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Electronic Supplementary Information:

ALGINATE BEADS CONTAINING LAYERED DOUBLE HYDROXIDE INTERCALATED WITH BORATE: A POTENTIAL SLOW-RELEASE BORON FERTILIZER FOR APPLICATION IN SANDY SOILS

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Table S1: Chemical characterization of the irrigation water collected in Hastings Agricultural Extension Center research farm located in Hastings, FL, U.S.

Element	Level	Element	Level
Nitrate (mg L^{-1})	0.28	Iron (mg L^{-1})	0.05
Phosphorus (mg L^{-1})	0.04	Manganese (mg L^{-1})	0.01
Potassium (mg L^{-1})	2.8	Sulfate (mg L^{-1})	0.02
Magnesium (mg L^{-1})	12.4	pH	8
Calcium (mg L^{-1})	96.47	Chloride (mg L^{-1})	23
Sodium (mg L^{-1})	15.27	Carbonate (mg L^{-1})	48
Boron (mg L^{-1})	0.12	Bicarbonate (mg L^{-1})	448.35

Total concentration of nitrogen (N) in the LDH-B-ALG and BA-ALG fertilizers:

LDH-B-ALG and BA-ALG presented a low fraction of N in their compositions. Nitrogen is a macronutrient required in relatively large amounts, and it is directly related to plant growth and development. The total N concentration was 15.0 g kg^{-1} in LDH-B-ALG (1.50% of N) and 6.0 g kg^{-1} in BA-ALG (0.60% of N). In the present study, the total N applied from LDH-B-ALG and BA-ALG was considered negligible. The total amount of LDH-B-ALG and BA-ALG was calculated to supply B, considering the plant's relatively low B requirement. The B rates applied in this study were 0, 0.5, 1.0, 3.0, and 5.0 mg dm^{-3} of B in the “Greenhouse experiment without leaching” and 2.0 mg dm^{-3} of B in the “Greenhouse experiment with leaching”. Under the highest B rate (5.0 mg dm^{-3}), the total N applied as LDH-B-ALG and BA-ALG corresponded to less than 1% of the total N supplied (200 mg dm^{-3} of N as urea source) in the first and second cultivations at pre-planting and sidedress. Therefore, the contribution of N from LDH-B-ALG and BA-ALG was not considered.

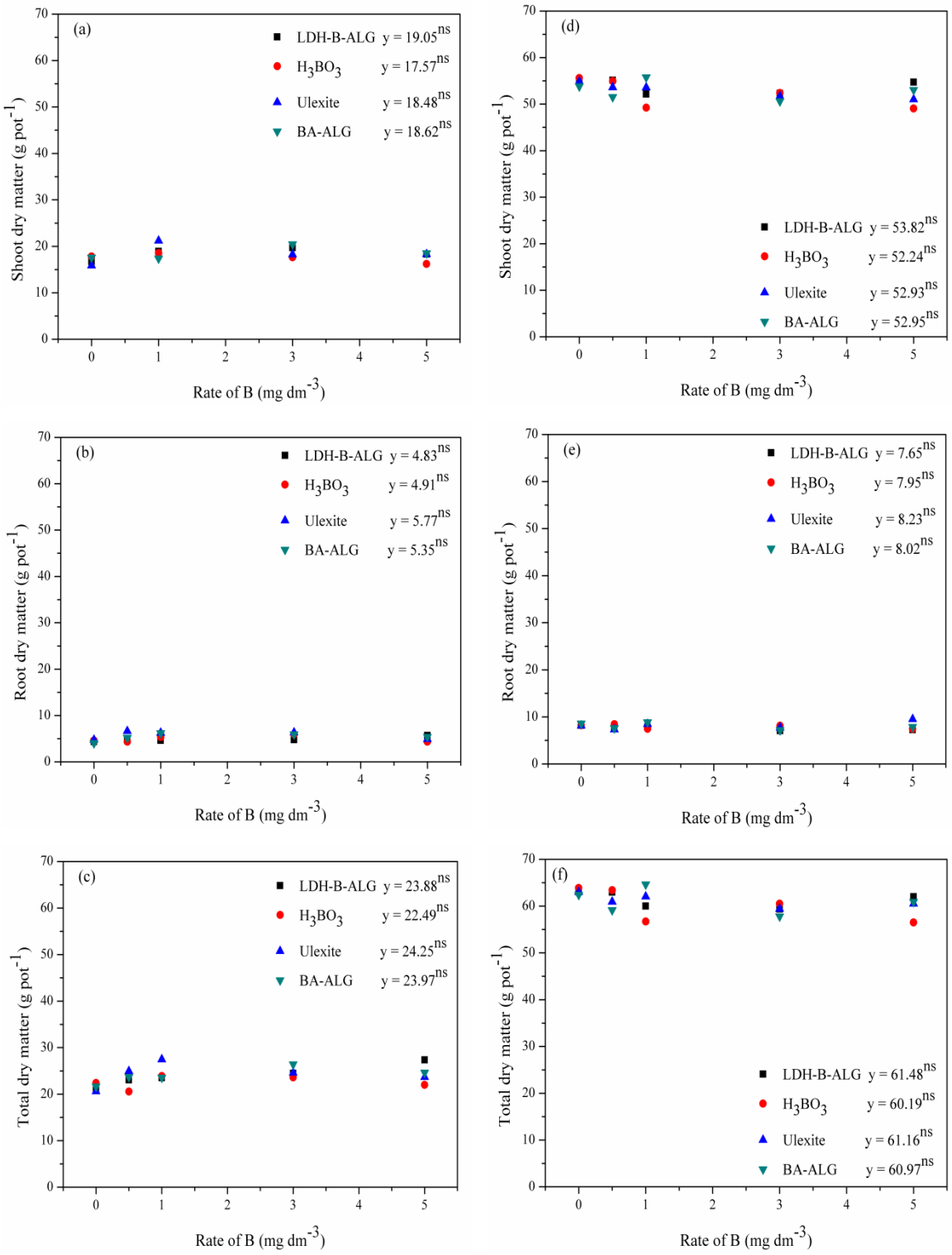

Fig. S1: Shoot, root and total dry matter as a function of the applied B (H_3BO_3, BA-ALG, Ulexite, and LDH-B-ALG) in first (a, b, and c) and second (d, e, and f) cultivation. ns = not significant.

Cumulative Release and Leaching of Boron from Mg_2Al-B-LDH, LDH-B-ALG, H_3BO_3 and BA-ALG:

The B release test was performed and adapted from the ''*in vitro*'' release method, described by Bin Hussein and coworkers.[1] A factorial 6 x 2 was established with six collection times (0, 0.5, 1, 2, 4, and 6 hours), and two B sources (LDH-B-ALG and Mg_2Al-B-LDH). The experiment was conducted in a randomized complete block design with four replicates. The water used in the boron release test was H_2O deionized-Milli-Q system. Using an Erlenmeyer's flask with 250 mL of capacity, 45 mg L^{-1} of total B from the B sources and 100 mL of the water were added. At pre-established times (0, 0.5, 1, 2, 4, and 6 hours), a slight agitation was performed to homogenize the solution and aliquots of 5 mL were withdrawn. Immediately afterwards, 5 mL of the water was added in order to keep the volume constant. The analyses of B concentration were performed according to the method described by López and coworkers.[2]

The leaching in soil columns was performed the same as described in section "2.2 Boron leaching in soil columns" of this manuscript, except for the boron sources (LDH-B-ALG and Mg_2Al-B-LDH) and incubation time (1, 5, 10, 15, 20, 25, and 30 days).

The B release and leaching tests were replicated comparing H_3BO_3 and BA-ALG sources. The collection and incubation times was the same previously described.

The cumulative release and leaching of B from LDH-B-ALG and Mg_2Al-B-LDH are shown in Fig. S2a. In the first collection, the total B released from LDH-B-ALG and Mg_2Al-B-LDH were equivalent to 0.6% and 0.7%, respectively of the total B. After 6 hours of LDH-B-ALG and Mg_2Al-B-LDH application, 54.7% and 100% of the B were released, respectively. LDH-B-ALG presented a cumulative B release significantly lower at 2, 4, and 6 hours of collection than Mg_2Al-B-LDH source. For H_3BO_3 and BA-ALG sources (Fig S2c), the B release from BA-ALG was significantly lower at 0.5, 1, and 2 hours compared to H_3BO_3. The total B released (100%) from H_3BO_3 and BA-ALG were at 2 and 4 hours of collection, respectively.

Regarding B leaching, as expected, the leachate had more quantity of B when Mg_2Al-B-LDH was applied (Fig. S2b). For the first leaching collection time, 1.7% and 5.2% of the total B applied were leached from the LDH-B-ALG and Mg_2Al-B-LDH sources, respectively. At 30 days, after the LDH-B-ALG and Mg_2Al-B-LDH

application, 67% and 88% of B was leached, respectively. The B leaching from LDH-B-ALG was significantly lower at 10, 15, 20, 25, and 30 days of incubation compared to Mg_2Al-B-LDH. These results showed a higher B leaching profile from Mg_2Al-B-LDH compared to LDH-B-ALG. The slow leaching profile was also confirmed for BA-ALG, in which in all incubation times the B leached was lower compared to H_3BO_3 (Fig. S2d).

The results presented by LDH-B-ALG in the release and leaching of B study, suggested a lower release and leaching profile by LDH-B-ALG compared to Mg_2Al-B-LDH, showing an advantage in producing LDH-B-ALG beads compared to the Mg_2Al-B-LDH in powder form.

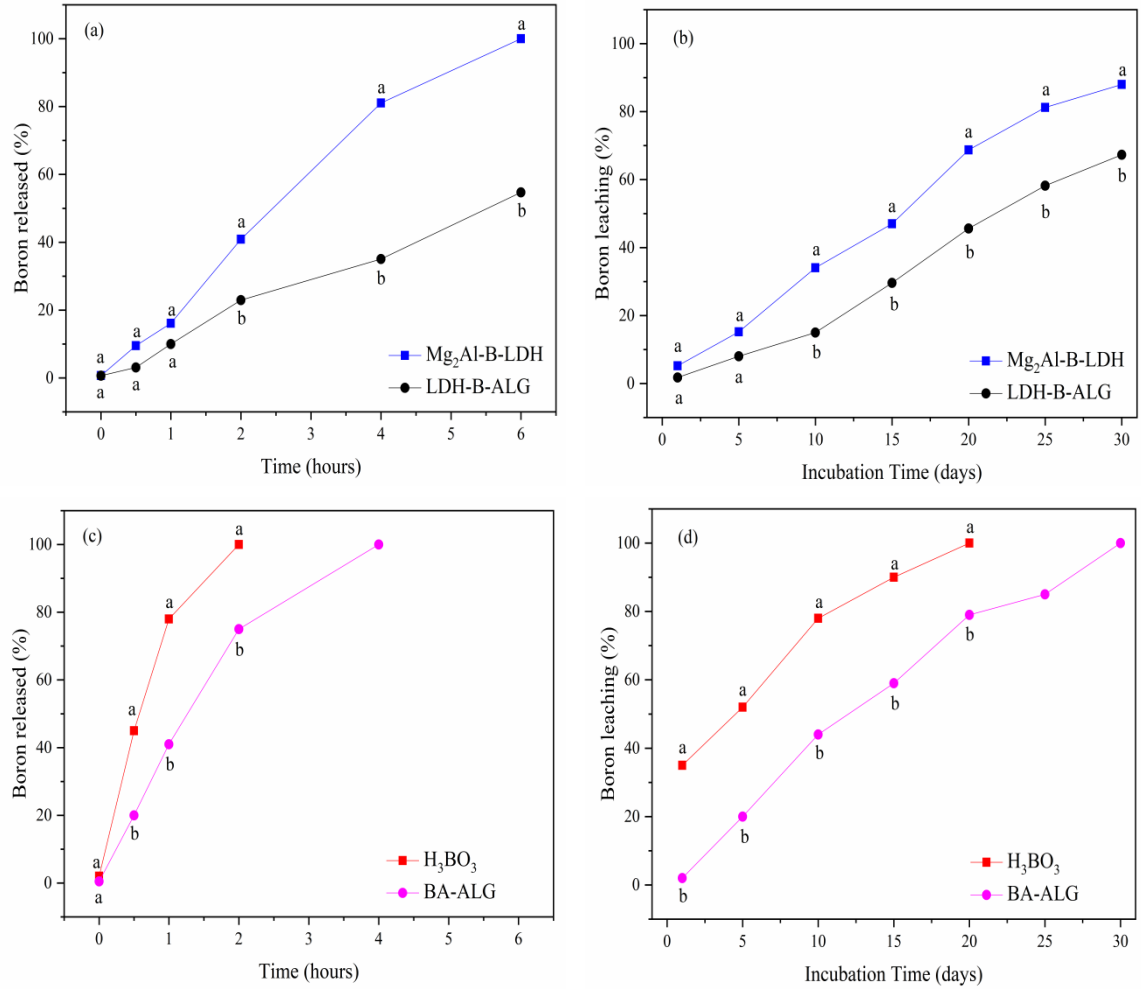

Fig. S2: Cumulative release (a and c) and leaching (b and d) of boron from Mg_2Al-B-LDH, LDH-B-ALG, H_3BO_3, and BA-ALG. Values followed by the same lowercase letter within each time (hours) and incubation time (days), indicate that the mean of release and leaching of B, are not significantly different at $p<0.05$ according to Tukey test between B fertilizer sources.

References

1 M. Z. bin Hussein, Z. Zainal, A. H. Yahaya and D. W. V. Foo, *Journal of Controlled Release*, 2002, **82**, 417–427.

2 F. J. López, E. Giménez and F. Hernández, *Fresenius Journal of Analytical Chemistry*, 1993, **346**, 984–987.