FY2025 Research Report

Black Shale

Shelburne Limestone Corporation

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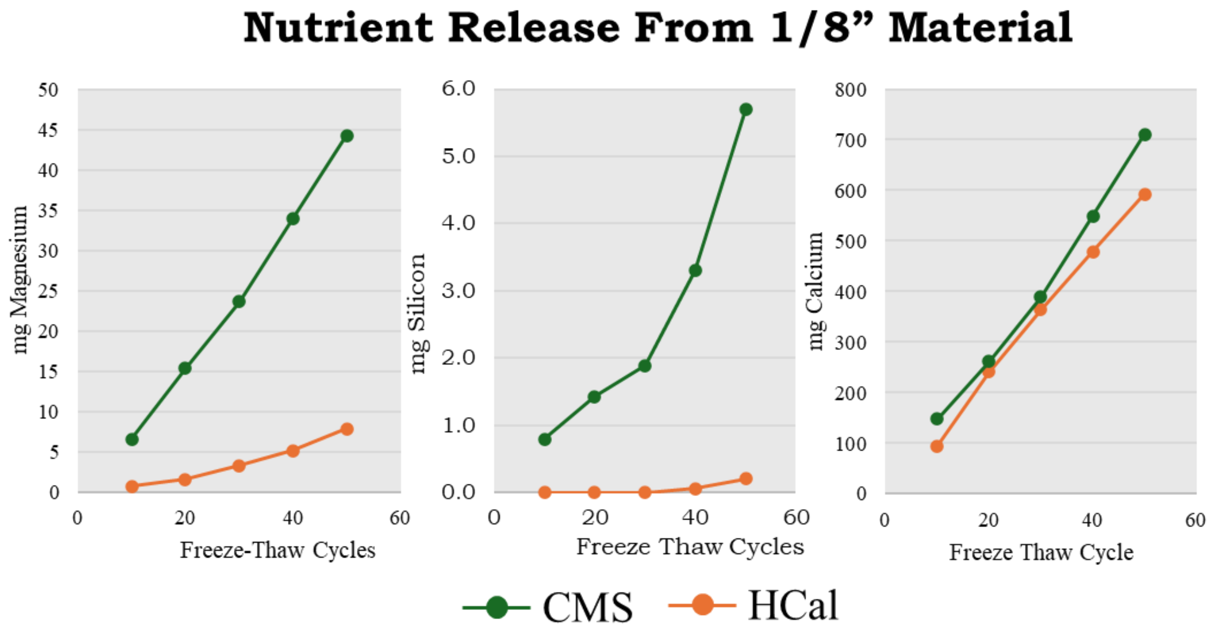
Executive Summary:

Carbonaceous Marine Shale (CMS) was compared to High-Calcium Limestone (HCal) or Humate in a series of test to determine differences in nutrient release and plant response to the materials. While plants did not show any significant differences in these trials, data from the freeze-thaw trials showed a substantial increase in magnesium and silicon release from the CMS material compared to HCal. Additionally, during a past AAPFCO meeting it was mentioned that Carbonaceous Shales are listed in the humic substance definition. *Test for the percent humic acid and/or fulvic acid fraction of the material may be warranted.* Taken together, labeling this product as a humic substance that releases calcium, magnesium, and silicon, supports an added value to Carbonaceous Marine Shale when compared to a standard high-calcium limestone.



Freeze-Thaw Trial:

In the freeze-thaw trial, 1/8” Carbonaceous Marine Shale (CMS) and High-Cal limestone (HCal) were added to plastic vials along with distilled water (**Fig. 1**). Following a 10-cycle freeze-thaw period distilled water was removed and stored at 4°C prior to testing. Additional water was added to the vial and another 10-cycle freeze-thaw period commenced. This was repeated 5 times for a total of 50 freeze-thaw cycles. A set of vials were also prepared similarly to those experiencing the freeze-thaw but were kept at room temperature for the entirety of the trial with no water removed or replaced.

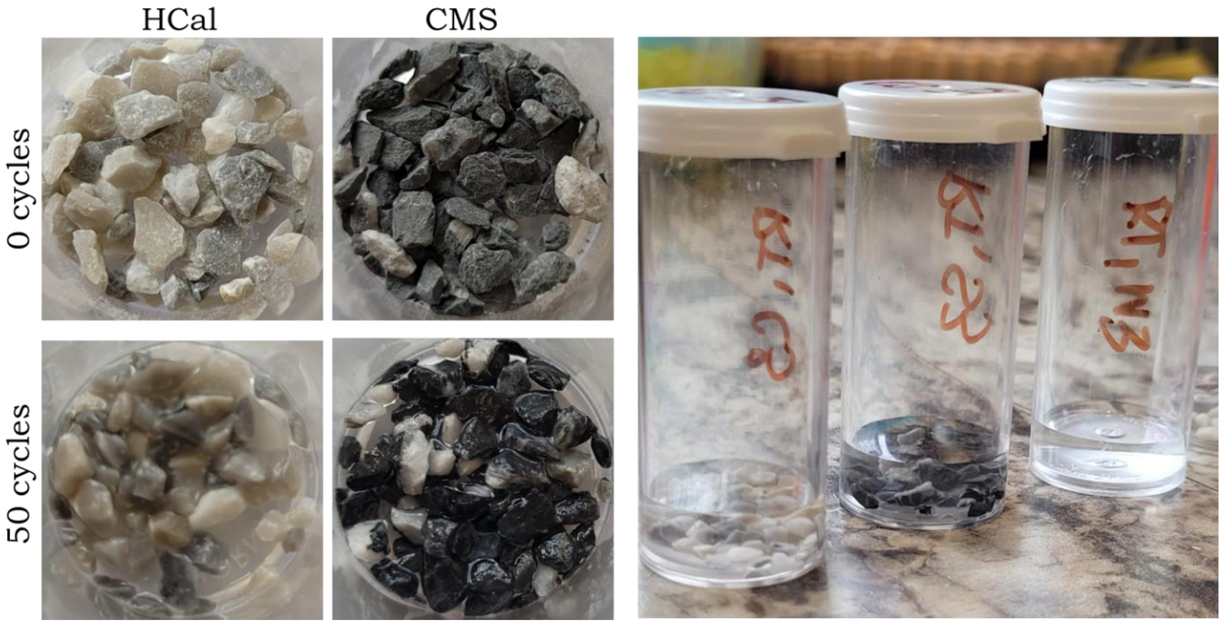


Figure 1: High-Calcium Limestone (HCal) and Carbonaceous Marine Shale (CMS) were added to plastic vials along with distilled water. The vials went through 50 freeze-thaw cycles. At the end of the 50 cycles, there was no observable difference in the material size.

The water solution was tested for calcium, iron, magnesium, silicon, and sulfur. Of these five nutrients, calcium, magnesium, and silicon were detected in the water solution.

Calcium release from both HCal and CMS was similar (**Fig. 2**). Overall, a significantly higher amount of calcium was released from the materials treated with freeze-thaw cycles compared to the amount released when kept at room temperature. This is likely due to the solubility of calcium in water as the room-temperature treatment was not replenished with fresh water and likely reached the maximum solubility at 125 mg/mL Ca.

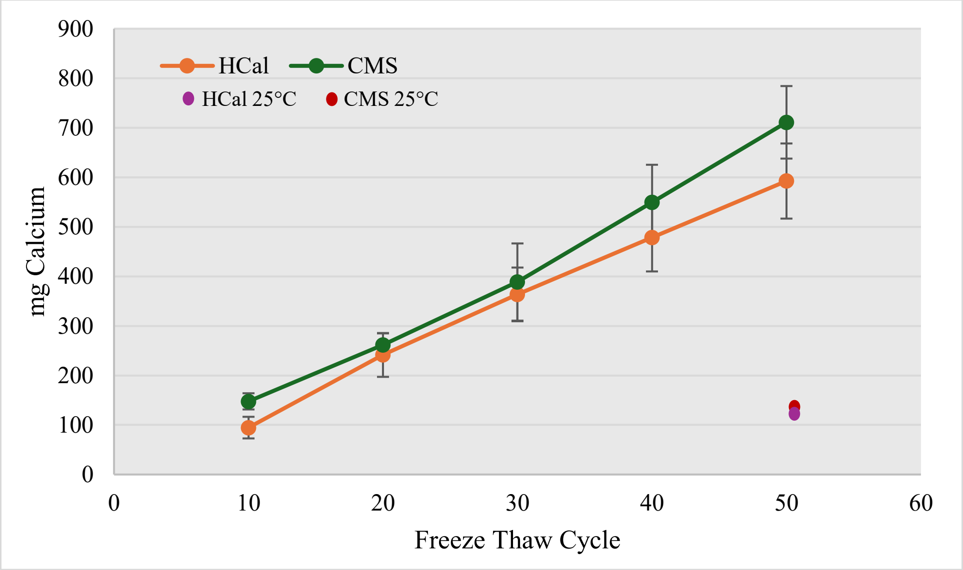


Figure 2: Cumulative calcium release from High-Cal (HCal, orange) and Carbonaceous Marine Shale (CMS, green) over 50 freeze-thaw cycles. Calcium release was similar between the two products throughout the entire experiment. Calcium release from material kept at room temperature during the study are also reported as single dots at 50 cycles for HCal (purple, average = 120 mg Ca) and CMS (red, average = 132 mg Ca). Error bars represent standard deviation with *n*=4 per treatment.

Silicon release from CMS was significantly higher than HCal with a total release of 3.8 mg Si after 50 freeze-thaw cycles compared to only 0.4 mg Si for HCal (**Fig. 3**). Silicon release for CMS at room temperature was lower at 50 cycles (3.8 mg Si) compared to the freeze-thaw treatments (5.7 mg Si). However, silicon release from HCal at room temperature was twice as much as that from the freeze-thaw cycles, at 0.4 mg Si and 0.15 mg Si, respectively. This data shows CMS releases a measurable amount of silicon compared to HCal and that its release begins to exponentially increase following 30 freeze-thaw cycles. *Future studies might look at silicon release over a longer period of time to capture the entire silicon-release curves for different grades of the CMS material.*

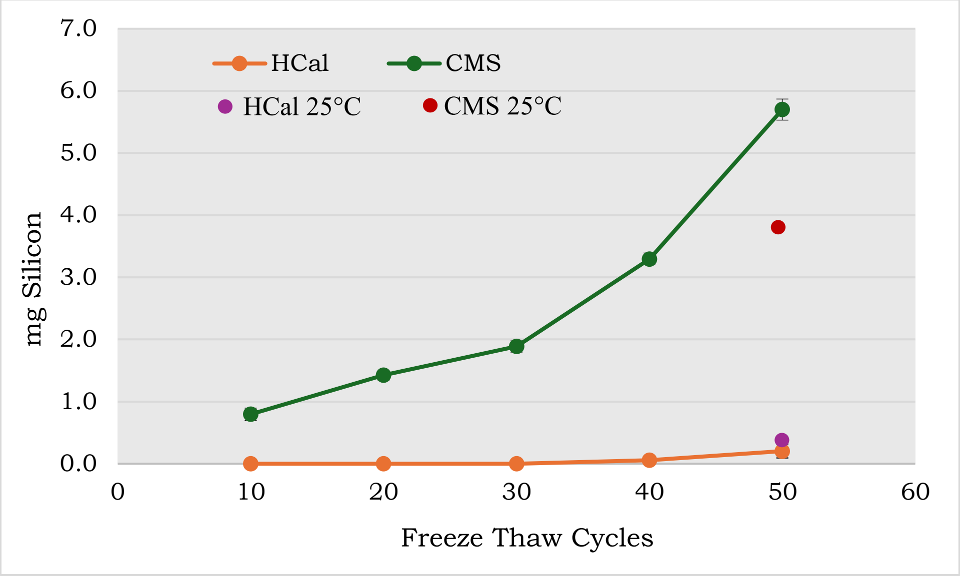


Figure 3: Cumulative silicon release from High-Cal (HCal, orange), Carbonaceous Marine Shale (CMS, green) over 50 freeze-thaw cycles. Silicon release from CMS was significantly higher than HCal at all time points. CMS at room temperature had a lower concentration of silicon compared to the freeze-thaw accumulation (red dot, average = 3.8 mg Si), which is likely due to the solubility of silicon. HCal at room temperature had about twice as much Si in solution compared to that accumulated through the freeze-thaw cycles (purple dot, average = 0.4 mg Si for room temperature HCal compared to 0.2 mg Si for freeze-thaw accumulation at 50 cycles). Error bars represent standard deviation with *n*=4 per treatment.

Magnesium release from CMS was significantly higher than HCal throughout all the freeze-thaw cycles (**Fig. 4**). Both CMS and HCal at room temperature had a lower magnesium concentration compared to the cumulative amount of magnesium at the end of 50 freeze-thaw cycles, which may reflect magnesium solubility in water. While the concentration of magnesium was lower than that of calcium, the steady increase in magnesium release could continue to increase if the time intervals were extended. *Future studies might look at magnesium release over a longer period of time to capture the entire magnesium-release curves for different grades of the CMS material.*

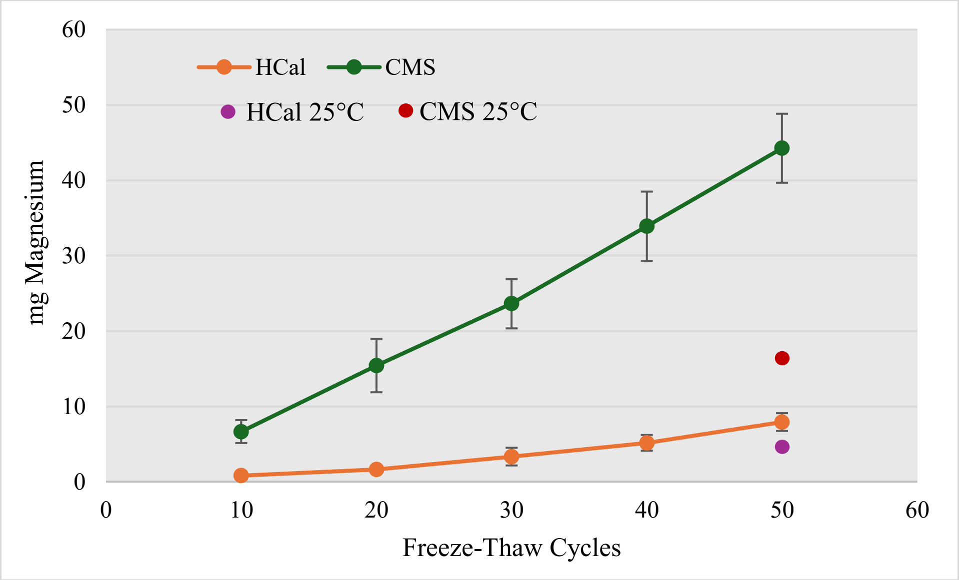


Figure 4: Cumulative magnesium release from High-Cal (HCal, orange) and Carbonaceous Marine Shale (CMS, green) over 50 freeze-thaw cycles. Magnesium release from CMS was significantly higher than from HCal at all time points. CMS at room temperature had a lower concentration of magnesium compared to the freeze-thaw accumulation (red dot, average = 17.6 mg Mg), which is likely due to the solubility of magnesium. HCal at room temperature had less Mg than the total amount released throughout the freeze-thaw cycles (purple dot, average = 4.3 mg Mg). Error bars represent standard deviation with *n*=4 per treatment.

While previous figures (**Figs. 2:4**) show the accumulated amount of each nutrient rising over time, if we were to look at the concentration of the nutrients at the time of collection, it shows different release patterns (**Fig. 5**). Magnesium released from CMS has a steady increase at each freeze-thaw interval, while silicon release from CMS has higher release at 40 and 50 freeze-thaw cycles. Calcium had consistent release at each of the freeze thaw cycles and was similar to the release reported at room temperature. This could suggest that the experiment only captured the beginning of the total release curves for magnesium and silicon. *A follow-up time-course study with the CMS and HCal with room-temperature or freeze-thaw cycles over a longer period of time (180 days, with samples collected weekly) could provide more data on how the material might behave throughout a growing season with respect to nutrient release.*

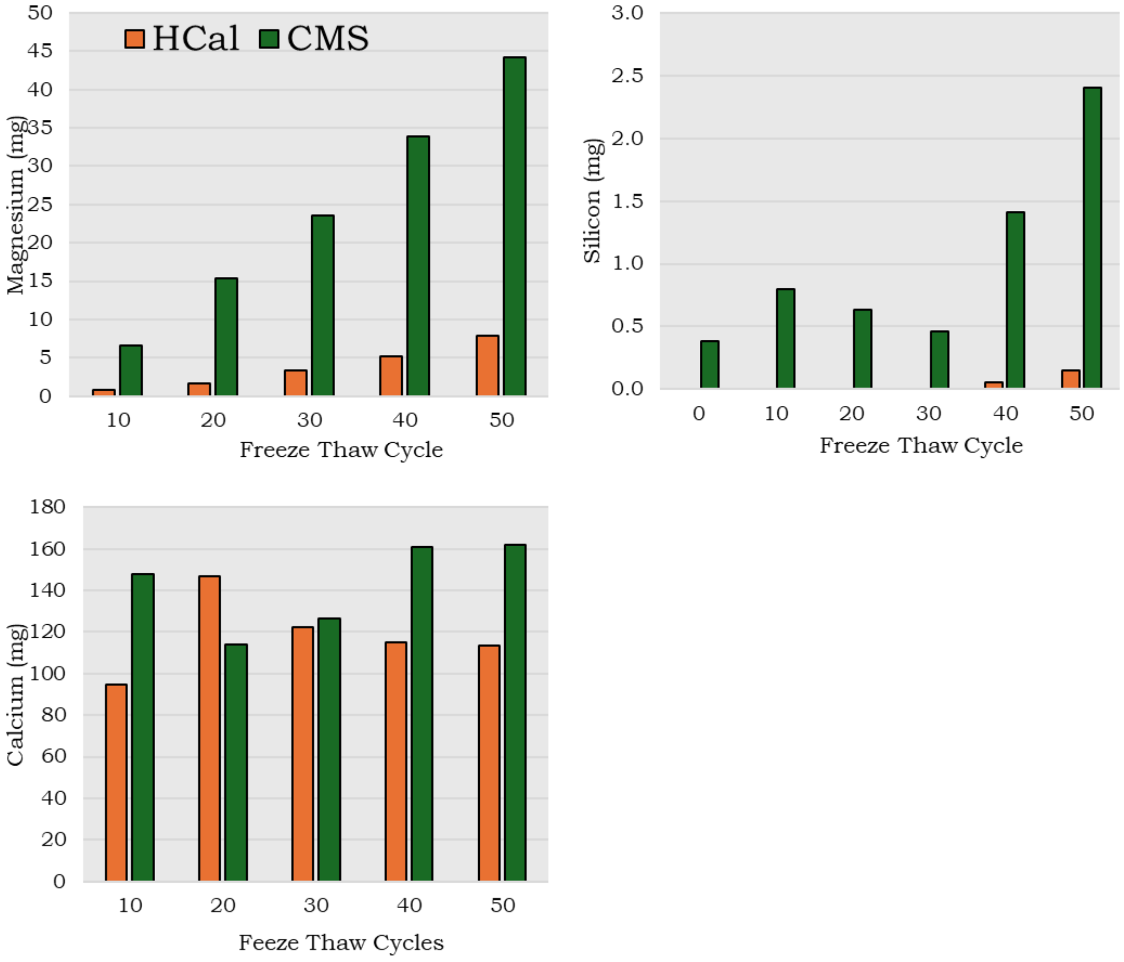


Figure 5: Average nutrient concentration (in mg) measured at the various freeze-thaw cycles released from High-Calcium Limestone (HCal, orange bars) or Carbonaceous Marine Shale (CMS, green bars).

No iron was detected in any of the collected solutions (data not shown). The sulfur test method did not work properly for the purpose of these tests and at this time the amount of sulfur release is concluded to be undetermined at this time.

Greenhouse Nutrient Release Trial:

Tomatoes were grown in a blended soil-less (peat:perlite) and clay-soil media containing varying amounts of super fine CMS and humate placed into a cotton teabag and added to the front of plastic containers (**Table 1, Fig. 6**). Root growth was monitored to determine if there was an increase in growth toward the material. An initial scan was made of each container and roots analyzed showing no significant difference across treatments or preference toward or away from the fertilizer material (**Fig. 7**). In the weeks following the initial scan, there were no observed differences between any of the treatments. Root growth was similar towards and away from CMS or CMS & humate combinations. No further analysis was carried out due to similar growth characteristics and no difference in root growth. The incorporation of soil-less media containing sphagnum peat could have masked the humate response in these trials. ***Future studies should try to reduce the concentration of humic substances present in the media or fertilization practice.***

Table 1: Experimental Design for CMS Tomato Trials

Trt #	%H	Trt	CMS tons	Humate lbs
1		Control	0	0
2	0%	SF	1	0
3	1%	SF+H	0.99	20
4	2%	SF+H	0.98	40
5	3%	SF+H	0.97	60
6	2%	H	0	40

CMS = Carbonaceous Marine Shale, H = Humate,
SF = CMS Super Fines,Trt = Treatment
n=6

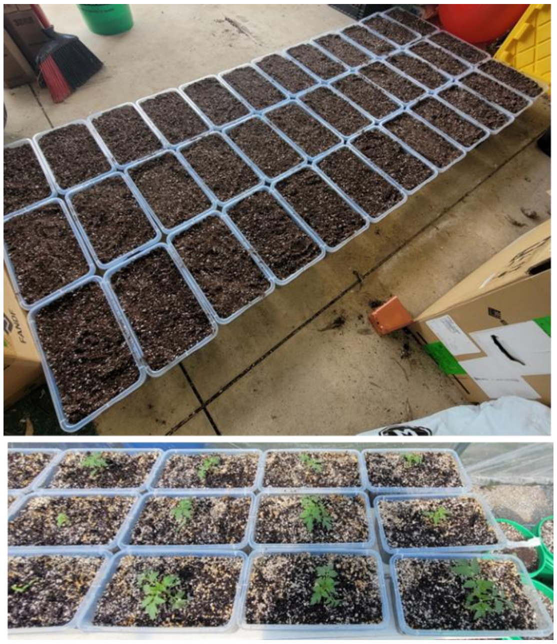


Figure 6: Custom media blend and early tomato growth.

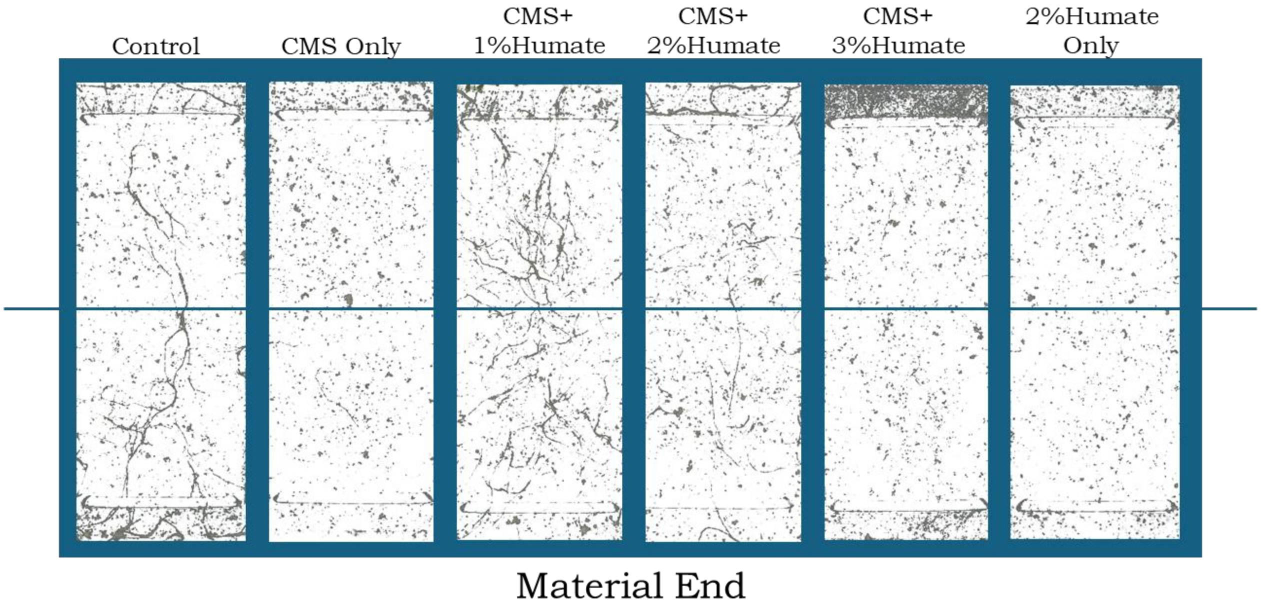


Figure 5: Representation of the initial screening of tomato root growth towards (below the thin blue line) or away (above the thin blue line) from the fertilizer material. Notice that for control and CMS+1% Humate root growth was similar in the two fractions of the container. These images were rendered in Photoshop to highlight areas of root growth.

Buried Bag Trial:

The goal of the buried bag trial was to follow the changes in material size over the course of multiple growing seasons. Carbonaceous Marine Shale (CMS) pellets and 1/8" High-calcium lime were added separately to tea bags and buried among tomato plants in a garden plot (**Fig. 6 A,B**). The soil was a Hoytville clay series with total exchange capacity of 15.42 meq, 6.2 pH, and 4.55% organic matter. After 14 weeks, bags were unburied. Unfortunately, the tea bags used in the experiment were degraded within this short time frame, resulting in material loss to the soil (**Fig. 6 C,D**). No further analysis of the material was carried out for this trial.

Figure 6: Buried bag trial using cotton tea bags (A) to hold the CMS and HCal material prior to being buried in clay soil between tomatoes (B). After 14 weeks, buried bags disintegrated under field conditions (C and D), resulting in loss of material. In some cases, a reminder of the material remained in the bag (C, CMS pellets are visible), while others have the material completely in contact with the soil (D, HCal).

AAPFCO Summary:

At the February Winter Annual AAPFCO Meeting, the MNP-12 Carbonaceous Marine Shale definition was voted to official by the board. This allows the use of carbonaceous marine shale as a description for labeling and marketing purposes. Interestingly, during the debate of this term, it was pointed out that carbonaceous marine shales are listed as humic substances (PMP-10 Humic Substance definition below). *A standard test to determine the percent humic acid and/or fulvic acid can be done in order to market this material as a humic substance.*

MNP-12 Carbonaceous Marine Shale: Black shale containing greater than 4% total carbon derived from marine sediment that may contain Ca, Mg, Co, Fe, Mn, and Ni (Tentative SA 2024, Official WA 2025).

PMP-10 Humic Substances: Constituents of soil organic matter and the aquatic environment, consisting of complex heterogeneous mixtures of carbon-based substances formed biochemical reactions during the decay and transformation of plant and microbial remains. They are primarily composed of three main fractions, called humic acids, fulvic acids, and humin, which are operationally defined by their solubility in dilute alkali and acid solutions. Sources of humic substances are commercially harvested from terrestrial deposits which include, but are not limited to, Leonardite, oxidized lignite, oxidized sub-bituminous coals, Humalite, **carbonaceous shales** (including humic shale), peat, and sapropel. (Tentative SA 2018, Official WA 2019)