

CO₂ sequestration by wollastonite-amended agricultural soils – An Ontario field study

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ABSTRACT

Terrestrial enhanced weathering is the spreading of silicate powder on land, and can sequester atmospheric CO₂ through carbonation of calcium- and magnesium-rich minerals. When applied to soils, at suitable geochemical conditions, alkaline minerals lead to accumulation of soil inorganic carbon as pedogenic carbonates. Agricultural land covers 37 % of the Earth's land surface, thus offering a natural sink for atmospheric CO₂. Wollastonite (CaSiO₃) has been commercialized in Ontario as an agricultural soil amendment for several years, but it is not known if or how much CO₂ is sequestered annually. In the present study, wollastonite-amended soils were collected from three commercial-scale fields located in Ontario: a leafy vegetables farm in the town of Paris (Field 1); a potato farm in the settlement of Alliston (Field 2); and a soybean farm in the city of Woodstock (Field 3). Chemical and mineralogical assessments of these soils were conducted to determine their carbonate content and the fate of the wollastonite. The soil inorganic carbon (SIC) content was higher in all soils that had been amended with wollastonite, compared to controls, and in Field 1 the SIC content was 2.6 times higher in soil amended thrice with wollastonite compared to a single application. Mineralogical analysis showed the presence of additional polymorphs of SiO₂, which may originate from the wollastonite after the dissolution of calcium. This work provides further evidence, here for the first time at a regional scale, that soil amendment with alkaline silicates can be an effective geoengineering tool for climate change mitigation.

1. Introduction

Liming is a widely used agricultural practice to ameliorate agricultural soil to increase productivity. Calcium carbonate (limestone), calcium-magnesium carbonate (dolomitic lime), calcium oxide (quicklime), or calcium hydroxide (slaked lime) are commonly used for liming (Tisdale et al., 1958; Meriño-Gerichevich et al., 2010). These calcium-salts increase the Ca content in the soil matrix, while increasing the soil pH to a range near 6–7, which is suitable for the availability of nutrients to plants (Osman, 2013; Goulding, 2016). Liming also improves the soil structure, as high calcium concentration increases the ionic strength in the soil solution, which further improves the flocculation of clay minerals, resulting in the formation of stable aggregates. In particular, the carbonates minerals have a cementing action on the soil structure (Doner and Lynn, 1989; Haynes and Naidu, 1998).

Naturally available Ca-rich silicate minerals are an alternative to increasing the pH of the soil while providing additional benefits compared to the traditional liming agents. Van Straaten (2006) has highlighted the potential of silicate rocks to supply soils with macronutrients and micronutrients, given their role in nutrient cycling and

biochemical processes at the root surfaces. Silicate minerals, upon weathering, release silica (SiO₂) to the soil, which in turn can accumulate in plants in the form of phytogenic silica (Keller et al., 2012). Keeping and Kvedaras (2008); Van Bockhaven et al. (2012), and Beerling et al. (2018) report on the use of silicon as a broad-spectrum insecticide and pesticide and as an environmentally friendly plant prophylactic that provides resistance to biotic and abiotic stresses. The deposition of phytogenic silica in epidermal layers creates a physical barrier against sucking insects and leaf-eating caterpillars, thus protecting the plant (Gomes et al., 2005; Ye et al., 2013). Thus silicate addition has the potential to boost plant resilience to stresses.

Washbourne et al. (2015) have studied the changes in soil inorganic carbon (SIC) content of an urban soil, prepared from demolition waste, at the city of Newcastle upon Tyne, UK, based on SIC measurements over 18 months and ¹⁴C dating. They reported that the prepared soil sequestered atmospheric CO₂ at an annual rate of 85 t CO₂ ha⁻¹. Manning et al. (2013) studied basalt-compost blends as a soil amendment for land restoration projects, and found that this blend supported the growth of several tested plants (including mustard, woolly thistle, white clover), and led to an annual SIC content augmentation of 36.7 t

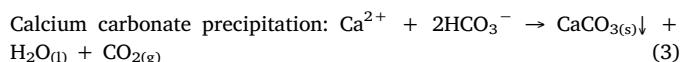
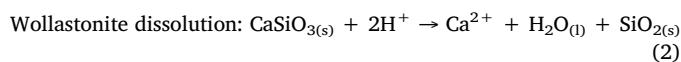
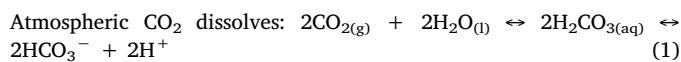
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$\text{CO}_2 \text{ ha}^{-1}$. Haque et al. (2019a) grew green beans and corn on a rooftop garden to test the effects of wollastonite amendment. Soil cultivated with beans showed a higher SIC accumulation over a period of 8 weeks, sequestering $24.3 \text{ t CO}_2 \text{ ha}^{-1} \text{ month}^{-1}$, and it was concluded that leguminous plants weather wollastonite faster due to liberation of acid compounds in the soil. Most recently, Amann et al. (2018) applied dunite to agricultural soils, and quantified that dissolved inorganic carbon (DIC) concentration in the soil solution increased after a year at a CO_2 consumption rate of $0.68 \text{ t CO}_2 \text{ ha}^{-1} \text{ year}^{-1}$.

Wollastonite (nominally CaSiO_3 , but commonly found in association with other minerals, such as diopside ($\text{CaMgSi}_2\text{O}_6$)) is a Ca-rich mineral that when weathered in soil can improve the soil fertility, by releasing calcium and other associated micronutrients into the soil, as well as forming calcium carbonate by reacting with the dissolved CO_2 present in the soil (Haque et al., 2019b). Amongst a wide variety of natural alkaline silicates for the terrestrial weathering process, wollastonite is one of the most promising candidates because of its simple chemistry, high weathering rate, and the ease of production of carbonated products due to the weaker bonding of Ca ions to the silica matrix (Palandri and Kharaka, 2004; Schott et al., 2012). Wollastonite is widely distributed around the world: China, Finland, India, Mexico, Spain, Canada, and the U.S., with a reserve size exceeding 100 million tonnes (Brioche, 2018). The main source of wollastonite in Ontario, Canada (where this study was conducted), is a quarry mine operated by Canadian Wollastonite in the village of Seeley's Bay, located 30 km north of the city of Kingston.

Eqs 1–3 shows how wollastonite can act as a liming agent. The CO_2 from the atmosphere and from microbial processes in the soil dissolves in available soil water forming carbonic acid (Eq. 1), which at near neutral to mildly acidic soil pH dissociates mainly into bicarbonate ions. Then, the dissolution of wollastonite in the carbonated water occurs (Eq. 2), and finally, calcium carbonate (CaCO_3) is precipitated (Eq. 3) (Hangx and Spiers, 2009).



These reactions show that wollastonite has the potential to sequester carbon dioxide (CO_2) from the surrounding environment, and that pedogenic carbonate content of soil can be used to verify the occurrence of wollastonite weathering (when soil pH is compatible with calcium carbonate accumulation, as verified by geochemical modeling by Haque et al. [2019a]). If this process occurs in agricultural soils, it would offer an attractive sequestration method in addition to the more well-known and frequently studied organic carbon sink in soils [Haque et al., 2019b]. Mineral carbonation, whereby CO_2 reacts chemically with calcium- and/or magnesium-containing minerals, either ex-situ (Gerdemann et al., 2007) or in-situ (Matter and Kelemen, 2009), has been recognized as a reliable way to form stable solid carbonate phases, and is deemed to be feasible at large enough scale that it can sequester a significant amount of global anthropogenic emissions (Lackner, 2003; Oelkers et al., 2008).

The novelty of the present ‘in the field’ work stems from assessing at the field-scale (i.e. in commercial farms in Ontario) if the application of wollastonite to agricultural land results in CO_2 sequestration in the form of verifiable accumulation of pedogenic carbonates in soil. Through communications with the Ontario Ministry of Agricultural, Food, and Rural Affairs (OMAFRA), it was found that wollastonite has been used as a soil remineralizer in Ontario since 2015, but no scientific study has been conducted to date on wollastonite-amended agricultural soils in the province. In our previous study (Haque et al., 2019a), a pot

experiment on a rooftop garden was used to investigate the co-benefits of wollastonite weathering in soil: namely, the accumulation of soil inorganic carbon, as well as improved plant growth (green beans and corn). In the present study, a field-scale wollastonite amendment experiment was conducted at a commercial soybean, for verification of CO_2 sequestration at field conditions, and two additional farms (leafy vegetables, and potato) that had used wollastonite amendment were also studied for evidence of CO_2 sequestration. There is no account of this kind of field study to date, and this marks the novelty of this work. This study provides a first step to understanding the in-field behavior of wollastonite in a variety of agricultural soils, used to grow a variety of field and horticultural crops. This study conducted chemical and mineralogical characterization of the sampled soils (wollastonite-amended and controls) to determine their inorganic carbon content and the fate of the wollastonite.

2. Material and methods

2.1. Study area and field trial procedures

The agricultural soils were sampled from three different commercial-scale fields located in Ontario, Canada (Fig. 1). The background information of each field is discussed in this section.

The first field, Field 1 located in the town of Paris ($43^\circ 04' 47.5''\text{N}$, $80^\circ 30' 37.9''\text{W}$), is used to grow leafy vegetables, including kale, lettuce, and romaine (Fig. 2a). Wollastonite, with a coarse texture, was added every Fall (August) as an alternate liming agent, and the soil was worked in 6–7 inches. Monoammonium phosphate (MAP) fertilizer was used during the growth period. In 2018, this field completed three applications of wollastonite, with $1.24 \text{ t hectare}^{-1}$ application in the first year (Aug. 2015), followed by $2.5 \text{ t hectare}^{-1}$ application, each time, in the second and third years (Aug. 2016 and Aug. 2017, respectively). Figure S1 in the Supplementary Materials shows the corresponding areas of the field that have received different applications, and additional information is given in Table S1. In total, 120 tonnes of wollastonite was added to 30 ha of land over three years, prior to this study’s sampling conduct in mid-July 2018.

The second field, Field 2 located in Alliston ($44^\circ 14' 57.3''\text{N}$, $79^\circ 49' 26.7''\text{W}$), is a potato field (Fig. 2b). The producer trialed wollastonite application on one of its fields as they were interested in the



Fig. 1. Mapped locations of the fields sampled in this study.



(a) Field 1 (Paris): Leafy vegetable field.



(b) Field 2 (Alliston): Potato field.



(c) Field 3 (Woodstock): Soybean field.

Fig. 2. Three Ontario commercial-scale agricultural fields studied.

potential benefit of wollastonite on potato growth, as potato plant prefers silica-rich soil, and the potential to reduce insect attack by boosting plant resilience with the released silica (Eq. 2). Wollastonite, with a finer texture, was applied on approximately half of the land area of 18 ha on May 30th 2018 at a rate of 1.24 t/hectare⁻¹. Earlier in the same growing season, on all the land area, dolomitic lime had also been applied as the liming agent, alongside a fertilizer (160 units of N and 80 units of K). The research team conducted soil sampling post-harvest on October 19th 2018, from both the land areas with and without (control) wollastonite application. Figure S2 in the Supplementary Materials shows how the field was divided into the control plot and the amended plot.

The third field, Field 3 located in Woodstock (43°08'57.7"N 80°37'29.8"W), is a soybean field (Fig. 2c) belonging to Baan Family Farms Inc. The producer worked together with the present research team to plan a field-scale trial to better understand the effects of wollastonite application in a soybean crop. A section of 2 ha of land (183 m by 110 m) was divided into four plots, 183m × 27m each. Three different application rates of coarse wollastonite (5 t/hectare⁻¹, 2.5 t/hectare⁻¹, 1.5 t/hectare⁻¹) was applied to three plots using a broadcast lime spreader (capable of covering 9.2 m in each pass), with the fourth plot reserved as a control, as shown in Fig. 3. In total, three passes of broadcast spreader were needed to cover the 27 m wide plot, thus

providing uniform spreading of wollastonite for each application rate. Following wollastonite application, soybeans seeds were planted at a rate of 420,000 seeds·hectare⁻¹ along with 0.2 t/hectare⁻¹ of muriate of potash. After a period of five months (June to October 2018), the soybeans were harvested, with the soybean yield weighed for each plot, and the soil was sampled several days later in late-October 2018.

All soils were sampled using a soil core sampler (JMC) down to 6 in. of soil depth, and the various cores collected from points distributed across each plot/field were thoroughly hand-blended in a bucket prior to storage under refrigeration and subsequent characterization analyses. Fields 1 and 2 were sampled using Directed Random Sampling (DRS) technique. In Field 1, DRS entailed randomly sampling distinct field locations where different amount of wollastonite had been applied in the past three years (Figure S1). In Field 2, DRS entailed randomly sampling two distinct areas adjacent to each other at one end of the field, one of which had received wollastonite application and the other not. Field 3 was sampled using Random Composite Sampling, which entailed collecting cores from across each plot following a zig-zag pattern along its length. From each field/plot, well over the traditionally minimum recommend number of cores (15–20) was collected (in the order of 100 cores per field/plot). This was done to ensure that enough soil was collected to be analyzed in replicates (triplicates), such that any difference observed could be attributed to wollastonite

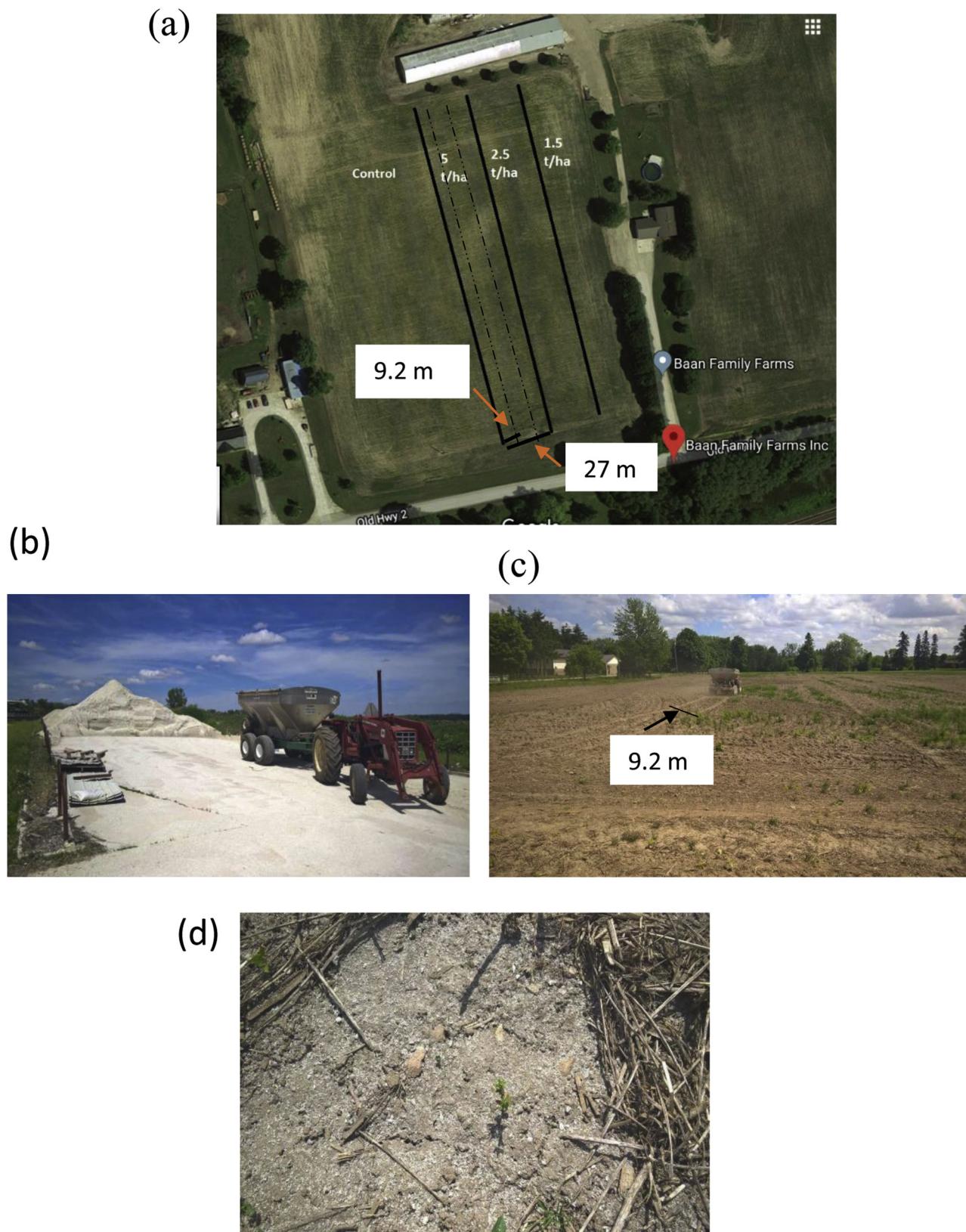
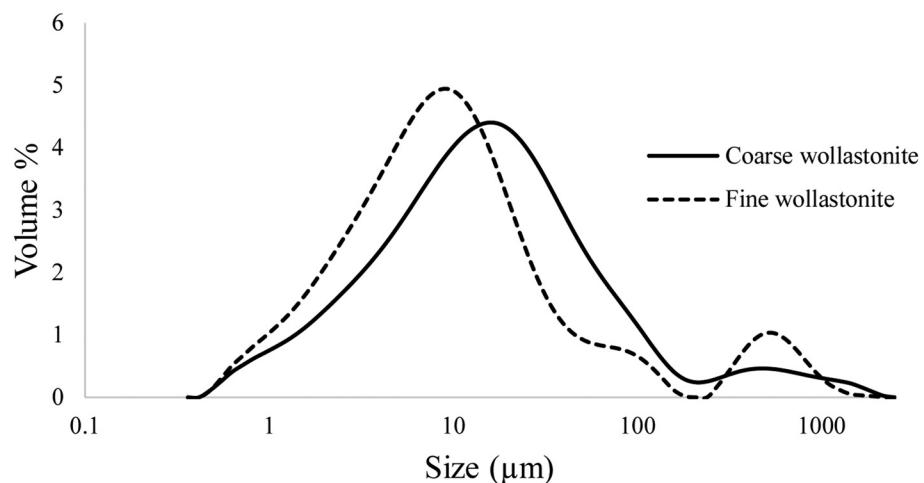


Fig. 3. a) Division of Field 3 into four plots, with three different application rates of wollastonite and a control; b) wollastonite powder used in Field 3; c) broadcasting wollastonite in Field 3 using a lime spreader; d) bare patch of soil in Field 3 after wollastonite application at highest application rate.

weathering. Accuracy in soil sampling is important to ensure that differences confirmed by statistical analyses are due to treatment effects rather than sampling bias.

Samples of the coarser and finer varieties of wollastonite used at

each location were obtained from the respective farmers. Wollastonite was sourced from Canadian Wollastonite's Ontario mine. Coarser-textured wollastonite was used in Fields 1 and 3, whereas finer-textured wollastonite was used in Field 2.



(μm)	Coarse wollastonite	Fine wollastonite
D [3,2]	5.8	4.4
D [4,3]	55.6	47.4
d (0.1)	2.3	1.8
d (0.5)	13.8	8.2
d (0.9)	83.7	63.7

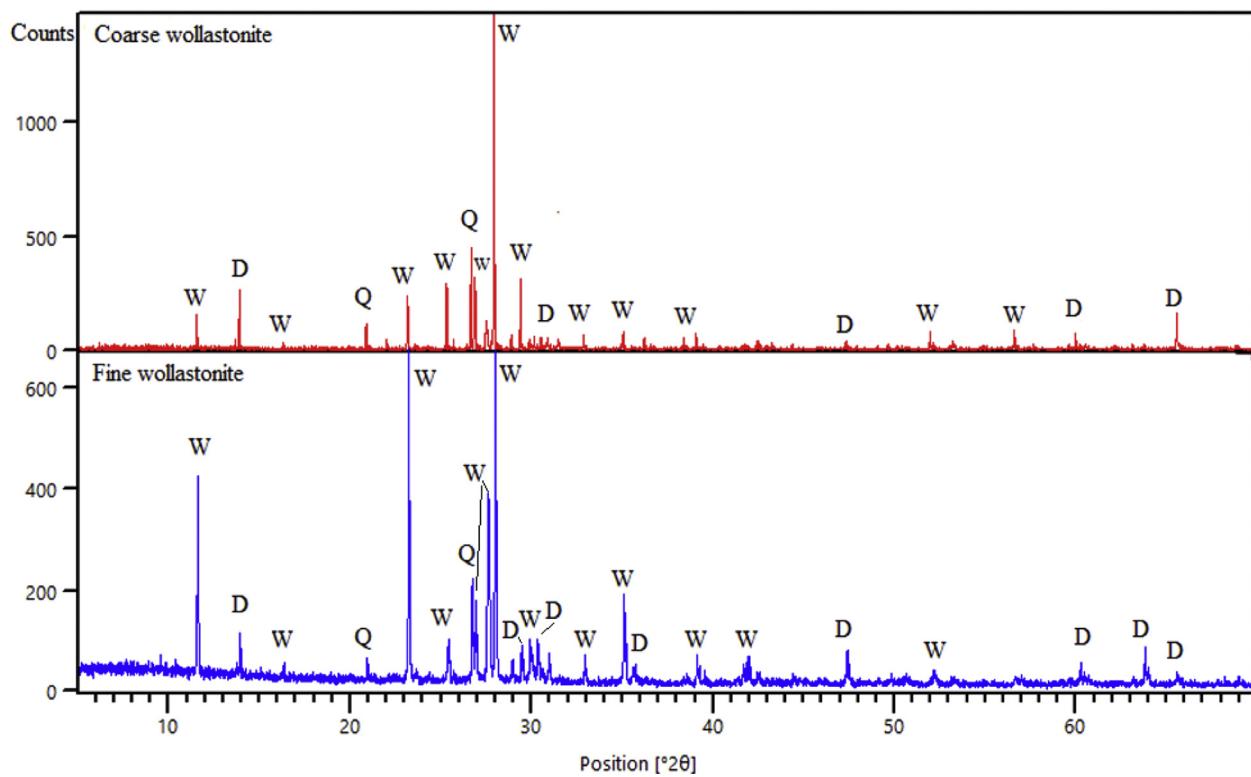


Fig. 4. a) Particle size distribution of coarse and fine wollastonite; b) XRD spectra of the coarse and the fine wollastonite with peak identification (W-wollastonite, D-diopside, Q-quartz).

2.2. Soil analyses

The sampled soils were characterized by the Agriculture and Food Laboratory Services (Guelph, Canada) to obtain the soil type, which was determined using the pipette method of sedimentary analysis, and the organic matter content via the Walkley-Black method. All other

tests were conducted by the University of Guelph research team. The pH of the samples was determined using a 1:5 ratio of soil and 0.01 M CaCl_2 solution, followed by 30 min shaking and 1 h settling time before taking the pH measurement of the clear supernatant (Pansu and Gautheyrou, 2006). The carbonate content (SIC calculated as $\text{gCO}_2(\text{kg soil})^{-1}$) was determined by a volumetric method called calcimetry. Soil

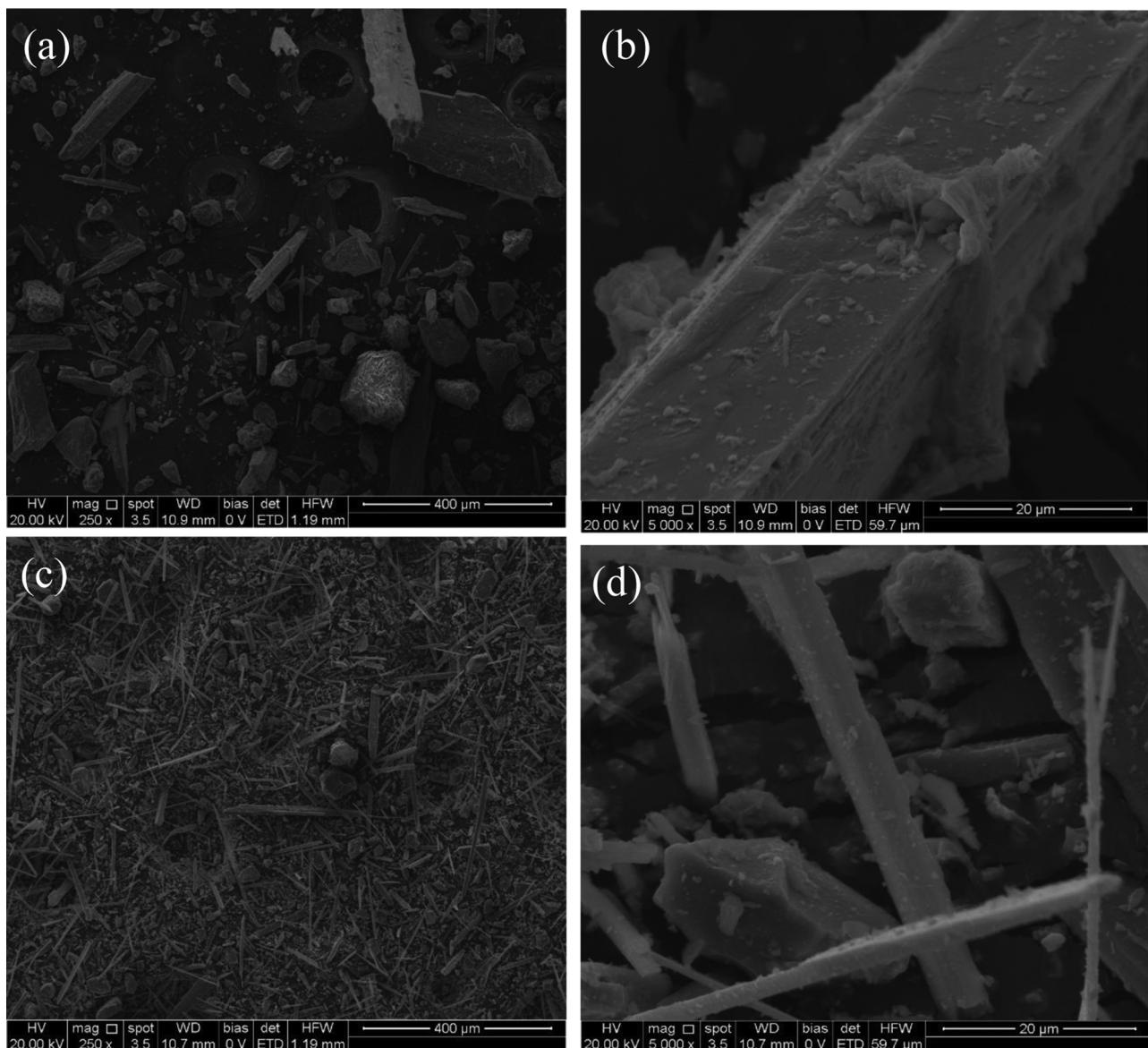


Fig. 5. Scanning electron micro images: a) Coarse wollastonite at low magnification; b) Coarse wollastonite at high magnification; c) Fine wollastonite at low magnification; d) Fine wollastonite at high magnification.

samples were suspended in MiliQ water (5 g in 20 mL), to which 7 mL of 7 M HCl was added within a sealed Erlenmeyer flask connected to a graduated water-filled manometer-style column that recorded the released CO₂ volume (Eijkenkamp Calcimeter 08.53) (Chen et al., 2015). The CO₂ sequestered as SIC of the sampled soils was estimated from the calcimeter results using Eq. 4, which assumes that all inorganic carbon is present in the form of calcium carbonate (CaCO₃). It is assumed that the soil density is 1300 kg m⁻³ (Singh and Devid, 2000), and that the sampled soil volume is the product of the sampling depth (0.1524 m) and the area of a hectare (100.0 m²).

$$\begin{aligned} & \text{CO}_2 \text{ sequestered as SIC (tonne CO}_2 \cdot \text{hectare}^{-1}) \\ &= \text{Calcimeter reading} \left(\frac{\text{g CO}_2}{\text{kg soil}} \right) \cdot \frac{1330 \text{ kg soil}}{\text{m}^3} \cdot \frac{1524 \text{ m}^3}{\text{hectare}} \cdot \frac{1}{\frac{1000 \frac{\text{g}}{\text{kg}}}{\text{kg}} \cdot \frac{1000 \frac{\text{kg}}{\text{tonne}}}{\text{tonne}}} \end{aligned} \quad (4)$$

Semi-quantitative determination of carbonate in the samples was also estimated using thermogravimetric analysis (TGA, Thermo Scientific Nicolet 700). The dried samples were placed in a crucible,

where approximately 20 mg was heated from ambient temperature to 1000 °C in nitrogen gas atmosphere at a heating rate of 10 °C/min. Nitrogen gas of high purity (99.99 %) was supplied at a constant flow rate of 100 mL/min as an inert purge gas. The calcium carbonate content is estimated based on weight loss between 500 °C and 800 °C (Huijgen et al., 2006).

2.3. Data analysis

All the analysis readings were taken in triplicates, and mean results reported herein have been represented along with standard deviations. The Field 1 data were statistically analyzed using one-way analysis of variance to draw multiple comparisons between the three-year soil data. For Field 2 and Field 3, paired *t*-test comparisons were made as control plots were available for these fields. P < 0.05 was used as the limit for statistical significance. Data analysis was done using IBM SPSS Statistics 26 software, and results are presented in Tables S2-S4 in the Supplementary Material.

Table 1

Soil composition analysis for carbonation evidences. **.

Sample	Weathering period (approx.)	Soil type	Organic matter content (wt% dry)	Irrigation	pH	SIC content (g $\text{CO}_2(\text{kg soil})^{-1}$)	CO_2 sequestered as SIC (tonne $\text{CO}_2\text{-hectare}^{-1}$)
Field 1 (Leafy vegetable field)							
Application year 3 (Field 1a)	36 months	Loamy sand (gravel 0.9 %, sand 83.1 %, silt 11.0 %, clay 5.9 %)	2.9	Yes	6.72 ± 0.04	2.99 ± 0.06	6.05*
Application year 2 (Field 1b)	24 months				6.62 ± 0.02	2.06 ± 0.12	4.17*
Application year 1 (Field 1c)	12 months				6.51 ± 0.02	1.16 ± 0.10	2.35*
Field 2 (Potato field)							
Soil (without wollastonite)	–	Sandy loam (gravel 0.5 %, sand 57.1 %, silt 35.9 %, clay 7.0 %)	1.7	Yes	5.92 ± 0.02	0.18 ± 0.02	–
Wollastonite amended soil (1.24 t/hectare ⁻¹)	5 months				6.14 ± 0.04	0.34 ± 0.03	0.32
Field 3 (Soybean field)							
Soil (without wollastonite)	–	Sandy loam (gravel 1.1 %, sand 55.1 %, silt 29.5 %, clay 15.5 %)	3.2	No	6.59 ± 0.06	0.30 ± 0.02	–
Wollastonite amended soil (5 t/hectare ⁻¹)	20 weeks				6.75 ± 0.04	0.49 ± 0.02	0.40
Wollastonite amended soil (2.5 t/hectare ⁻¹)	20 weeks				6.64 ± 0.02	0.41 ± 0.06	0.22
Wollastonite amended soil (1.5 t/hectare ⁻¹)	20 weeks				6.60 ± 0.02	0.35 ± 0.01	0.11

* Control not available, thus these are SIC contents simply converted into tonne $\text{CO}_2\text{-hectare}^{-1}$.

** Refer to Table S1 in the supplementary material for more information.

2.4. Materials characterization

The main crystalline mineral phases in wollastonite and soil samples were identified using X-ray diffraction (XRD, Panalytical Empyrean) and HighScore Plus software (Malvern Panalytical). The diffractometer operated with Cu K α radiation at 45 kV and 40 mA, and the diffraction patterns were collected over a 20 range of 5–70°. The particle size distribution of wollastonite was determined by laser diffraction (Malvern Mastersizer SM). The multipoint BET surface area was determined using a physisorption analyzer (Quantachrome Autosorb iQ) conducted with N₂ adsorption at 77 K on samples previously degassed in vacuum consecutively at 120 °C (30 min soaking time) and 350 °C (300 min soaking time). The morphological structure of the two types of wollastonite and the sampled soils was visualized with scanning electron microscope (SEM, FEI Inspect S50), which was equipped with energy dispersive spectroscopy (EDS, Oxford X-Max20 SSD) used for chemical (elemental) composition analysis of individual particles. Prior to SEM-EDS analysis, the samples were sputter-coated with gold.

3. Results and discussion

3.1. Characterization of the wollastonite

The particle size distribution (Fig. 4a) gives information on the active surface area, which is important for the enhanced weathering reactions, and is inversely proportional to particle size. The surface area-based Sauter mean diameter (D[3,2]) of the coarser wollastonite is $5.8 \pm 0.16 \mu\text{m}$ whereas that of the finer wollastonite is $4.4 \pm 0.06 \mu\text{m}$. The smaller particle size of the finer wollastonite provides a greater surface area for the silicate dissolution reaction (Eq. 2) to occur. The d (0.9) values were also determined from the size distribution, with 90 % of coarser and finer wollastonite particles (by volume) being less than 83.7 μm and 63.7 μm , respectively. The multipoint BET surface area of the finer wollastonite is $3.48 \text{ m}^2/\text{g}$, which is higher than that of the coarse wollastonite ($2.07 \text{ m}^2 \text{ g}^{-1}$).

The CaCO₃ content (calcimeter reading) in coarse and fine wollastonite was found to be 20.9 g CaCO₃ kg⁻¹ mineral (or 9.2 g CO₂ kg⁻¹) and 38.2 g CaCO₃ kg⁻¹ mineral (or 16.8 g CO₂ kg⁻¹), respectively. Field 3 (soybean field) used the highest application rate of coarse wollastonite at 5 t/hectare⁻¹, and the amount of added CaCO₃ in this amendment is equivalent to 0.03 wt%, thus indicating negligible added carbonate content in the amended soil at the time of wollastonite application. Similarly, in this study, the lowest application rate of

1.24 t/hectare⁻¹ contained a negligible amount of 0.008 wt% CaCO₃.

The main mineral phases identified by XRD are shown in Fig. 4b. Both varieties of wollastonite (sourced from the same mine) are mainly comprised of wollastonite (CaSiO₃), diopside (CaMgSi₂O₆) and quartz (SiO₂). SEM analysis of wollastonite samples showed the characteristic needle-shaped (acicular) grains (Huijgen et al., 2006), with much smaller (shorter and narrower) needles observed in case of fine wollastonite (Figs. 5c and 5d), as compared to the coarse wollastonite (Figs. 5a and 5b). The nominal elemental composition (> 0.2 wt%) of the sourced material is (Canadian Wollastonite, 2017): 25.8 wt% Si; 18.9 wt% Ca; 4.0 wt% Mg; 2.3 wt% Al; 1.6 wt% Fe; 1.3 wt% K; 1.1 wt% Na; and 0.8 wt% S. Trace amounts (< 0.2 wt%) of Ti, N, and P are likely present.

3.2. Evidence of CO₂ sequestration in the soils

The soil type, organic matter content, soil pH, SIC content, and the amount (control deducted, where available) of CO₂ sequestered as pedogenic carbonates in the different fields is tabulated in Table 1. Field 1 soil type was found to be loamy sand, whereas both Field 2 and Field 3 had sandy loam soil, with a difference in organic matter content of 1.5 wt% from the highest to the lowest. From Field 1, three sets of data were obtained based on the number of wollastonite applications received in each part of the farm. The amount of carbonate accumulated in the soil with three years of application (Application year 3) was found to be 2.6 times higher than that of the soil with a single application in the most recent year, and 1.5 times that of the soil with two consecutive years of application. Multiple comparisons between the Application year 1, 2 and 3 SIC data using Tukey's HSD (honestly significant difference) test shows (Table S2) that the difference between each year SIC content is statistically significant ($p < 0.05$). The greater amount of wollastonite added explains why the soil pH is higher for the Application year 3 soil by 0.21 pH units. The amount of CO₂ sequestered by Field 1, calculated using Eq. 4, was found to be 2.35–6.05 tonne $\text{CO}_2\text{-hectare}^{-1}$, thus implying that consecutive applications of wollastonite to the same soil results in greater accumulation of pedogenic carbonates. There was part of Field 1 that had not been treated with wollastonite, so this limited the possibility to understand the change in the soil carbonate composition in comparison with a control plot (as could be done with Fields 2 and 3). Given that dolomitic lime was applied to these fields, it is entirely possible that some of the SIC content originates from residual dolomite.

Field 2 and Field 3 maintained a control plot without wollastonite,

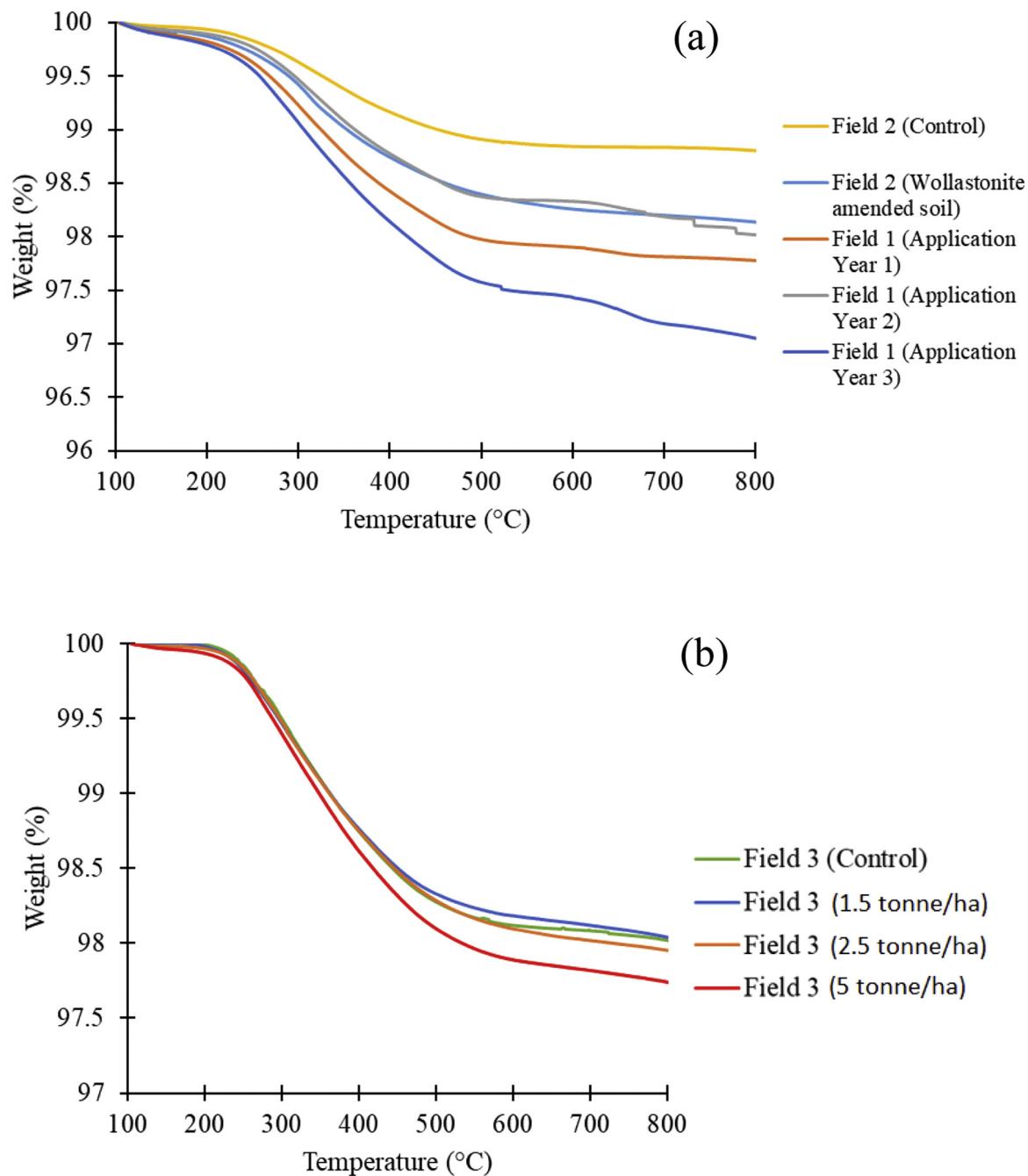


Fig. 6. TGA curve of the soil samples from: a) Field 1 (Leafy vegetable) and Field 2 (potato); and b) Field 3 (soybean).

and the SIC content in the wollastonite amended soil in Field 2 was 89 % higher than that of the control, and in case of Field 3 it was 63 % higher for the plot amended with the highest application rate of wollastonite. For these two amended plots, paired *t*-test showed (Tables S3 and S4) that the wollastonite amended plots had significantly higher SIC content compared to the control plot ($p < 0.05$). Field 2 used fine wollastonite at a slightly lower application rate than the lowest application rate used on Field 3, however Field 2 achieved a significantly greater CO_2 sequestration or SIC accumulation, by nearly 3 times. This can be due to the type of wollastonite used, as the small particle size and high surface area of the fine wollastonite should result in faster weathering reaction. Secondly, Field 2 was well irrigated (a requirement of potato farming in Ontario) whereas Field 3 depended solely on rainwater. As can be seen from Eqs 1–3, water plays an important role in the weathering reaction for dissolving atmospheric CO_2 , providing

the protons for wollastonite dissolution, as well as carrying the bi-carbonates for calcium carbonate formation. Thus irrigation may have enhanced the weathering of wollastonite in that agricultural field, and is an important parameter (together with chemical properties of the irrigation water) to study in future field studies.

The effect of three different wollastonite application rates was studied in Field 3. Table 1 shows that as the application rate increased, the SIC augmentation followed. It should be noted that statistically, Field 3 plots amended with less wollastonite, paired *t*-test showed (Table S4) significant differences at slightly lower confidence levels than 95 %, given p values of 0.059 and 0.076. For the highest application rate in Field 3, with p value 0.007, the CO_2 sequestration (as a result of SIC) of 0.4 t CO_2 per hectare obtained over five months is equivalent to a monthly accumulation of $0.079 \text{ t CO}_2 \text{ ha}^{-1} \text{ month}^{-1}$, for a soil depth of ~15 cm. Manning et al. (2013) reported a rate of inorganic carbon

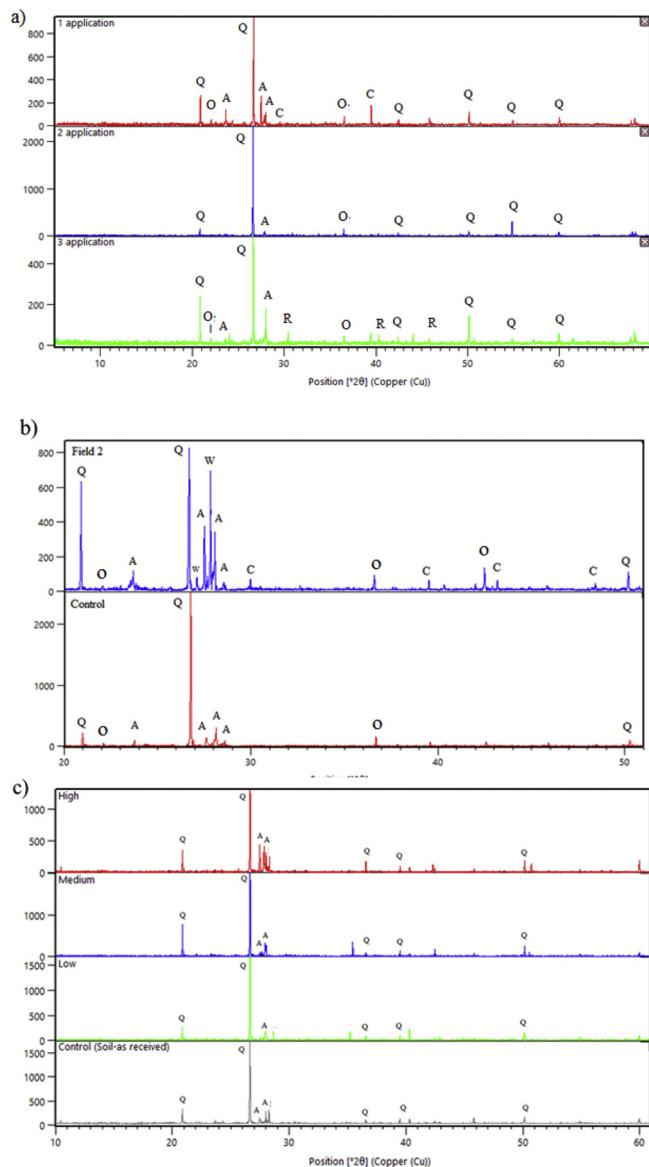


Fig. 7. XRD diffractograms of soil samples from: a) Field 1; b) Field 2; and c) Field 3. (Q: quartz, O: opal, A: albite, R: rutile, C: calcite, W: wollastonite).

accumulation for plots that used carbonate-free crushed rock (basaltic quarry fines) to be $1.47 \text{ t CO}_2 \text{ ha}^{-1} \text{ month}^{-1}$ to a depth of 30 cm. The results of the present study compare favorably to these once it is realized that the available calcium content of the wollastonite amended soil after a single application is substantially less than that of the artificial soils used by Manning et al. (2013).

The presence of greater quantities of SIC in the wollastonite amended soils can be confirmed from the TGA graphs (Fig. 6). The decomposition temperature range for CaCO_3 is approximately $500 - 800^\circ\text{C}$ (Huijgen et al., 2006), and the TGA graph shows a greater mass loss in this high-temperature range for wollastonite amended soil (0.26 wt.% in case of Field 2) versus the control untreated soil (0.11 wt. %) (Fig. 6a). For Field 1, the mass loss at the high temperature range progressively increased from the application year 1 sample to application year 3 sample, though quantitative conclusions about CO_2 sequestration still cannot be made with the lack of a control plot. The TGA data of the soils from Field 3 (Fig. 6b) show that as the wollastonite application rate increases, greater mass loss above 500°C resulted, which is in agreement to the increase in the SIC content determined by calcimetry (Table 1). In the present study, the calcimetry

results are deemed more precise and accurate given the larger mass of sample analyzed (5 g versus 20 miligrams), the triplicate readings obtained, and the use of pure calcium carbonate as the method standard.

From the data of inorganic carbon accumulation and CO_2 sequestration in these three different field scenarios, it can be seen that several field conditions and parameters attribute to the wollastonite weathering mechanism. These include the hydrology and leveling of the agricultural land, the type of plant grown, agricultural practice (irrigation, tilling), and the particle size of the wollastonite used, to name some. For example, the type of plant grown can drive the weathering mechanism. Field 1 grew a variety of leafy vegetables, Si-favoring potato was grown on Field 2, whereas root nodule-forming soybeans were grown on Field 3. In a previous study, Haque et al. (2019a) found that the type of plant affects the weathering of wollastonite. It was reported that nitrogen-fixing plants (such as soybeans) can enhance the weathering dissolution by providing excess protons that facilitate the dissolution of wollastonite.

Farmers from Field 1 confirmed that they had better produce with wollastonite amended soil, and their seedlings suffer less transplantation shock when grown with wollastonite. The potato farmers from Field 2 confirmed that their wollastonite amended soil resulted in improved soil compaction, and the potato plant had a sturdier stalk as compared to the one grown on the control plot. In terms of soybean yield (Field 3), the data provided by the farmer confirmed that wollastonite addition had no negative impact on the growth yield. The yield for the control plot recorded was $53.2 \text{ bushels acre}^{-1}$, whereas the wollastonite amended plots showed higher yield by 4.5%–9.1%, with the medium application rate plot showing the highest yield ($58.1 \text{ bushels acre}^{-1}$), and the other two plots showing similar yields of $55.7 \text{ bushels acre}^{-1}$. These yields are typical of Southern Ontario. The difference in the trends of CaCO_3 accumulation (greatest with highest amendment) and yield (greatest with medium application rate) can be attributed to differences in the hydrology and leveling of the agricultural land. Further studies on why and by how much wollastonite amendment can boost crop yield are warranted as this can provide added incentive for using this CO_2 -sequestering mineral. Farmers from all the three fields also observed that bug and insect attack was minimized when wollastonite was used, and this is another potential benefit that warrants further study as it could lead to reduced use of pesticides, which can provide both monetary relief and environmental protection benefits.

To account for the net CO_2 sequestration, the carbon cost involved in the production of wollastonite needs to be quantified. A detailed analysis is not within the scope of this study, but it is interesting to estimate the net carbon price that could potentially be involved in a commercial implementation. The cost of wollastonite production can be estimated based on the main processes involved, as discussed herein; the prices are based on the study of Huijgen et al. (2007). The first process includes mining which comprises of investment cost (\$/tonne of wollastonite rock) and operation and maintenance (\$/tonne). Secondly, crushing and grinding is another step that contributes to the overall cost, as grinding the rock to a finer particle would involve higher cost as more energy will be required. The wollastonite size used in this study is between $63.7 - 83.7 \mu\text{m}$. Therefore, assuming a particle size of $50 \mu\text{m}$, energy of 0.07 GJ/tonne at an electricity cost of $\$24/\text{GJ}$ would account for $\$1.7/\text{tonne}$ for crushing and grinding. For transportation and spreading of the wollastonite on the field, the distance between the mining site (Kingston, Ontario), and all the three fields in this study is approximately 300 km, hence contributing $\$12/\text{tonne}$ to the total cost of wollastonite application. The total economic cost of wollastonite, based on the above processes comprising mine to field application, is thus estimated to be $\$44/\text{tonne}$. This value is somewhat lower than the value reported by Brioche (2018), of $\$80/\text{tonne}$ or over, as typical applications of wollastonite infer extra processing costs (to control composition and morphological properties) and extra transport costs (as the main mines of wollastonite are far from the industries that

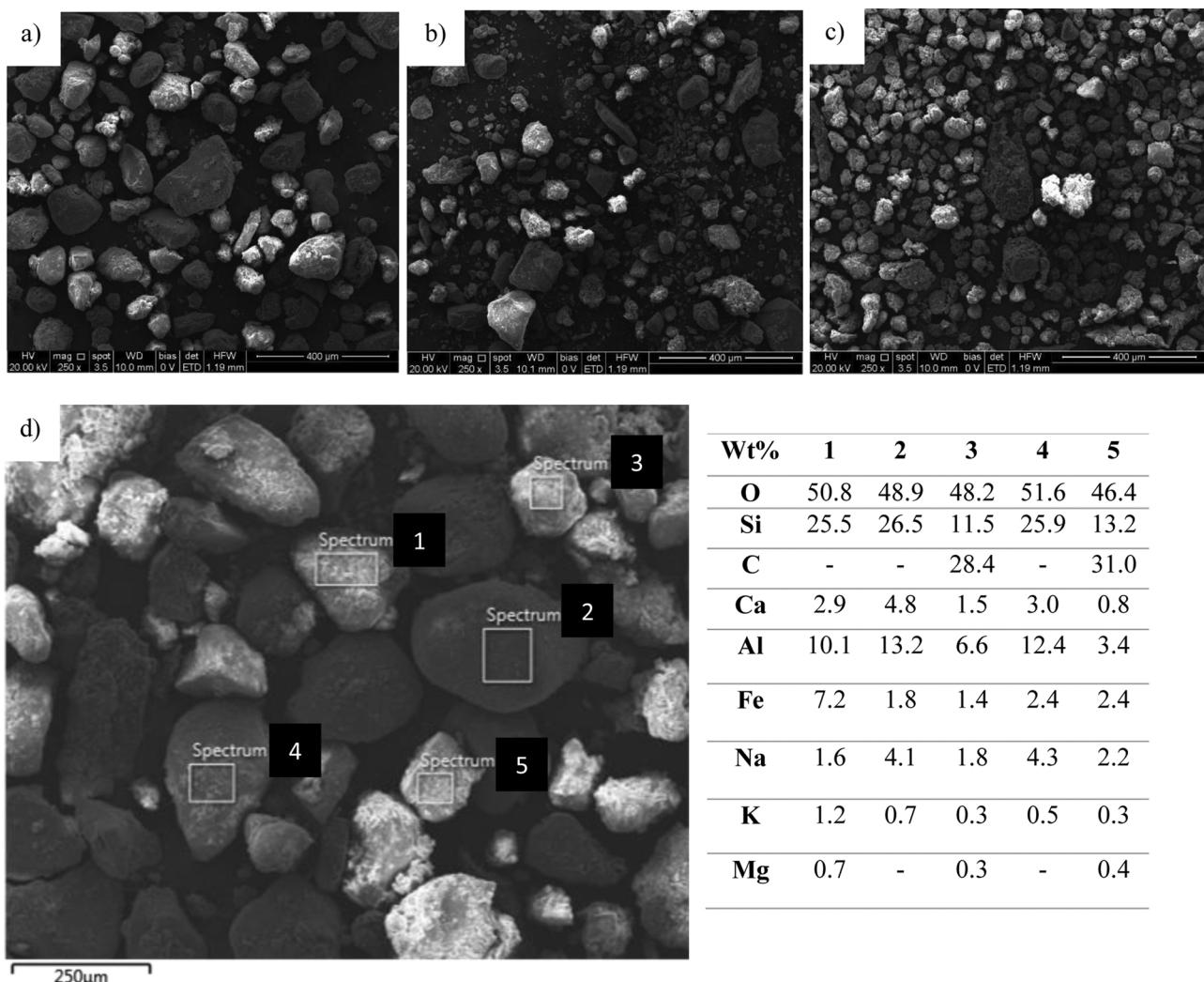


Fig. 8. SEM image of the soil sample from Field 1: a) Application Year 1; b) Application Year 2; c) Application Year 3; and d) EDS analysis of Application Year 3 soil.

use it). Assuming the cost to farmer, in Ontario, of \$44/tonne, and assuming a net sequestration of 0.2 t CO₂ per tonne of wollastonite (Moosdorff et al., 2014), to account for CO₂ emissions from mine to farm, the net cost of CO₂ sequestration as a result of wollastonite application is estimated at \$240/tonne CO₂. At present in Ontario, the carbon price for CO₂ emission is \$20/tonne of CO₂ emission exceeding the limit in 2019, rising by \$10 each year up to a maximum of \$50/tonne in 2022 (Pricing carbon pollution from industry, 2019). As such, carbon credits alone may not cover the cost of wollastonite application, but would off-set its cost when wollastonite is used to deliver additional benefits to soil and plants Haque et al. (2019a,2019b), as wollastonite is presently marketed and with research to confirm such benefits still ongoing by several research groups.

3.3. Microstructural analyses

3.3.1. XRD results

Fig. 7 shows the XRD diffractograms of the wollastonite amended soils from the three fields. Since the soil composition is complex, quantification of the different mineral phases is a challenge, therefore the peaks were qualitatively identified. Fig. 7a shows the XRD diffractogram of Field 1 for the three application years (1, 2, and 3). Characteristic peaks for quartz (SiO₂) and albite (NaAlSi₃O₈), which are predominant in Canadian soils (Schönenberger et al., 2012), are present in the soil samples. The amended soils showed peaks for calcite

(CaCO₃), as well as opal, a SiO₂ polymorph, and rutile (TiO₂). Ti likely originated from wollastonite, as its chemical composition include trace amounts of Ti. The three predominant peaks of rutile match well the position of several new peaks formed in the soil with three applications of wollastonite, suggesting that subsurface-originated wollastonite could be the source of this mineral.

XRD diffractogram of the wollastonite amended soils from Fields 2 and 3 were compared with their respective controls in Figs. 7b and 7c. These provide a better understanding on how the soil mineralogy is changing when weathering reactions occur due to wollastonite amendment. The Field 2 amended sample showed peaks for wollastonite, which was applied to the soil, as well as opal and calcite, which are also not present in the control plot sample, hence suggesting that these phases have formed later as a result of the weathering reactions. In Fig. 7c, new peaks are seen in the Field 3 amended soil in the 20 regions of 27–29° and 34–36°. These soil samples showed characteristic peaks for quartz and albite, with increased intensity for albite in the soil samples with highest wollastonite application rate. Albite is a silicate mineral, and likely originates from the wollastonite used, as its chemical composition includes minor amounts of sodium (1.06 wt%). In comparison, the calcium content of the mined wollastonite is 18.9 wt% versus 23.2 wt% for pure wollastonite.

According to Eq. (2), the carbonation of wollastonite not only results in the production of CaCO₃, but SiO₂ is also formed as a result of wollastonite dissolution. This explains the appearance of SiO₂

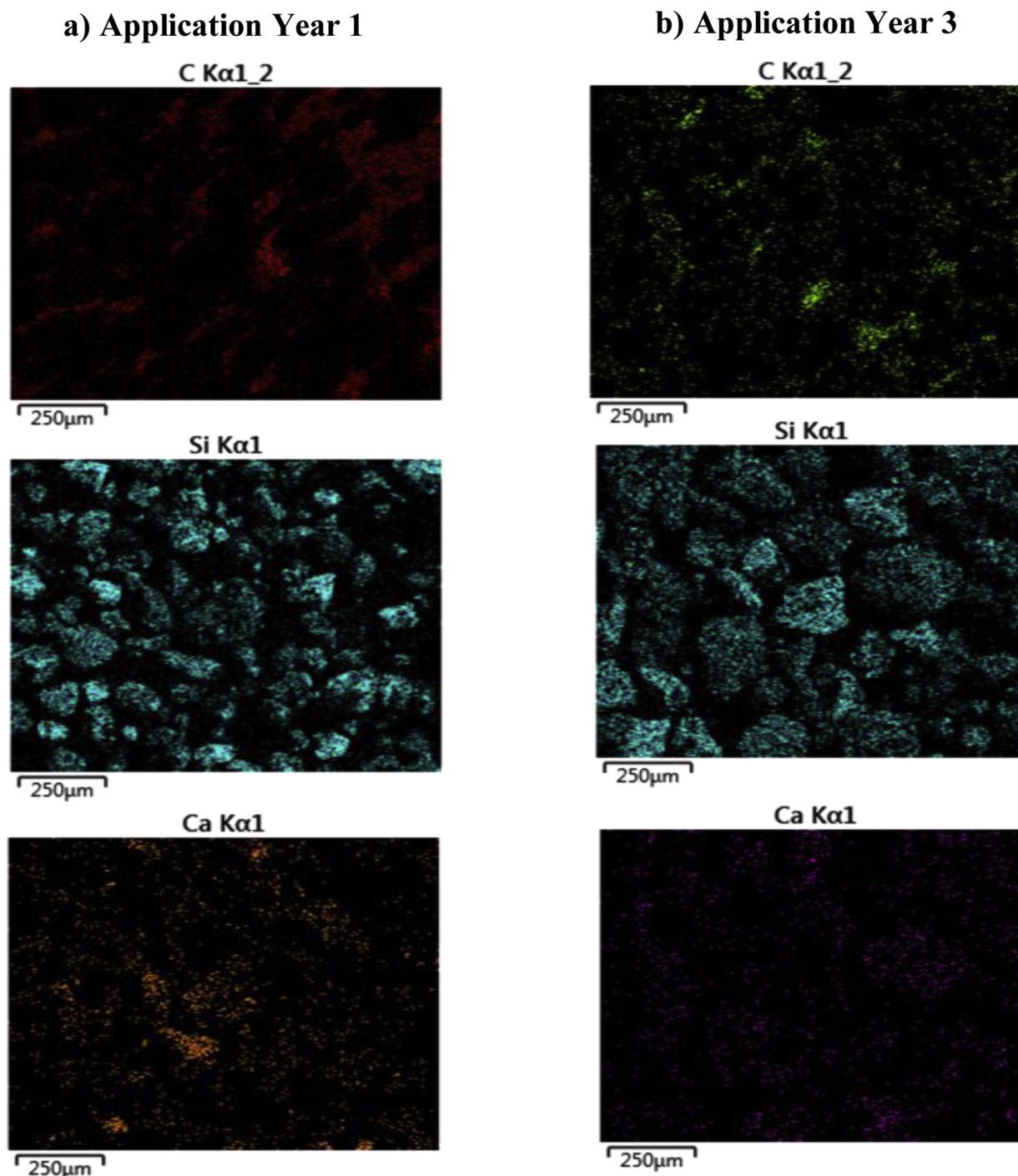


Fig. 9. Elemental mapping (C, Si, Ca) of the soil samples from the Field 1: a) Application Year 1; and b) Application Year 2.

polymorphs, which is an added advantage for the soil's physical properties. Silica plays an important role as a cementing material to increase the soil strength, prevent soil loss, and overall contributes towards soil improvement (Walker and Pavía, 2011). The high SIC content of amended soils verified by calcimetry and TGA can be linked from the XRD data to the formation of the calcite polymorph, though it is also possible that amorphous calcium carbonate is also present (Versteegh et al., 2017). Thus, the XRD study confirms that wollastonite weathering occurred in agricultural soils, which resulted in the formation of new mineral phases in the amended soils.

3.3.2. SEM-EDS results

Fig. 8 shows the SEM images of the soils sampled from Field 1 (leafy vegetable). To isolate the wollastonite particles from the amended soil is a challenge, so it was difficult to understand if the observable wollastonite particles had reacted and if calcite had formed on its surface or as separate particles. Limited by this condition, SEM-EDS study was used to understand how the soil composition changed in terms of morphology and structure. The soil amended with wollastonite thrice (Application year 3, Fig. 8c) consisted of more irregular shaped fragments and was denser compared to the one treated once (Application year 1, Fig. 8a), giving the former a compact structure. The consecutive applications of wollastonite may have altered the soil morphology over

time. The XRD analysis confirmed the formation of new mineral phases, and these may contribute to the increased occurrence of irregular shaped structures in the amended samples. The denser soil structure with irregular morphology observed in wollastonite amended soil is either attributable to the formation of CaCO_3 , or more generally to the weathering of alkaline silicates in soils.

The recorded EDS data for the Application Year 3 sample (Fig. 9d) reveals the chemical profile of five different fragments. The probed spectrum regions mainly consisted of O, Si, Ca, Al, Fe, Na, and K (elements found in all regions). Calcium concentrations were low in all regions, so it cannot be stated with certainty if any of these regions contained wollastonite or calcium carbonate derived from it. In addition, spectrum regions 1, 3, and 5 contained Mg, and spectrum regions 3 and 5 contained C. The detected carbon constitutes the soil carbon composition, which includes organic and inorganic components, thus again this analysis cannot verify the presence or formation of pedogenic carbonates. Fig. 9 shows elemental mapping of the Application Year 1 and Year 3 samples. Here it can be better visualized that no distinct regions that could be attributed to the presence of any of the mineral phases detected by XRD can be reliably identified. As much of the carbon content is likely organic matter, regions with Si and Ca but no C may be residual particles of wollastonite, and regions with Ca and C but no Si could be pedogenic carbonates. The spatial resolution of the analysis contributes to these uncertainties, and the use of electron probe microanalysis (EPMA) is a technique with superior spatial resolution for elemental mapping worth exploring in future soil amendment studies.

4. Conclusion

Results of this study are of significance to confirm the potential of wollastonite as a soil amendment to find acceptance in the agricultural sector. Consecutive annual applications of wollastonite should result in an increase in soil inorganic carbon content, as seen in the case of Field 1 where wollastonite has been regularly applied over three years, leading to 2.6 times increased carbonate content. Also, the particle size of the wollastonite used, coarse or fine grains, also has an impact on the weathering reactions, as seen in Field 2, where fine wollastonite was used but showed 89 % increase in the soil inorganic carbon content, as compared to the coarse wollastonite used in the Field 3 where 63 % increase was observed. SEM-EDS study, and in particular XRD data, also confirm the presence of additional mineral phases after wollastonite amendment, including polymorphs of SiO_2 and calcite that originate from wollastonite weathering reactions in the soils. These results are in agreement with smaller scale experiments conducted by the present research team and other research groups around the world. The results obtained from these fields study will help to convince producers, especially those of high-value crops like leafy vegetables and potatoes, to effectively use wollastonite on their lands to contribute toward global climate change mitigation without compromising on their yield. It is concluded from this study that amending agricultural soils with wollastonite is an effective geoengineering tool applicable at regional to global scales that has the potential to store significant amounts of carbonates and help to mitigate atmospheric CO_2 levels alongside other carbon capture, utilization and sequestration approaches.

CRediT authorship contribution statement

Fatima Haque: Methodology, Formal analysis, Investigation, Writing - original draft. **Rafael M. Santos:** Conceptualization, Methodology, Writing - review & editing, Supervision, Funding acquisition. **Yi Wai Chiang:** Conceptualization, Methodology, Resources, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.ijggc.2020.103017>.

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