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

Working title: CCU and soil improvement

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

Abstract

With industrial CO_2-emission reduction the heart of carbon capture enabling technologies, we report on a solution engineered to potentially redress the issues of soil improvement and sustainable use of fresh water for food production. In a laboratory-scale pilot study, we demonstrate the capabilities of an innovative and novel product utilising carbon-capture to restore soil properties critical for crop production. In the first study of its kind, the carbon-initiated mode-of-action resulted in changes to soil physical and chemical properties. Soil water retention in a range of soil types was significantly increased by up to 62%; soil pH increased by 0.7 to 1.1 units: soil microbial colonisation increased by ~20% over the short term and crop biomass was enhanced by up to 38%. These results give impetus for developing CCU technologies to address environmental issues.

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

1. Introduction

Climate change and environmental degradation currently present humanity with an enormous and varied array of challenges. CO_2 emission reduction has progressed over recent years with respect to changes in energy use. In the UK a reduction of coal fired power stations has led to an average annual emission reduction of 16% between 2012 and 2016, however, other sectors (industry, transport, buildings and agriculture) have contributed only 1% over the same time period [1]. It is recognised that innovative state-of-the-art technologies have the potential to improve emission reductions, but also to act synergistically with other priorities [1]. Two key priority environmental challenges are becoming increasingly urgent. The first is soil degradation with associated impacts on agricultural production and global food security. The second is access to fresh water resources and the competing factors that impose a constraint on food production [2-4]. Furthermore, these challenges have relevance over a range of spatial scales from the individual small-holder/gardener, medium to large-sized horticultural enterprises producing food under glass, to industrial scale agricultural production.

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

The second challenge is the availability of fresh water resources required to facilitate the use of land across all spatial scales for food production while competing with demands from other economic sectors; industry [4], energy [10] and increasing urban water demand [11]. Water availability and accessibility are the largest constraining factors on crop production, with strong relationships between these and output capacity [4]. While it is known that productivity can be improved with irrigation even in humid climates, for example, the UK where wheat yield could be increased by an average of 25% [12], the failure to reach full potential yield is a consequence of deteriorating soils [3] rather than a lack of water.

Clearly, novel and innovative solutions are required to rapidly address present and future losses to agricultural capacity providing a sustainable approach to the management of soil. We have developed an engineering process which can directly fix CO_2 at source to procure a compound that has the potential to manipulate soil physico-chemical properties and substantially contribute to re-establishment of soil ecosystem services while also adopting Climate-Smart Agricultural practices to reduce greenhouse gases [13].

It has been recognised that carbon capture and sequestration (CCS), as a readily available source of carbon, has potential for crop productivity improvement via CO_2 storage materials (CO_2SMs) as demonstrated for glasshouse crops [14]. Soil improvement can be achieved by the crop sequestration of CO_2 and subsequent reincorporation of crop residues into soil [15]. This however, requires that land be left for residues to be naturally broken down over time. Carbon capture and utilisation (CCU) technologies have been engineered to efficiently capture industrial CO_2 and safely convert it into materials with the potential to restore and enhance the ability of soils to resist degradation via soil OC amendment. Using this technology we have engineered a novel CCU product comprising of a matrix derived from cellulosic waste feedstock (e.g. straw/paper pulp/digestate) that is coated in a nitrogenous material which facilitates capture of industrial CO_2 at source (see section 1.2.1). The matrix is then stabilised as a carbonate which has potential to re-introduce an OC-element to degraded soils. The product (denoted CCm hereafter) can be tailored to specific chemical compositions i.e. carbon to nitrogen ratio and/or the form it takes, powder, pellet or granular. It can also be produced to replicate commercial fertilizers with the addition of waste or recycled materials; nitrogen and potassium (from anaerobic digestate) and phosphate (from slaughterhouse waste), giving outputs greater sustainable credibility. The production of each tonne of CCm generates up to 6.5 tonnes less CO_2 than a typical conventional fossil-fuel based fertiliser supply route i.e. the Haber-Bosch process, which can contribute as much as 40% of C-emissions in the production of bread [16]. There is, therefore, potential to provide remediation of both soil OC status, structural integrity and associated water retentive capabilities over significant (catchment wide) areas, while the use of recycling waste streams results in more sustainable supply chains.

2. Materials and methods

2.1. The engineered process

The process for procurement of CCm has been developed to utilise recycled materials as far as possible and is shown schematically in Figure 1. A cellulose based waste material is fed to the mixer; at the same time a solution of aqueous ammonia is fed to the reactor together with industrially sourced CO_2 entrained within flue gas. Potential contaminants in the industrial gas stream include NO_x and SO_y, however, measured concentrations of both in flue gas are below 500 ppm in the analysed systems and are therefore, negligible. Furthermore, due to the presence of ammonia in the capture reaction, any NO_x and SO_y present are converted to ammonium nitrate and ammonium sulphate, which are well established fertiliser materials.

The gas reacts with the ammonia. A solution of aqueous calcium nitrate is fed to the reactor where it forms a suspension of calcium carbonate in the ammonium nitrate solution. This reaction is highly exothermic and importantly, the heat produced can be recovered for ancillary processes, reducing energy needs. The suspension is injected into the mixer to be absorbed by the cellulosic matrix. Further CO_2 may be fed to the mixer in order to complete the reaction process. Plant nutrients may be subsequently added to the mixer during the completion phase prior to pelletisation.

Equation 1 shows the reaction pathway between ammonia-calcium nitrate solution and gaseous CO_2. The concentration of CO_2 at the inlet is approximately 10% on average. A portion of the flue gas emitted is fed through the system, where it is circulated until the CO_2 concentration drops below 1%. The amount of CO_2 captured as a proportion of the reactants is about 13%. however, products of the reaction (ammonium nitrate and calcium carbonate), and therefore the amount of CO_2 captured, are dependent on the concentration of reagents and the reaction conditions, particularly gas injection rate and bubble size, agitation speed, temperature, pressure and residence time, all of which can be manipulated.

$$\begin{array}{c}
\mathrm{NH_3}_{(g)} + \mathrm{H_2O}_{(l)} \rightleftharpoons \mathrm{NH_4^+OH^-}_{(aq)} \\
\big\downarrow \mathrm{CO_2}_{(g)} \\
\mathrm{(NH_4)HCO_3}_{(aq)}\,;\,\mathrm{(NH_4)_2CO_3}_{(aq)} \\
\big\downarrow \mathrm{Ca^{2+}(NO_3^-)_2}_{(aq)} \\
\mathrm{NH_4NO_3}_{(aq)} + \mathrm{CaCO_3}_{(s)} \downarrow + \mathrm{H_2O}_{(l)}
\end{array}$$

$Ca(NO_3)_2$ is used as NH_4HCO_3 and $(NH_4)_2CO_3$ are not stable long-term and readily revert to ammonia and CO_2, which is unsuitable and unsafe to be sold as a fertiliser product, and is sourced from fertiliser materials suppliers. CO_2 is converted to $CaCO_3$, which acts as both a binder for the pellets, as well as nutrients for plants. The stability of stored CO_2 and residence time in soil is beyond the scope of this pump-priming study and will require long-term experiments, inclusive of soil biota, to be measured.

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

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

2.2. Experiments

2.2.1. Standardised soil

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

2.2.2. Physico-chemical properties with addition of CCm

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

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

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

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

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

2.2.3. Soil water retention in different substrates

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

2.2.4. Soil matric potential

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

2.2.5. Plant interactions

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

2.2.6. Microbial interactions

JI was autoclaved twice (with 3 days between) to reduce microbial content to a baseline level and allow re-colonisation under experimental conditions. A test of effectiveness of autoclaving was carried out. 5g samples of freshly autoclaved and non-autoclaved (control) soil were weighed into centrifuge tubes. 20 mL sterile buffer (10mM $MgSO_4$ + 0.01% Tween 40 [20] was added to the tube and vortexed for 1 min. Serial dilutions from 200 μmL to x7 dilution were plated onto bacterial agar (VWR Chemicals, BDH, UK) sterile petri-dishes and incubated over 7 days at 28 ^{o}C (LMS cooled incubator). Daily counts of colonies were recorded. This gave suitable dilutions for the end of the experiment as 50 and 25 μL per plate.

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

Statistics

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

3. Results

3.1. Soil water retention in standardised soil

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

3.2. Soil water retention in different substrates

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

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

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

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

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

3.5. Plant and microbe interactions

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

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

4. Discussion

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

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

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

The day of maximum difference from controls also differs between substrates (Table 2), and surprisingly, there is a larger effect in both degraded (mid-field) and marginal agricultural soils. Both soils hold ~28 and ~18% less water than standardised composts (M3 and JI) respectively when dry (days 17 and 37), indicative of degradation as mechanically degraded soils have a higher bulk density which can severely impact on water retentive properties [20]. This was measured in the mid-field soil as 1.15g cm^{-3} and the marginal soil as 1.05g cm^{-3}. The mid-field soil shows correspondingly lower water content and demonstrates the link between bulk density and water retention [19]. Both M3 and JI have bulk densities of 0.48 g cm^{-3} (M3) and 0.53 g cm^{-3}, again with correspondingly higher water content than agriculturally damaged soils. Mean increases above controls over the experimental time show a range of between 20 and 62% (Figure 3f) with both agricultural soils showing better improvement in water retention over time with CCm addition than either of the standardised soils (M3 and JI). In comparable laboratory pot experiments, recent studies using the nearest equivalent soil improvement additive, biochar, in natural soils have reported increased available water of between 21 and 38% [21], water volume increases of ~11% [22] or no effects on soil moisture [23]. This demonstrates that soil variability, as well as climatic differences can affect the remediation of soil carbon. A more direct comparison is afforded by a study using biochar in sand at three doses which does give comparable increases in water retention of between 44 and 68% [24], however production of biochar involves feedstock materials, such as miscanthus or wood chips, which are slow-burned (pyrolysed) producing non-condensable gases, including CO_2 [25], whereas CCm technology involves direct capture of CO_2.

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

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

FC was breached in all treatments within 18 days. In pots containing wheat, this occurred 5 to 12 days earlier than with the addition of CCm with wheat. Interestingly, in M3 control and M3 with CCm but without wheat, this occurred earlier than treatments with wheat plus CCm. It is thought that the uncovered soil surface (no plant cover) allowed a greater loss of water initially and that root development was insufficient to exert an effect on Ψ. Watering was carried out, therefore, on days 20, 24 and 26 to allow sufficient root growth. This is manifested as slight increases (less negative) in Ψ in Figure 4a (shorter time and smaller scale for detail). PWP is not breached in pots containing no plants over the experimental time frame, however, PWP is breached in all pots containing wheat demonstrating the rapid depletion of available water through plant uptake. Addition of CCm affords a delay in PWP of 9 (M3) and 5 (JI) days with a difference of 99% and 88% in Ψ respectively, in the presence of plants (Table 3) by day 37 (Figure 4b, Table 3). These results also demonstrate the effect of soil type and structure with respect to Ψ. M3, an organic soil with a high content of large particulates (decayed plant material) and pore spaces, held water more readily initially but at the end of 37 days had a final Ψ of ~-85,000 kPa in the presence of wheat. By contrast, JI, a mineral based soil with much smaller particles and pores, including a clay/silt component, held water more steadily over time, reaching a final Ψ of ~-12,000 kPa. The addition of CCm acts to make both of these soils more uniform with respect to Ψ (Figure 4). No direct comparisons for this experiment were found in the literature, however, the delay afforded by CCm to reach the PWP may prove decisively beneficial at critical growth stages when crops become more sensitive to water deficit e.g. cereal grain filling or root crop tuber initiation [29].

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

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

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

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

4.4. Plant and microbe interactions

As CCm substantially maintains Ψ at beneficial levels in both soil types M3 and JI (Figure 4), this raised the question of whether the additional water retained was freely available to plants or held within the CCm/soil matrix. To address this question wheat was grown in a dose-dependent study over 29 days. At the end of the experiment gravimetric soil water loss revealed that soil water loss decreased with application rate, therefore water retention increased linearly (Figure 6a). Mean biomass (fresh and dry weight) of wheat leaves shows a dose dependent response up to a 3.34g L^{-1} level of applied CCm (Figure 6b) and that harvested leaves contained more water (Figure 6c), both statistically significant as a function of CCm application rate (Table 4).This demonstrates that the product does not retain available water at the expense of crop needs, despite the plants having no water for the last 10 days of the experiment.

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

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

5. Conclusions

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

We recognise that trials conducted in this preliminary study utilise small-scale closed laboratory systems under controlled environment conditions, and it is fully acknowledged that mechanisms linking OC, soil water retention and interactions with living components in real-world soil systems are not simple (Minasny and McBratney 2018), however, results presented here provide impetus to further investigate mechanisms that produce and maintain soil beneficial properties for development of the product to maximise effects over a full range of scales within horticultural/agricultural settings.

Furthermore, the engineered technology for efficient capture of otherwise 'lost-to-atmosphere' industrial CO_2, gives a strong greenhouse gas reduction impetus which can be incorporated into methods for increasing sustainable use of finite resources and in particular to move toward a more sustainable approach to agricultural production.

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Author contribution

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

Competing interests

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

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

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

Soil type	**sand**	**agricultural margin (soil)**	**agricultural mid-field (soil)**	**Levington's M3 compost**	**JI no. 2 compost**
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

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

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

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

	One way ANOVA				
factor	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

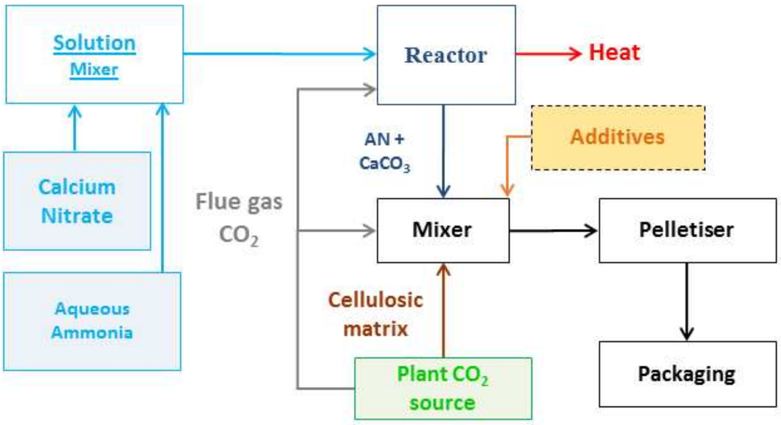

Figure 1. Schematic of the process of CO_2 capture and conversion into CCm pellets. AN = ammonium nitrate, additives are specified plant nutrients (nitrogen, potassium, phosphate) as required and do not affect the CO_2 capture process.

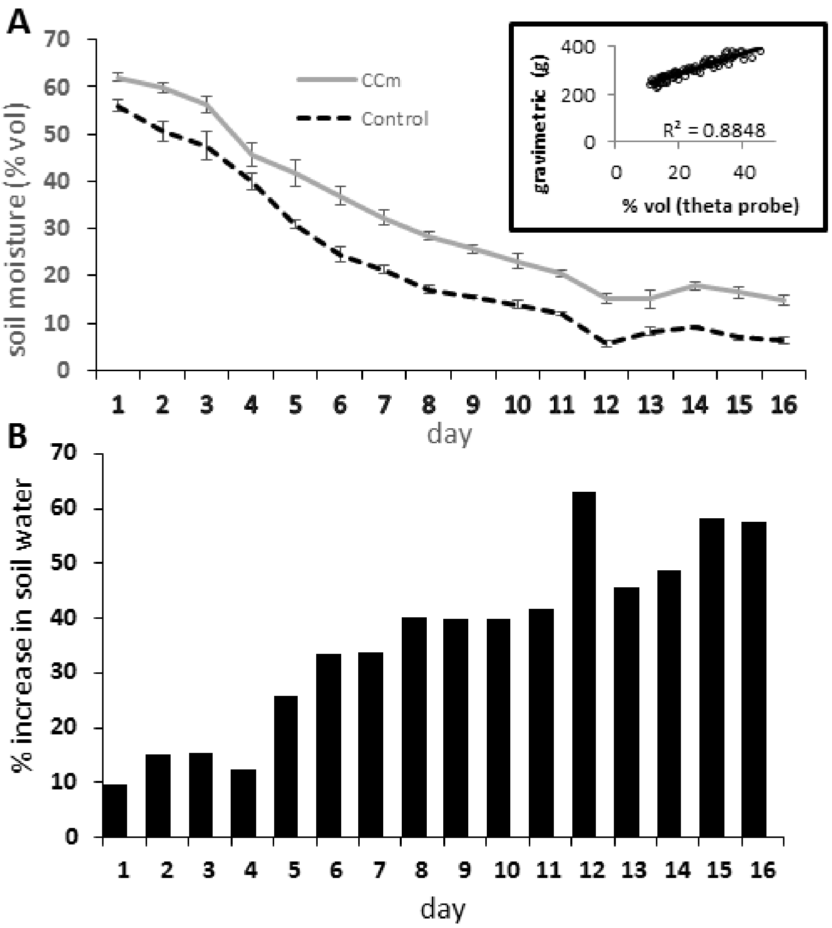

Figure 2. Water retention of M3 under controlled conditions with addition of CCm over 16 days drought. A) mean soil moisture (% vol water) measured by theta probe. (insert: gravimetric water content correlation with theta probe measurements; regression analysis $R^2 = 0.866$, Pearson's correlation co-efficient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

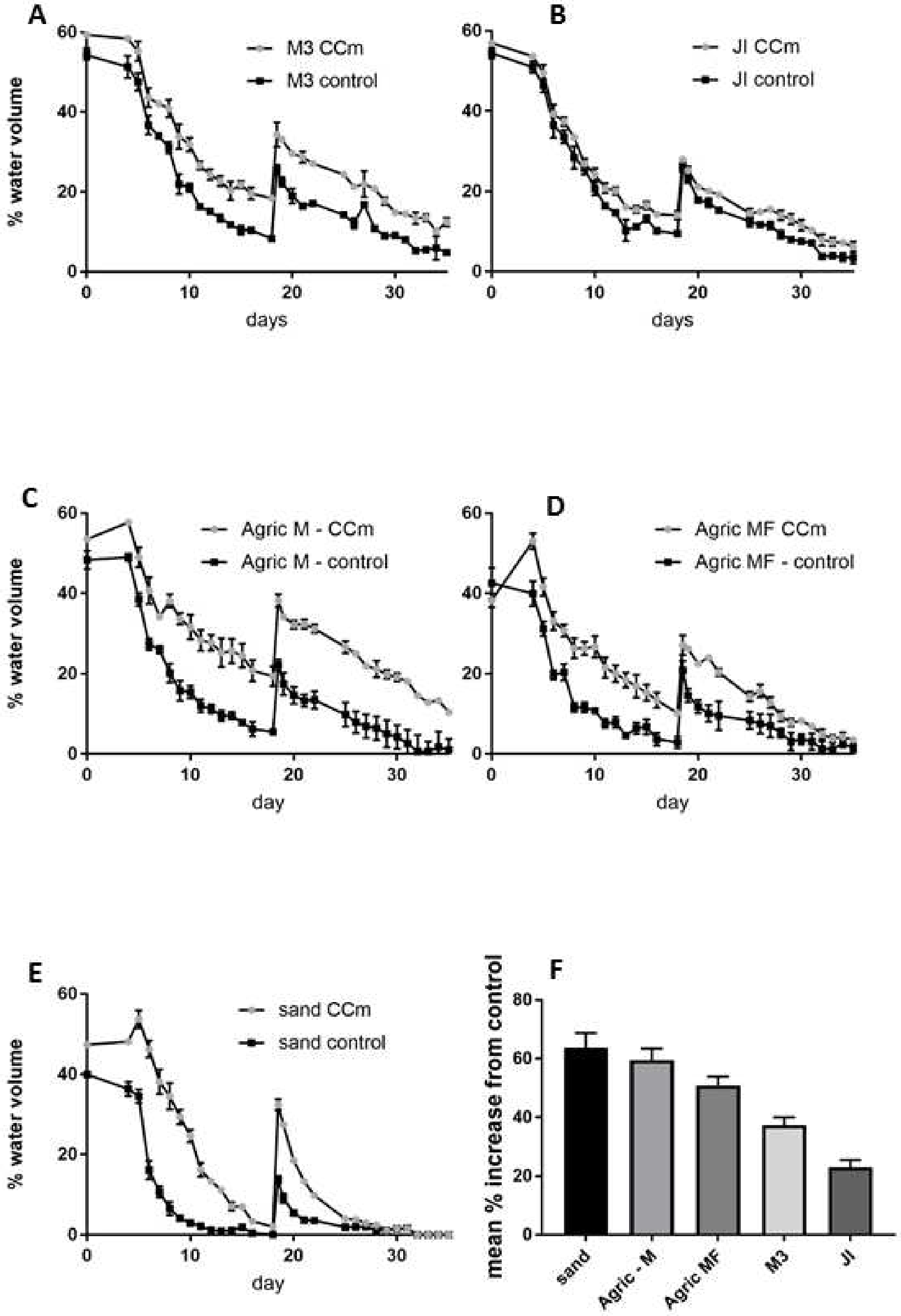

Figure 3. A – E) % water volume of different substrates over 35 days (Agric M is marginal soil, Agric MF is mid-field soil) F) mean % increase from controls over the same period.[n = 3, bar = SEmean]

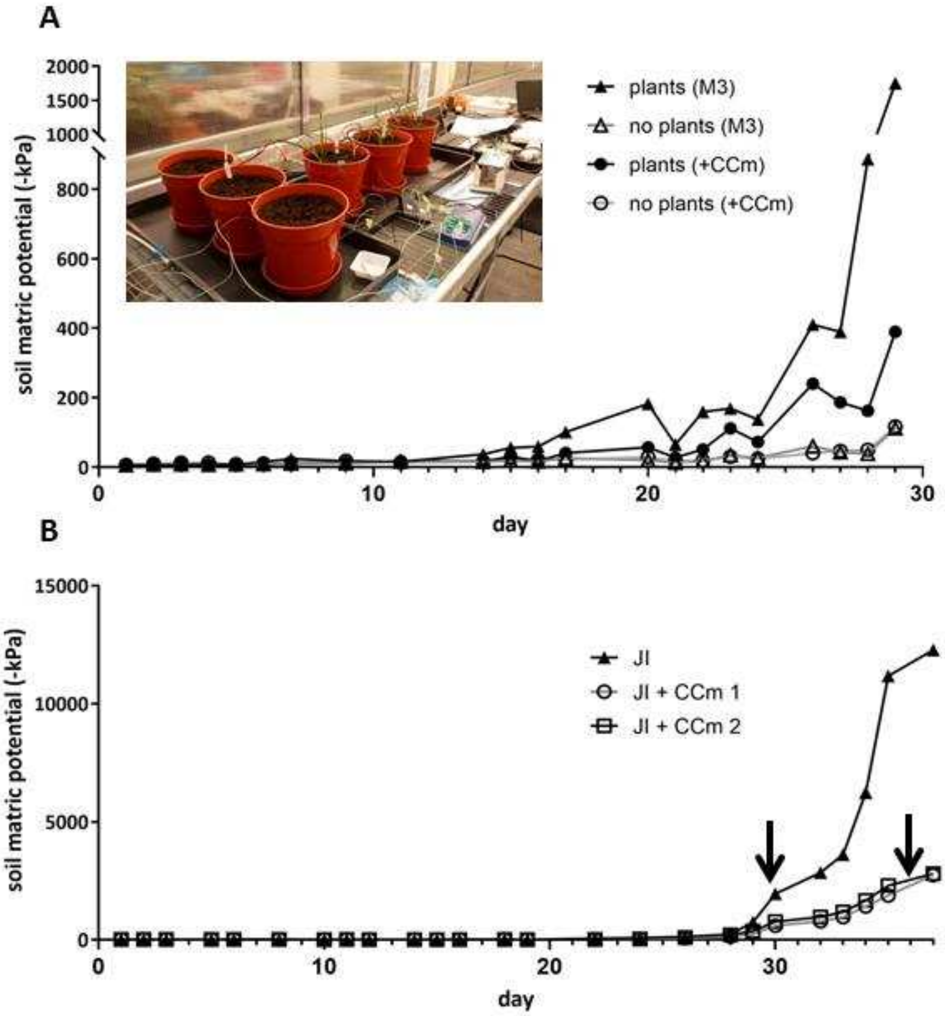

Figure 4. A): Soil matric potential (Ψ) logged over 29 days using M3 incorporating CCm and wheat. B) Effect of wheat on soil matric potential over 37 days in a repeated experiment using JI (JI + CCm 1 & 2 are replicates; arrow denotes permanent wilt point at -1,500 kPa)

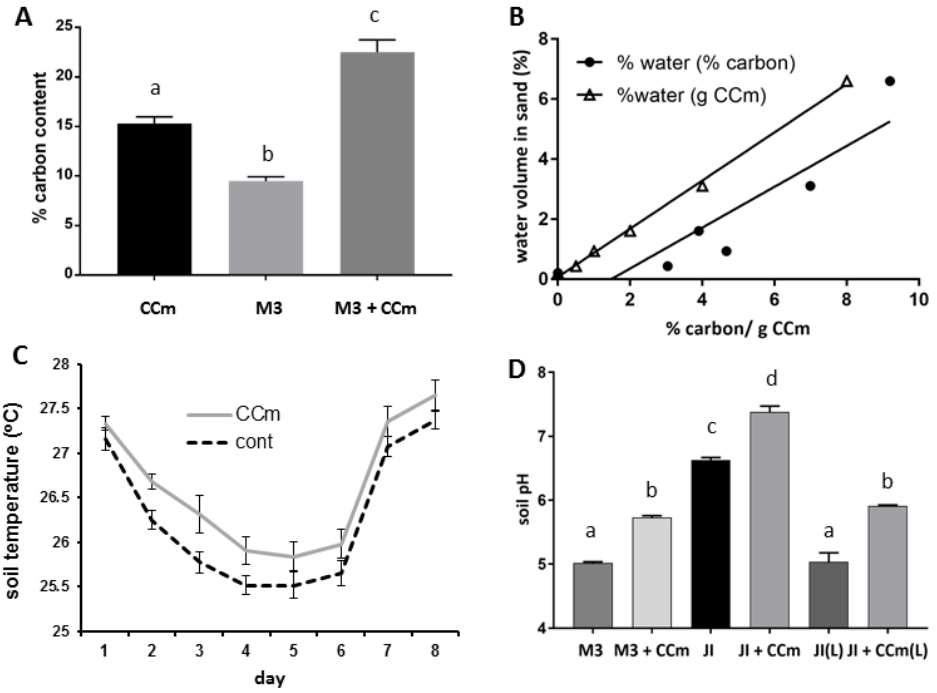

Figure 5: A) Total carbon content (%) of CCm (raw product), M3 and M3 + CCm [n= 3, bar = SEmean]; B) regression analyses of correlations between water content and % carbon and between water content and CCm (g) added to sand (% carbon = $R^2 = 0.808$, Pearson's correlation coefficient = 0.911, p = 0.015;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

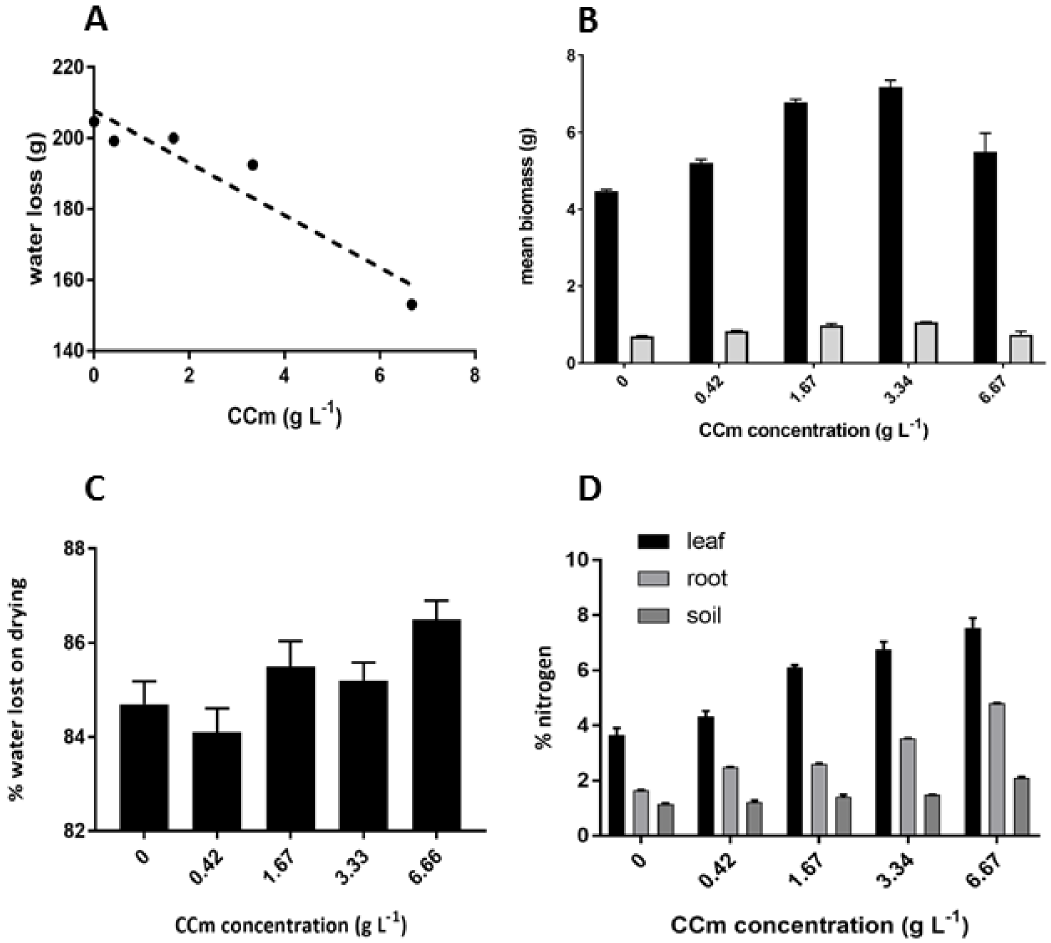

Figure 6. A) Correlation between gravimetric water loss on day 29 and CCm concentration (regression analysis $R^2 = 0.91$, Pearson's correlation co-efficient = -0.95, $p = 0.014$); B) % water loss from of wheat leaves; C) mean biomass of leaves [black = fresh weight, grey = dry weight]; D) % nitrogen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

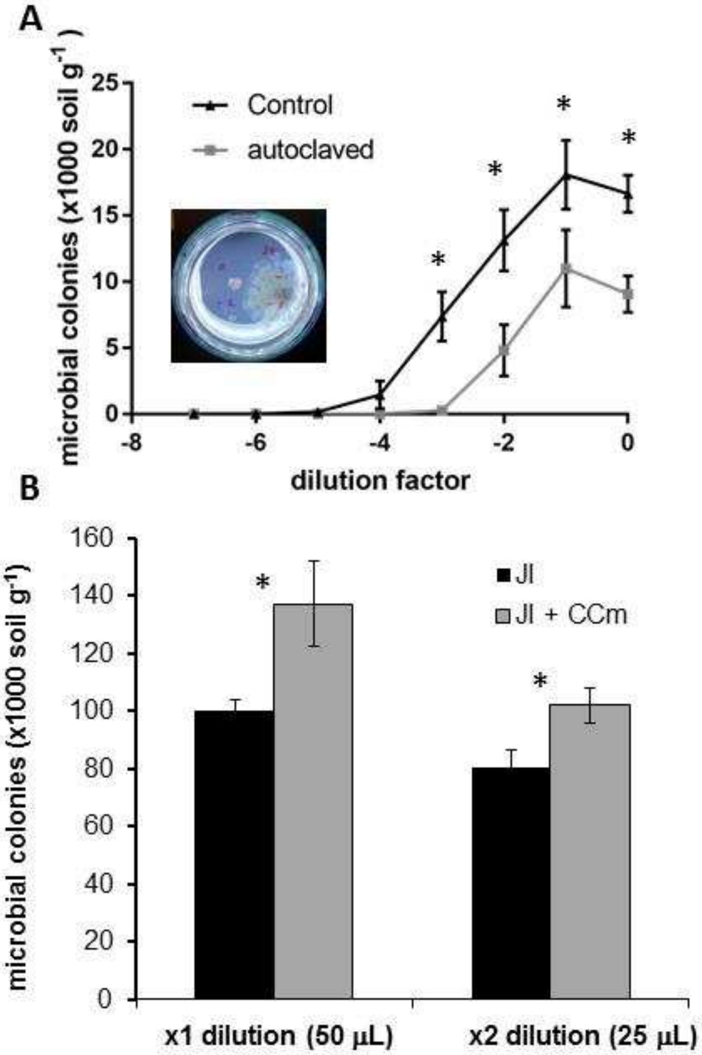

Figure 7. A) Autoclave test of microbial numbers of autoclaved and non-autoclaved JI. B) Microbial colonies from soil samples at the end of experiment following addition of CCm [n = 5, bars = SEmean, * $p = <0.05$ time point Student's t-test].

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

Day number	**Soil water volume (%)**		
	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

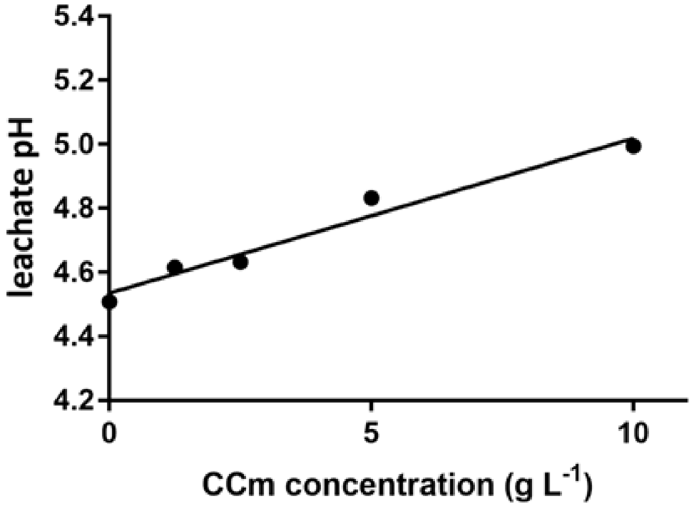

Figure S1. Dose-dependent pH response to CCm in M3 soil leachate [n = 5, regression analysis of correlation $R^2 = 0.965$, Pearson's correlation co-efficient = 0.98, p = 0.0029]