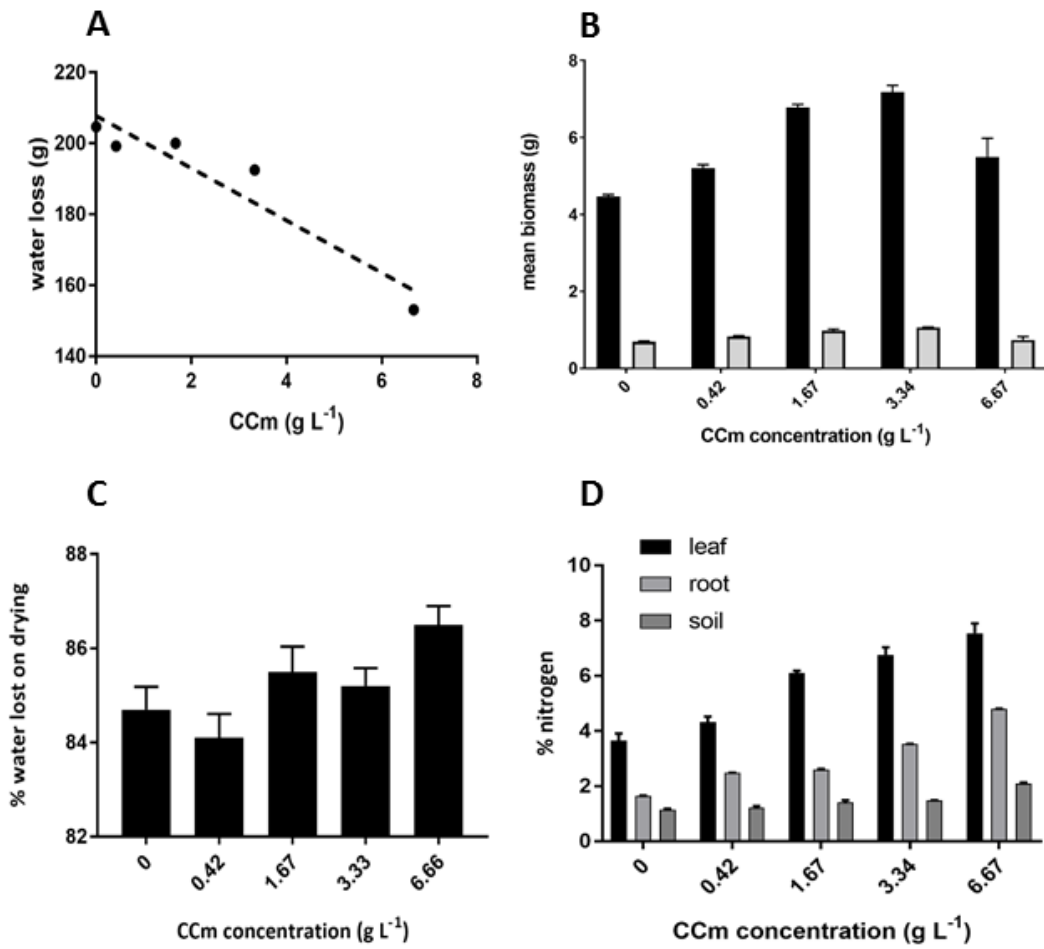
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**Figure 5:** A) Total carbon content (%) of CCm (raw product), M3 and M3 + CCm [n= 3, bar = SEmean]; B) regression analyses of correlations between water content and % carbon and between water content and CCm (g) added to sand (% carbon =  $R^2 = 0.808$ , Pearson's correlation coefficient = 0.911,  $p = 0.015$ ; g CCm =  $R^2 = 0.998$ , Pearson's correlation coefficient = 0.98,  $p = <0.0001$ ); C) soil temperature of M3 and M3 + CCm over 8 days [n= 5, bar = SEmean]; D) soil pH of M3 and Jl with and without CCm, L = soil leachate [n= 5, bar = SEmean, letters denote significance  $<0.05$ , significance levels for soil temperature in Table 1].

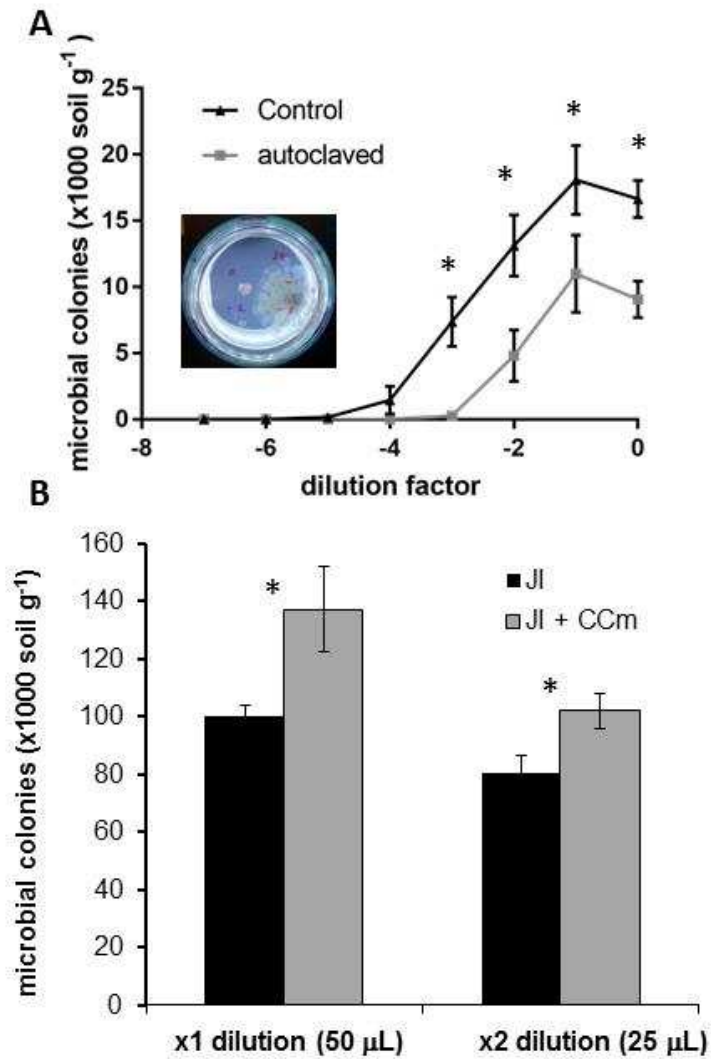
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**Figure 6.** A) Correlation between gravimetric water loss on day 29 and CCm concentration (regression analysis  $R^2=0.91$ , Pearson's correlation co-efficient = -0.95,  $p = 0.014$ ); B) % water loss from of wheat leaves; C) mean biomass of leaves [black = fresh weight, grey = dry weight]; D) % nitrogen of leaves roots and soil over at a range of CCm concentrations. [ $n = 5$ , bars = SEmean, statistics see Table 4]

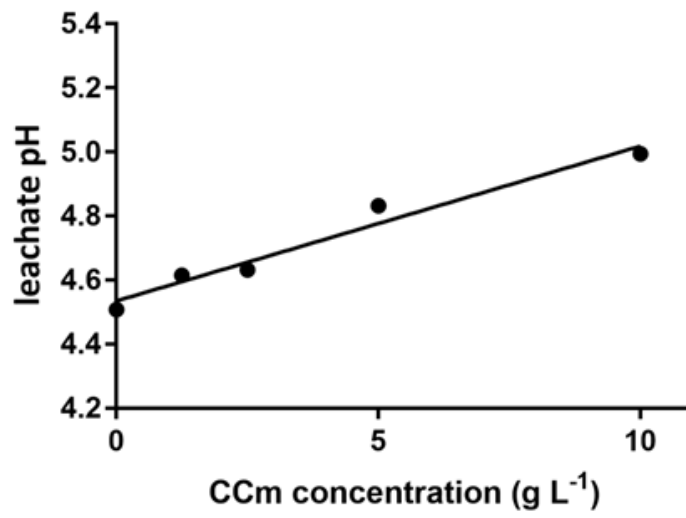




**Figure 7.** A) Autoclave test of microbial numbers of autoclaved and non-autoclaved JI. B) Microbial colonies from soil samples at the end of experiment following addition of CCm [n = 5, bars = SEmean, \* p = <0.05 time point Student's t-test].

**Supplementary Table S1.** Raw data for experiment 1: M3, M3 + CCm, M3 + vermiculite.

<b>Day number</b>	<b>Soil water volume (%)</b>		
	CCm added	Vermiculite added	M3 control (no addition)
1	62.1	59.14	56.06
2	59.9	55.14	50.74
3	56.34	51.16	47.58
4	45.68	42.24	39.98
5	41.68	34.3	30.86
6	36.92	28.08	24.54
7	32.3	23.64	21.36
8	28.44	17.3	17.02
9	25.64	17.32	15.42
10	23.14	16.26	13.92
11	20.54	13.88	11.94
12	15.16	7.4	5.6
13	15.08	9.88	8.2
14	17.9	10.94	9.16
15	16.52	9.34	6.92
16	14.92	9.38	6.34



**Figure S1.** Dose-dependent pH response to CCm in M3 soil leachate [n = 5, regression analysis of correlation  $R^2 = 0.965$ , Pearson's correlation coefficient = 0.98, p = 0.0029]