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Influence of brick air scrubber by-product on growth and development of corn and hybrid poplar

Carla N. Thomas [a], William L. Bauerle [b,*], Tom O. Owino [c], John P. Chastain [c], Stephen J. Klaine [a]

[a] Institute of Environmental Toxicology, Clemson University, 509 Westinghouse Rd., Pendleton, SC 29670, United States
[b] Department of Horticulture, Clemson University, Clemson, SC 29634, United States
[c] Department of Agricultural and Biological Engineering, Clemson University, Clemson, SC 29634, United States

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Abstract

Studies were conducted to determine the effects of spent reagent from air pollution control scrubbers used at a brick manufacturing facility on emergence, growth, and physiological responses of corn and hybrid poplar plants. Scrubber by-product was obtained from General Shale Brick, Louisville, KY. Potting substrate was weighed and quantities of scrubber by-product were added to the substrate to obtain treatments of 0%, 6.25%, 12.5%, 25%, 50%, 75%, and 100% scrubber by-product (w:w) for the corn study. Each treatment mix was potted into nine replicate polyethylene pots and four corn seeds were sown per pot. The pots were randomized in a greenhouse at Clemson University and the number of seedlings emerging from each treatment, dark-adapted leaf chlorophyll *a* fluorescence, and shoot heights were measured at the end of a 21-day growth period. Then, dry shoot biomass was determined for plants from each treatment and plant tissues were analyzed for selected constituents. For the poplar study, nine-inch cuttings of hybrid poplar clone 15–29 (*Populus trichocarpa* × *P. deltoides*) and clone OP367 (*P. deltoides* × *P. nigra*) were planted in treatments of scrubber by-product-potting soil mixes of 0% , 5% , 10% , and 25% w:w. Leaf chlorophyll *a* fluorescence was measured over six weeks and cumulative leaf area, dry biomass, and nutrient content of tissues were determined upon harvest. Results of these studies indicate that percent seedling emergence for corn plants decreased with increasing scrubber by-product application rates. Application rates up to 12.5% scrubber by-product w:w had no adverse effect on corn seedling emergence. Shoot elongation, biomass production, and the status of the photosynthetic apparatus of the seedlings were also not severely impaired at applications below this level. A critical value of 58.2% w:w scrubber by-product was estimated to cause 25% inhibition of seedling emergence. Biomass production, cumulative leaf area, and chlorophyll *a* fluorescence of hybrid poplar plants were not affected by scrubber by-product applications of up to 5% w:w.

Keywords: Scrubber by-product; Corn; Hybrid poplar; Chlorophyll fluorescence; Physiological stress

1. Introduction

Several gases are released during brick manufacturing processes including hydrogen fluoride (HF), sulfur oxides (SO_x), nitrogen oxides (NO_x), carbon monoxide (CO), carbon dioxide (CO_2), and hydrogen chloride (HCl). The combustion products, including SO_2, NO_x, CO, and CO_2, are typically released from fuel combustion in brick kilns and some brick dryers (US EPA, 2003). The raw materials of brick often contain sulfur and fluoride compounds and are the primary source of SO_2 and HF emissions from brick kilns during the firing process. Emissions of these gases vary considerably due to the high variability in sulfur and fluoride contents of shales and clays. The US Environmental protection agency (EPA) has established national emission standards for hazardous air pollutants which require all major sources, including brick manufacturing plants, to

* Corresponding author. Tel.: +1 864 656 7433; fax: +1 864 656 4960.
E-mail address: bauerle@clemson.edu (W.L. Bauerle).

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implement a maximum achievable control technology (MACT) to reduce emissions (US EPA, 2003).

Brick plants utilize several techniques to extract and neutralize acid gases from their exhausts, which are classified as either wet or dry scrubbing processes. In dry scrubbing systems, the emphasis of this study, Dry Lime Scrubbers (lime injection/baghouse) are used to remove both HF and SO_x, combustion exhaust gases present in significant quantities. Injection of limestone and or hydrated lime in a Venturi reactor followed by collection of the reaction product in a baghouse results in a waste product (scrubber by-product). The constituents of the scrubber by-product differ due to the variability in the raw materials used in the brick manufacturing process as well as differences in the parent extractant used in the scrubber system. Scrubber by-product is presently disposed of in landfills, however, there exists the potential for its re-use as a cost effective resource in agricultural production. Although scrubber by-product had not been applied in a commercial agriculture setting, physical and chemical characteristics of the material indicate that scrubber by-product addition to soil could result in improved soil structure, improved water holding capacity, increased pH (under acidic soil conditions), as well as increased micro- and macronutrient supply. The by-product might contain high levels of potentially toxic trace elements, which when added to the soil may exceed the recommended concentration guidelines (EPA, 1994) (Table 1). It is crucial, therefore, that studies are conducted to effectively assess the potential risks and benefits of the re-use of scrubber by-product.

Table 1
Physical and chemical characteristics of brick scrubber by-product

Parameter	Mean
NO_3-N	563 (72.2)
Kjeldahl-N	1100 (57.7)
P	57 (27.7)
K	900 (57.7)
S	135783 (4305.9)
Mg	7483 (1021.3)
Cu	6.2 (3.5)
Zn	18.3 (5.8)
Mn	25.1 (2.9)
Ca	321000 (3702.6)
Se	62.3 (2.3)
Al	3535 (927.2)
Fe	1848 (140.9)
Ni	8.43 (4)
Pb	5.4 (1.2)
Cr	6.64 (1.7)
B	38.6 (8.7)
Be	0.25 (0.01)
Co	9.5 (0.12)
As	34.2 (7.5)
Cd	0.32 (0.02)
Na	451 (36.4)
Cl	19367 (1454.4)
pH	11.53 (0.14)
$CaCO_3$ equivalency (%)	23.4 (0.29)
Bulk density (g/cm^3)	0.67 (0.005)
% Moisture content	0.91 (0.02)

All data are in mg/kg except pH, $CaCO_3$ equivalency, bulk density, and moisture content; standard errors are in parentheses.

The aim of this study, therefore, was to assess the direct effects of physiological stress potentially imposed by brick scrubber by-product on plants, which can be evaluated through measures of changes in micro-parameters such as chlorophyll fluorescence (Maxwell and Johnson, 2000; Bauerle et al., 2003).

The objective of this study was to quantify the effects of the brick scrubber by-product on emergence, growth, photosynthesis efficiency, and accumulation of nutrients and trace elements in corn seedlings and photosynthesis efficiency, biomass production, leaf area, and nutrient uptake of hybrid poplar plants.

2. Methods

2.1. Physical and chemical characterization of scrubber by-product

Brick scrubber by-product was obtained in powdered form from a brick manufacturing plant that utilizes the dry scrubber system (General Shale Brick, Louisville, KY). Samples were transported to Clemson University in 55-gallon drums and stored in a cool dry place until analyzed. The bulk density and moisture content of the scrubber by-product were measured in pre-weighed aluminum containers. Each of three replicate containers was completely filled with scrubber by-product and weighed. The containers were dried to constant weight in a drying oven at 120 °C and bulk density and moisture content were computed on a mass difference basis. Replicate samples of the scrubber by-product were analyzed for selected constituents by the Agricultural Service Laboratory and the Crop and Soil Science Laboratory at Clemson University. Analytical procedures included a wet ash procedure with nitric acid and Kjeldhal digestion for total nitrogen followed by quantification using inductively coupled plasma analysis (ICP).

2.2. Plant species

The plant species assessed in this study were selected based on their agricultural and forestry importance. The plant species were *Zea mays* hybrid 3223 (field corn) and hybrid poplar clones 15–29 (*Populus trichocarpa* × *P. deltoides*) and OP367 (*P. deltoides* × *P. nigra*).

2.3. Exposure procedures

Toxicity tests were conducted in a controlled environment greenhouse at Clemson University where growth conditions were maintained at a temperature of 25 ± 3 °C and a relative humidity of 51.5 ± 5%. The growing substrate used in these studies was a commercial artificial mix (2P blend) obtained from Fafard Soils (Anderson, SC). To conduct the seedling emergence study, corn seeds were obtained from

Pioneer Hi-Bred International, Inc. (Johnson, IA). Potting substrate was weighed and quantities of scrubber by-product were added to the substrate to obtain treatments of 0%, 6.25%, 12.5%, 25%, 50%, 75%, and 100% scrubber by-product (w:w). Each treatment mixture was thoroughly mixed to ensure homogeneity and the pH of each treatment level was determined using a standard pH electrode (HI 9810, Hanna Instruments, Woonsocket, RI). Four seeds were planted in 119 cm^3 containers to a depth of 2.5 cm and allowed to grow for 21 days. Each container was replicated nine times per treatment.

To conduct the rooting and growth study, hybrid poplar cuttings were obtained from Frank Gomez Hybrid Poplar Trees Nursery (Glenmoore, PA) as nine-inch cuttings. Potting substrate was treated with scrubber by-product and pH measured in a similar fashion to the procedure used for the corn studies, however, treatment levels used in this study were 0%, 5%, 10%, and 25% scrubber by-product (w:w). Each cutting was planted in a 12 L pot with scrubber by-product-treated substrate and each treatment was replicated six times. Plants were allowed to grow for six weeks.

2.4. Measured endpoints

The endpoints selected as indicators of changes induced in the plants by the scrubber by-product were different for both plant species due to differences in the cultivation method and plant morphology. The effect of scrubber by-product on the emergence of corn seedlings was evaluated by recording the number of seedlings emerging from each treatment after a 21-day growth period. This was further expressed as a percentage of the total number of seedlings sown for each treatment. Individual corn shoot heights and tissue dry masses were determined at the end of the 21-day growth period.

The effect of the scrubber by-product on leaf chlorophyll *a* fluorescence was determined by using a modulated fluorometer (model OS5-FL, Opti-Sciences, Tyngsboro, MA) to assess the status of the photosynthetic apparatus of treated and untreated intact corn and hybrid poplar leaves under dark-adapted conditions. To evaluate changes in leaf chlorophyll parameters the most recently expanded leaf of each plant was selected and tagged. Leaves were dark adapted by leaving a specially designed leaf clip on each selected leaf for 30 min. Following dark adaptation, the fluorometer was used to measure dark-adapted fluorescence parameters, which included initial fluorescence (F_o), maximal fluorescence (F_m), and quantum efficiency of photosystem II (F_v/F_m), where F_v is the variable fluorescence.

Upon dark-adapting leaves, the photosystem II (PSII) electron acceptors become oxidized. Subsequent exposure to light results in a rapid rise to the F_o level, which is a measure of the fluorescence emission from chlorophyll antenna molecules before energy has migrated to the PSII reaction center. Fluorescence from the PSII chlorophyll *a* antenna molecules increases to F_m when the first stable electron acceptor is fully reduced. The reduction of PSII electron acceptors is represented by F_v and is derived from F_m–F_o. Effects of environmental stressors on the PS II apparatus result in changes in the F_v/F_m ratio (an estimate of the quantum efficiency of the plant). A complete description of chlorophyll fluorescence is beyond the scope of this article, however, interested readers are referred to Maxwell and Johnson (2000) for a comprehensive review of chlorophyll fluorescence principles.

A Licor 3100 leaf area meter (Licor Inc., Lincoln, NE) was used to measure the cumulative leaf area of hybrid poplar plants immediately after a destructive harvest. After leaf area determination, plants were oven dried at 70 °C until weight was stable. Each hybrid poplar plant was partitioned into leaves and stems and the mass of each portion was determined separately. Corn and Hybrid Poplar plant material harvested from each treatment was analyzed for selected constituents (N, P, K, Ca, Mg, S, Cl, Mn, Zn, Cu, B, Al, Cr, Ni, Sb, As, Se, Cu, Cd) by the Agricultural Service Laboratory and the Crop and Soil Science Laboratory at Clemson University.

2.5. Statistical analysis

Plant response data were analyzed using SAS (SAS Institute, Cary, NC, 2003). One-way Analysis of Variance (ANOVA) was used to analyze the significance of main effects (F-test at $p < 0.05$) and differences between means were analyzed by least significant difference (LSD) at $p < 0.05$ (Little and Hills, 1978). The rates of scrubber by-product (% w:w) resulting in 25% and 50% inhibition of seedling emergence, shoot height, and shoot biomass were estimated using a log logistic analysis. Confidence intervals were estimated using the principle of Fieller's theorem (Finney, 1971).

3. Results and discussion

3.1. Effects of scrubber by-product on seedling emergence, growth, and biomass production of corn and hybrid poplar plants

3.1.1. Corn seedling emergence study

The physical and chemical characteristics of the scrubber by-product and potting substrate are presented in Tables 1 and 2, respectively. As compared to potting

Table 2
Physical and chemical characteristics of potting substrate

Parameter	Mean (mg/kg)	Standard error
NO_3-N (mg/kg)	437	30.2
P (mg/kg)	7	0.8
K (mg/kg)	115.5	6.1
Mg (mg/kg)	51	4.1
Ca (mg/kg)	43.5	3.7
B (mg/kg)	0.025	0.004
pH	6.15	0.04
Bulk density (g/cm^3)	0.16	0.02

substrate, the characteristics of the scrubber by-product are a high pH, Ca, Mg, and B level. In the right proportion, these components can act to improve soil fertility. However, the addition of too much of any of these scrubber by-product constituents could potentially cause phytotoxic effects. The number of corn seedlings emerging from treatments of scrubber by-product as a percentage of the total sown for each treatment was relatively unaffected by scrubber by-product treatments up to 12.5%, with only a two percent difference in emergence between treated and untreated plants. The percentage seedling emergence decreased gradually thereafter over the 25–75% scrubber by-product addition and no emergence of seedlings was obtained from the 100% application rate. Although higher levels of by-product addition to substrate inhibited seedling emergence, these effects were absent when scrubber by-product was first stabilized in dairy lagoon sludge (Thomas et al., 2006). Table 3 shows the rates of scrubber by-product resulting in 25% and 50% inhibition of seedling emergence, shoot height, and shoot biomass. This decline was best described by a log logistic analysis from which a critical value of 58.2% w:w scrubber by-product was estimated to cause 25% inhibition of seedling emergence. The percent scrub- ber by-product that reduced seedling emergence by 50% (EC50) was 67.9% w:w (95% confidence interval: 62.3–73.5%).

Although we do not have substrate pH and electrical conductivity values, Table 1 indicates that the decrease in percentage seedling emergence with increasing scrubber by-product application rates may be attributed to increasing salinity and pH, as well as the potential toxic influence of some ions. A consequence of these factors is a decrease in the osmotic potential of the soil media, which subsequently results in water deficits in plant tissue and imbalances in the uptake of essential plant nutrients required for optimal germination (Garg and Gupta, 1997; Ramoliya and Pandey, 2003; Huang et al., 2003). The prevailing soil conditions can also reduce protein hydration (Kramer, 1983) and induce changes in enzyme activities in germinating seeds (Dubey and Rani, 1990; Garg et al., 1993).

A general decline in seedling heights was observed with increasing scrubber by-product treatment with the exception of the 12.5% treatment level, which produced seedlings with longer shoots (averaging 30.42 cm/plant) than plants growing in untreated substrate (Fig. 1). This shoot height, however, was not statistically different from controls. Application rates up to 50% scrubber by-product resulted in a 23% reduction in shoot height when compared with untreated plants, whereas a 65% reduction was obtained from the 75% treatment level.

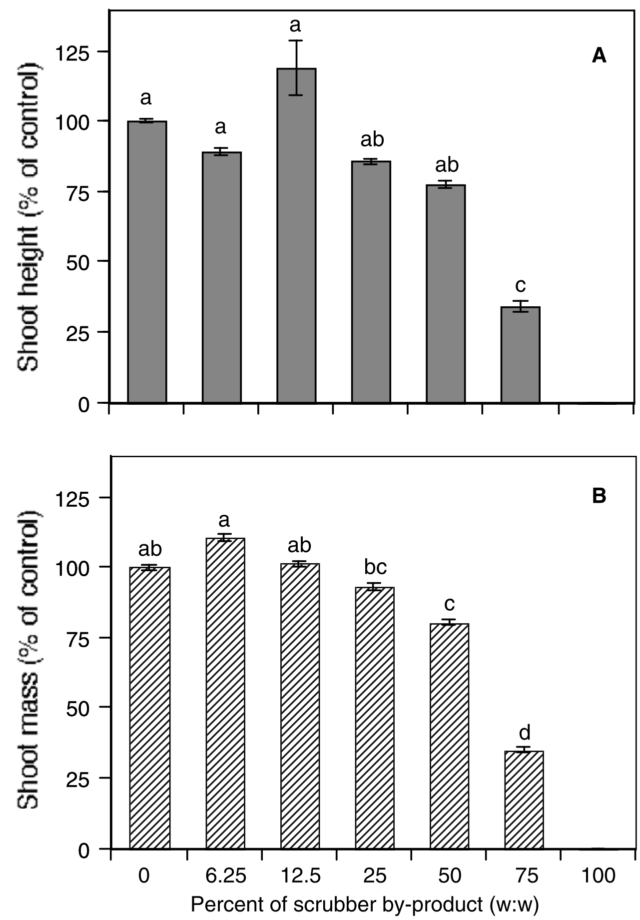

Fig. 1. Percent of control of shoot height (A) and shoot mass (B) in relation to scrubber by-product application for corn seedlings after a 21-day growth period. Vertical bars represent standard errors. Means with the same letter are not statistically different from each other at $p = 0.05$.

The results indicate that treatment levels up to 25% scrubber by-product had no significant effect on mean tissue mass per plant when compared with the control plants (Fig. 1). Treatment levels above 25%, however, produced plants with significantly lower plant tissue mass than the control plants. Mean dry tissue mass of plants ranged between 0.17 and 0.20 g per plant for treatment levels up to 25% scrubber by-product and decreased significantly to 0.15 g at the 50% application level and 0.065 g at the 75% treatment, indicating a 2.5-fold decrease when compared with untreated plants.

Table 3
Effect rate estimates (ER_{25} and ER_{50}) for inhibition of measured end-points by scrubber by-product in corn study

Parameter	ER_{25} (95% confidence interval)	ER_{50} (95% confidence interval)	Slope (Std. error)
Emergence	58.23 (1.73–68.17)	67.86 (21.83–82.76)	16.54 (5.61)
Shoot height	52.03 (35.80–75.61)	63.84 (49.29–82.68)	12.36 (5.07)
Shoot mass	54.02 (33.20–2.61)	65.25 (52.51–76.35)	13.40 (3.15)

The rates of scrubber by-product (% w:w) resulting in 25% and 50% inhibition of seedling emergence, shoot height, and shoot biomass were estimated using a log logistic analysis. Confidence intervals were estimated using the principle of Fieller's Theorem Finney (1971).

3.1.2. Hybrid poplar growth study

Dry tissue mass of leaves and stems from plants of hybrid poplar clone OP367 growing in mixtures of potting substrate and scrubber by-product up to 10% w:w were statistically similar ($p > 0.05$) to that of untreated plants. Mean leaf and stem dry weights of untreated plants averaged 19.24 and 13.48 g per plant, respectively. The 25% treatment level, however, produced leaves and stems with significantly lower masses averaging 12.81 and 7.41 g per plant, respectively (Fig. 2). The results indicate that scrubber by-product application rates of up to 10% did not significantly affect the mean leaf biomass of hybrid poplar clone 15–29 and mean biomass of leaves decreased only slightly from 19.60 g per plant to 17.44 g per plant over application rates of 0–10% w:w, respectively. The 25% treatment level, however, produced plants with an average dry leaf mass of 14.07 g per plant, indicating a 28% decrease in tissue mass compared with untreated plants. The mean stem mass of plants that were grown in the 5% treatment mix (12.30 g per plant) was not statistically different ($p > 0.05$) from control plants (15.13 g per plant) but the 10% and 25% treatment mixes produced plants with significantly lower average stem masses (9.18 and 6.21 g, respectively) than the control plants.

The cumulative area of leaves harvested from hybrid poplar clone OP367 decreased with increasing scrubber by-product treatment (Fig. 3). Significantly lower cumulative leaf area values were obtained for all the plants grown in treated substrate when compared with untreated plants, with the exception of the 10% treatment plants for which the leaf area was not statistically different from the controls. Average cumulative leaf area of control plants was 4131.7 cm^2 per plant, while leaf areas of plants from treated substrate averaged 2333.7, 3064.9, and 2087.3 cm^2

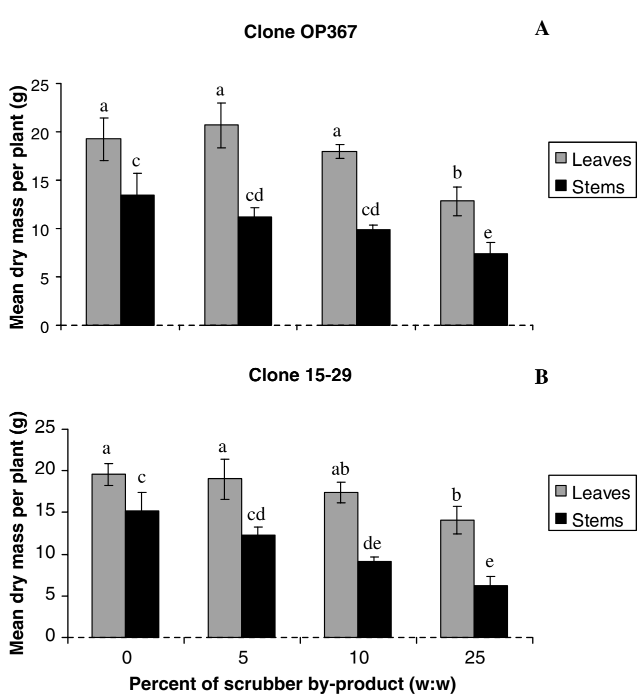

Fig. 2. Effects of scrubber by-product on mean dry mass of leaves and stems of plants of Hybrid Poplar clone OP367 and clone 15–29. Vertical bars represent standard errors. Means with the same letter are not statistically different from each other at $p = 0.05$ for each clone.

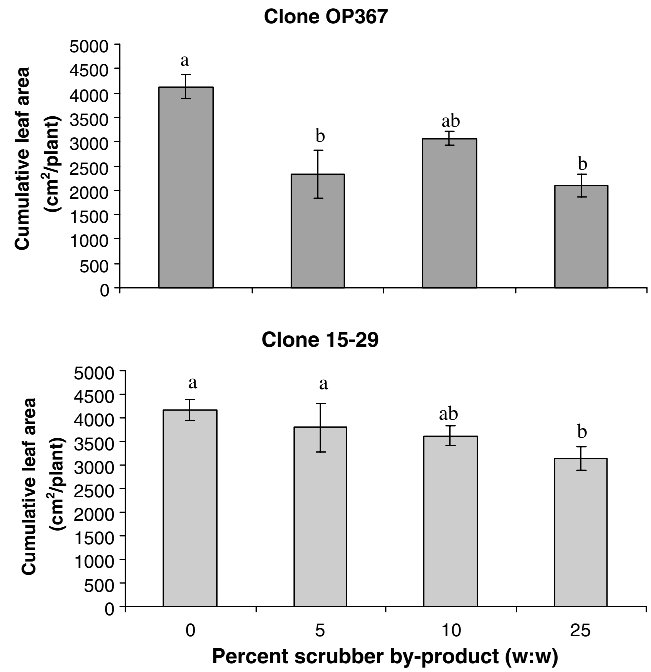

Fig. 3. Effect of scrubber by-product on cumulative leaf area of plants of hybrid poplar clone OP367 and clone 15–29. Vertical bars represent standard errors. Means with the same letter are not statistically different from each other at $p = 0.05$ for each clone.

per plant at the 5%, 10%, and 25% treatment levels, respectively.

The cumulative area of harvested leaves from hybrid poplar clone 15–29 decreased with increasing scrubber by-product treatment mixes (Fig. 3). Plants grown in untreated potting substrate produced leaves with cumulative leaf area averaging 4174.2 cm^2 per plant. The leaf area of plants grown in the 5% treatment level (3797.9 cm^2 per plant) was not significantly different ($p > 0.05$) from that of plants grown in untreated substrate. Significantly lower leaf areas of 3618.3 and 3128.9 cm^2 per plant were, however, obtained for plants of this clone grown in the 10% and 25% scrubber by-product mixes than were obtained for plants in untreated substrate.

3.2. Effect of scrubber by-product on chlorophyll fluorescence of corn and hybrid poplar plants

3.2.1. Corn seedling emergence study

Mean photosynthesis parameters obtained from dark-adapted chlorophyll fluorescence on intact corn leaves are presented in Table 4. The quantum efficiency of photosynthesis is represented by the F_v/F_m parameter. The results indicate that 13-day old plants growing in the 6.25%, 12.5%, and 25% scrubber by-product had significantly higher quantum efficiencies than control plants as indicated by the average F_v/F_m values. Plants grown in the 50% treatment had the lowest F_v/F_m value. The 75% treatment level at the time did not allow plants to produce sufficient foliage for determination of this parameter.

Table 4
Initial fluorescence (F_o), maximal fluorescence (F_m), and quantum efficiency (F_v/F_m) values for dark-adapted leaves of corn plants

Day	Treatment	Mean F_o	Mean F_m	Mean F_v/F_m
13	0	154.72 (4.32)	547.59 (8.67)	0.72 (0.01)
	6.25%	146.54 (2.96)	576.79 (7.68)	0.75 (0.00)*
	12.5%	137.67 (2.06)	560.37 (8.55)	0.75 (0.00)*
	25%	151.68 (3.4)	574.28 (10.88)	0.74 (0.00)*
	50%	157.35 (6.09)	535.41 (15.26)	0.71 (0.01)
	75%		NL	
18	0	146.24 (2.17)	593.30 (8.74)	0.75 (0.00)
	6.25%	155.7 (2.45)	565.53 (13.33)	0.72 (0.01)*
	12.5%	149.58 (2.31)	558.03 (5.84)	0.73(0.01)*
	25%	143.46 (2.21)	524.00 (7.45)	0.73 (0.01)*
	50%	146.50 (3.43)	587.54 (18.69)	0.75 (0.01)
	75%	170.83 (14.13)	497.83 (74.94)	0.61 (0.07)*
21	0	147.73 (4.54)	484.09 (20.18)	0.68 (0.01)
	6.25%	147.16 (4.86)	511.00 (13.48)	0.71 (0.01)*
	12.5%	153.29 (3.90)	573.68 (12.72)	0.73 (0.01)*
	25%	146.81 (3.08)	556.15 (14.13)	0.73 (0.01)*
	50%	153.17 (5.37)	596.21 (12.35)	0.74 (0.01)*
	75%	138.00 (6.56)	554.60 (38.62)	0.75 (0.01)*

Means are presented with standard errors in parentheses.
NL—No leaves.
* Significantly different from controls at $p \leqslant 0.05$.

The F_v/F_m values obtained for the 18-day old corn plants growing in scrubber by-product substrate were significantly lower than the values for plants growing in untreated substrate. These values fluctuated with scrubber by-product application rates with the highest F_v/F_m values obtained for plants growing in the 50% treatment mix (average $F_v/F_m = 0.745$), while the lowest value was obtained for the 75% treatment where F_v/F_m averaged 0.612. The 75% treatment was likely biologically meaningful and the response to phytotoxic levels of scrubber by-product. The fluctuations in F_v/F_m at treatments below 75% addition, although significant, did not appear to show an obvious detrimental response.

Measures of F_v/F_m for the 21-day old plants were higher for the scrubber by-product treated plants than for the untreated plants, which had an average F_v/F_m value of 0.683. The values increased with increasing scrubber by-product application rates with an average F_v/F_m value of 0.712 obtained for the 6.25% treatment level and increased slightly thereafter to 0.749 for the 75% treatment level. The increase could be attributed to the nutrition benefits of scrubber by-product.

3.2.2. Hybrid poplar growth study

Mean F_o, F_m, and F_v/F_m values for dark-adapted leaves of hybrid poplar clone 15–29 over a six-week growing period are presented in Table 5. There were no significant differences between mean F_v/F_m values for plants growing in scrubber by-product treated substrate compared with controls over the first three weeks. During the fourth week, however, plants growing in the 10% treatment mix had a significantly lower mean F_v/F_m value than the control plants. Overall, lower mean F_v/F_m values were recorded for all plants during week 5 when compared with previous weeks. Mean values for treated plants were, however, not significantly different ($p > 0.05$) from that of untreated plants. Mean F_v/F_m values for all treated levels after week 6 of growth were not significantly different from untreated plants. Values for all treatments were lower than the values recorded at the start of the study. Taken together, the results do not indicate a negative response to the addition of scrubber by-product, but do indicate F_v/F_m decline in all treatments over time. Leaf aging is a possible explanation for this response.

Table 5
Initial fluorescence (F_o), maximal fluorescence (F_m), and quantum efficiency (F_v/F_m) values for dark-adapted intact leaves of clone 15–29 hybrid poplar plants

Week	Treatment	Mean F_o	Mean F_m	Mean F_v/F_m
1	0	123.75 (3.64)	666.58 (18.55)	0.81 (0.01)
	5%	116.67 (7.36)	667.67 (15.18)	0.83 (0.01)
	10%	108.00 (2.21)	611.38 (12.76)	0.82 (0.00)
	25%	106.71 (4.00)	618.00 (8.05)	0.83 (0.00)
2	0	114.67 (2.84)	659.33 (14.99)	0.83 (0.00)
	5%	121.10 (6.20)	709.50 (13.86)	0.83 (0.01)
	10%	123.30 (2.63)	690.00 (12.65)	0.82 (0.01)
	25%	110.10 (2.50)	669.50 (17.11)	0.83 (0.01)
3	0	112.60 (3.80)	706.60 (5.59)	0.84 (0.01)
	5%	110.11 (5.18)	681.11 (13.62)	0.84 (0.01)
	10%	118.27 (4.72)	674.18 (10.01)	0.83 (0.01)*
	25%	104.75 (3.10)	665.88 (20.71)	0.84 (0.01)
4	0	124.11 (4.158)	697.11 (9.53)	0.82 (0.01)
	5%	125.30 (3.20)	719.90 (12.52)	0.83 (0.00)
	10%	135.90 (4.43)	704.60 (18.78)	0.81 (0.00)*
	25%	119.22 (4.38)	680.44 (14.56)	0.82 (0.01)
5	0	137.11 (6.76)	623.22 (20.66)	0.78 (0.01)
	5%	153.20 (10.78)	688.80 (39.19)	0.77 (0.02)
	10%	169.60 (8.39)	690.50 (20.23)	0.76 (0.01)
	25%	144.89 (8.52)	656.44 (18.59)	0.78 (0.01)
6	0	133.33 (7.28)	586.22 (19.96)	0.77 (0.01)
	5%	137.90 (5.81)	591.30 (16.13)	0.77 (0.01)
	10%	130.20 (5.55)	582.40 (19.81)	0.78 (0.01)
	25%	147.13 (8.27)	635.75 (19.73)	0.77 (0.01)

Means are presented with standard errors in parentheses.
* Significantly different from controls at $p \leqslant 0.05$.

Dark-adapted values of F_v/F_m for hybrid poplar clone OP367 were slightly lower in treated plants than in untreated plants during week 1 but only plants growing in the 5% treatment level recorded a significantly lower mean F_v/F_m value when compared with the controls (Table 6). These values were higher for the treated plants than for untreated plants in week 2 but differences were not significant when compared to controls. Over the next two weeks, F_v/F_m values increased with increasing scrubber by-product application rates and were significantly higher than the mean value for control plants. This trend continued over week 5 but only plants grown in the 10% and 25% treatment levels recorded significantly higher F_v/F_m values than their respective controls. Significantly higher values of F_v/F_m were obtained for plants growing in the 5% and 10%

Table 6
Initial fluorescence (F_o), maximal fluorescence (F_m), and quantum efficiency (F_v/F_m) values for dark-adapted intact leaves of clone OP367 hybrid poplar plants

Week	Treatment	Mean F_o	Mean F_m	Mean F_v/F_m
1	0	112.00 (7.79)	619.00 (9.27)	0.82 (0.01)
	5%	130.67 (5.39)	596.56 (11.65)	0.78 (0.01)*
	10%	120.67 (7.48)	604.33 (12.70)	0.80 (0.01)
	25%	113.88 (5.17)	613.50 (17.16)	0.81 (0.01)
2	0	111.40 (3.24)	633.90 (13.46)	0.82 (0.01)
	5%	105.10 (4.18)	666.10 (23.09)	0.84 (0.00)
	10%	107.10 (3.78)	651.80 (31.70)	0.83 (0.01)
	25%	107.50 (3.34)	666.10 (9.48)	0.84 (0.01)
3	0	114.70 (4.61)	699.60 (12.58)	0.84 (0.01)
	5%	104.20 (2.67)	687.70 (15.39)	0.85 (0.00)*
	10%	98.44 (2.49)	690.11 (12.28)	0.86 (0.00)*
	25%	102.78 (2.98)	685.67 (13.37)	0.85 (0.00)*
4	0	105.80 (3.62)	617.00 (10.43)	0.83 (0.01)
	5%	110.44 (3.70)	667.78 (15.07)	0.83 (0.01)*
	10%	106.90 (4.24)	666.20 (15.44)	0.84 (0.01)*
	25%	106.09 (3.09)	666.64 (15.15)	0.84 (0.00)*
5	0	131.30 (5.30)	626.70 (14.32)	0.79 (0.01)
	5%	121.11 (4.60)	614.67 (13.75)	0.80 (0.01)
	10%	130.0 (4.99)	694.00 (11.43)	0.81 (0.01)*
	25%	124.18 (4.41)	687.91 (17.57)	0.82 (0.00)*
6	0	150.90 (8.51)	632.50 (29.66)	0.76 (0.02)
	5%	121.89 (4.85)	606.22 (23.01)	0.80 (0.01)*
	10%	142.80 (10.05)	670.30 (30.01)	0.79 (0.01)
	25%	132.73 (5.68)	680.00 (25.42)	0.80 (0.01)*

Means are presented with standard errors in parentheses.
* Significantly different from controls at $p \leqslant 0.05$.

growing substrate than in untreated plants during week 6. The summation of the results for OP 367 F_v/F_m values are similar to those observed in clone 15–29. The more consistent increase in treatment F_v/F_m values over controls could be attributed to a nutrient benefit of the scrubber by-product.

Although we do not have data for substrate metal levels after the addition of scrubber by-product, the leaf chlorophyll fluorescence data indicate that scrubber by-product affects the photosystem apparatus of corn and hybrid poplar plants to varying degrees. If metals contained in the scrubber by-product exceed a tolerable threshold, they can disrupt CO_2 fixation thus impacting photosynthesis (e.g., Bertrand and Poirier, 2005). Photophosphorylation or enzyme activities have also been reported to be inhibited by metals in photosystem II (PSII). Additionally, some metals such as Zn, Cd, and Cu can interfere with pigment biosynthesis, which can lead to reduced chlorophyll content and subsequent inhibition of photosynthesis (Clijsters and Van Assche, 1985; Prasad and Stzalka, 2002; Macinnis-Ng and Ralph, 2003; Bertrand and Poirier, 2005).

The scrubber by-product was shown to have an adverse effect on chlorophyll fluorescence of 18-day old corn plants. This effect was reversed, however, on day 21, which may indicate that while the constituents of scrubber by-product may disrupt the normal functioning of the photosynthetic apparatus, permanent damage may not result (Prasad and Stzalka, 2002).

In general, the scrubber by-product did not adversely impact the photosynthetic apparatus of hybrid poplar plants. In fact, higher F_v/F_m values were obtained for some of the treated plants than for the untreated plants. This observation may be due in part to the hybrid poplar utilization of the essential elements in the scrubber by-product and excluding or sequestering potentially toxic constituents such as Na. There are reports of suppression of photosynthesis due to salt stress (AliDinar et al., 1999; Romeroaranda et al., 2001; Kao et al., 2001). Conversely, it has been shown by other authors (Rajesh et al., 1998; Kurban et al., 1999) that salinity has no effect on photosynthesis and can even be stimulatory.

3.3. Tissue concentrations of selected elements in corn and hybrid poplar plants

The concentrations of selected constituents in corn plant tissue grown in scrubber by-product are given in Table 7. Concentrations of the elements essential for normal plant growth were all within the sufficiency range for corn plants with only a few exceptions. The sufficiency ranges for Ca, S, and Mn in corn plants are 0.21–1.01%, 0.20–0.50%, and 35–300 mg/kg, respectively (Bergmann, 1992; Jones, 1998). The optimum pH range for maximum availability of N is 6–8 (Foth, 1990). Outside of this range, N uptake is reduced in most plants. Therefore, the uptake of N by corn plants in the higher scrubber by-product treatment levels can be impaired by the high pH of these treatments (see pH data in Tables 7–9). Populus sp. and their hybrids, however, have been reported to have exceptional N uptake and utilization properties (Liu and Dickmann, 1992; Heilman and Xie, 1994; Ibrahim et al., 1997; Coleman et al., 1998; Cooke et al., 2005). Hence, the different physiology of corn and hybrid poplar plants could explain their differences in N tissue concentrations. Despite the lower corn N tissue concentrations in the scrubber by-product treated plants, as compared with controls, no visible signs of N deficiency was observed. A complete description of sufficient nutrient ranges is beyond the scope of this article, however, interested readers are referred to Bergmann (1992) and Jones (1998) for an in depth review. Calcium concentration in the plant tissue increased with increasing scrubber by-product application rates and exceeded the sufficiency range in plants from treatments above 12.5% w:w. Tissue concentrations of S were also higher than normal in all treatments. Manganese concentration in plants from the 75% treatment was however below the sufficiency range. Of the non-essential trace elements analyzed, only chromium exceeded the maximum suggested level for corn plants (Jones, 1998).

Calcium and Cl were the only two elements that increased continuously with increasing scrubber by-product application rates. In fact, strong negative correlations ($p < 0.01$) between tissue concentrations and scrubber by-product applications were obtained for some elements,

Table 7
Concentrations of selected constituents in whole corn plant tissues from each treatment of scrubber by-product

Element	Scrubber by-product treatment					
	Control (6.2)	6.25% (7.9)	12.5% (8.2)	25% (8.3)	50% (8.7)	75% (9.2)
P (%)	0.69 (0.02)	0.25 (0.009)*	0.26 (0.01)*	0.26 (0.01)*	0.28 (0.003)*	0.51 (0.01)*
Mg (%)	0.68 (0.01)	0.61 (0.04)*	0.79 (0.009)*	0.66 (0.01)	0.48 (0.02)*	0.28 (0.03)*
Ca (%)	0.54 (0.005)	0.99 (0.02)*	1.18 (0.03)*	1.23 (0.03)*	1.48 (0.07)*	2.09 (0.01)*
S (%)	0.81 (0.03)	0.98 (0.01)	1.22 (0.02)	0.83 (0.35)	0.91 (0.06	0.63 (0.02)
Cl (%)	0.89 (0.05)	1.82 (0.14)*	2.14 (0.25)*	2.27 (0.18)*	2.90 (0.48)*	0.38 (0.03)
NO_3-N (mg/kg)	1254 (0.00)	490 (13.00)*	450.66 (12.17)*	165.73 (47.49)*	407.00 (81.00)*	477.50 (22.5)*
Mn (mg/kg)	179.67 (0.88)	143.33 (7.51)*	132.33 (9.02)*	99.77 (8.51)*	51.87 (4.42)*	14.95 (1.25)*
Zn (mg/kg)	58.93 (3.04)	25.77 (1.51)*	27.23 (0.34)*	23.87 (1.11)*	27.03 (2.45)*	34.50 (1.10)*
Cu (mg/kg)	7.39 (0.42)	4.28 (0.31)*	5.88 (0.09)*	4.49 (0.47)*	6.14 (0.51)*	5.85 (0.08)*
B (mg/kg)	147.67 (9.82)	133.13 (29.76)	145.10 (32.39)	126.67 (18.82)	120.70 (14.08)	94.20 (1.90)
Al (mg/kg)	25.11 (4.85)	22.17 (1.04)	24.87 (2.67)	32.60 (1.61)	23.13 (1.27)	13.00 (0.40)*
Cr (mg/kg)	26.27 (6.87)	18.50 (3.42)	16.20 (1.87)	15.63 (3.55)	7.81 (0.16)*	3.49 (0.16)*
Ni (mg/kg)	9.44 (1.55)	8.53 (0.89)	9.34 (0.75)	9.16 (1.32)	6.27 (0.15)*	3.12 (0.10)*
Sb (mg/kg)	2.51 (0.35)	1.15 (0.15)*	2.40 (0.17)	1.60 (0.26)	1.16 (0.53)*	–
As (mg/kg)	2.13 (0.58)	1.67 (0.85)	3.08 (0.83)	0.47 (0.05)*	0.56 (0.23)	–
Se (mg/kg)	0.96 (0.00)	1.39 (0.75)	0.12 (0.12)	1.25 (0.16)	0.18 (0.18)	–
Co (mg/kg)	0.27 (0.09)	0.60 (0.07)	1.34 (0.10)*	2.37 (0.26)*	2.19 (0.11)*	1.30 (0.13)*
Cd (mg/kg)	0.15 (0.07)	0.07 (0.04)	1.66 (0.84)*	1.60 (0.26)*	1.16 (0.53)	–

Substrate pH values are in parenthesis next to by-product treatment percentage. Means are presented with standard errors in parentheses.
* Significantly different at $p \leqslant 0.05$.

Table 8
Concentrations of selected constituents in stems and leaves of hybrid poplar clone 15–29

Element	Scrubber by-product treatment			
	Control (6.2)	5% (6.6)	10% (7.7)	25% (8.5)
N (%)	1.49 (0.05)	1.55 (0.04)	1.5 (0.03)	1.80 (0.04)*
K (%)	2.56 (0.03)	2.69 (0.02)	2.37 (0.02)	2.15 (0.19)*
Mg (%)	0.50 (0.02)	0.36 (0.01)*	0.37 (0.03)*	0.44 (0.02)
S (%)	0.39 (0.03)	0.52 (0.02)	0.52 (0.03)	0.95 (0.07)*
P (%)	0.22 (0.02)	0.20 (0.005)	0.12 (0.005)*	0.09 (0.005)*
Ca (%)	0.80 (0.04)	1.19 (0.03)*	1.29 (0.08)*	1.51 (0.005)*
NO_3-N (mg/kg)	519.5 (133.5)	673.50 (70.50)	592.0 (22.0)	595.5 (35.5)
Na (mg/kg)	355.5 (29.5)	306.5 (76.5)	259.0 (27.0)	159.0 (6.0)*
Fe (mg/kg)	223.5 (20.5)	176.5 (15.5)	171.5 (21.5)	163.0 (7.0)
Mn (mg/kg)	105.5 (7.5)	241.0 (3.0)*	242.0 (37.0)*	128.0 (18.0)
Al (mg/kg)	100.0 (0.0)	109.0 (9.0)	102.0 (4.0)	74.0 (3.0)*
Zn (mg/kg)	41.5 (3.5)	45.0 (4.0)	32.0 (1.0)	21.0 (3.0)*
B (mg/kg)	27.0 (3.0)	43.0 (1.0)*	40.0 (0.0)*	43.5 (1.5)*
Cu (mg/kg)	2.0 (0.0)	2.0 (0.0)	2.5 (0.5)	2.0 (0.0)

Substrate pH values are in parenthesis next to by-product treatment percentage. Means are presented with standard errors in parentheses.
* Significantly different at $p \leqslant 0.05$.

notably Mg, Mn, B, Cr, and Ni. This decrease in tissue elemental composition with increasing scrubber by-product application rates is a consequence of changes in the chemistry of the growth substrate as the application rates increased. Increasing pH levels of the growing substrate can result in the unavailability of some of the constituents of the scrubber by-product for uptake by the corn plants. This may be due to decreased solubility and or adsorption of the ions to particles of the growth substrate (Stumm and Morgan, 1996; Su and Wong, 2004). A comparison of shoot masses with plant tissue content of selected macronutrients showed that shoot dry mass decreased with increasing Ca and P concentrations, but increased with increasing Mg and S concentrations.

The concentrations for the macro and micronutrients in shoots of hybrid poplar plants are given in Tables 8 and 9. Plants of both clones had lower than normal N tissue concentrations for all the treatments, while the S content in plants from the 75% treatment exceeded the sufficiency range. Additionally, the phosphorus concentration in tissues from the 10% and 25% treatments were less than sufficient for both clones (Bergmann, 1992). Tissue concentrations of each element were similar for both clones with the exception of Na which was present at higher concentrations in hybrid OP 15–29.

An assessment of the ratios of plant nutrients is essential when evaluating the nutritional status of plants. For example, Fe/Mn ratios > 1 are considered ideal when characteriz-

Table 9
Concentrations of selected constituents in stems and leaves of hybrid poplar clone OP367

Element	Scrubber by-product treatment			
	Control (6.2)	5% (6.6)	10% (7.7)	25% (8.5)
N (%)	1.56 (0.05)	1.48 (0.13)	1.28 (0.08)	1.57 (0.09)
K (%)	2.35 (0.08)	2.33 (0.15)	1.88 (0.07)*	1.69 (0.08)*
Mg (%)	0.43 (0.01)	0.33 (0.01)*	0.27 (0.03)	0.32 (0.03)
S (%)	0.31 (0.05)	0.42 (0.04)	0.38 (0.03)	0.84 (0.17)*
P (%)	0.21 (0.02)	0.15 (0.01)*	0.10 (0.00)*	0.08 (0.01)*
Ca (%)	0.75 (0.08)	1.04 (0.03)	0.52 (0.42)	1.42 (0.18)
NO3-N (mg/kg)	556.5 (47.5)	605.0 (55.0)	491.0 (3.0)	472.0 (10.0)
Na (mg/kg)	267.5 (36.5)	158.0 (23.0)*	160.5 (9.5)*	233.5 (1.5)
Fe (mg/kg)	143.5 (4.5)	110.5 (20.5)	82.0 (1.00	182.0 (43.0)
Mn (mg/kg)	105.5 (19.5)	172.0 (12.0)*	138.5 (1.5)	102.5 (4.5)
Al (mg/kg)	70.5 (3.5)	61.5 (10.5)	55.5 (5.5)	82.5 (11.5)
Zn (mg/kg)	40.0 (2.0)	40.5 (4.5)	27.0 (2.0)*	21.0 (0.0)*
B (mg/kg)	26.5 (0.5)	41.5 (0.5)*	40.0 (2.0)*	40.0 (2.0)*
Cu (mg/kg)	2.0 (0.0)	1.5 (0.5)	2.0 (0.0)	2.0 (0.0)

Substrate pH values are in parenthesis next to by-product treatment percentage. Means are presented with standard errors in parentheses.
* Significantly different at $p \leqslant 0.05$.

ing nutrient sufficiency levels (Campbell and Plank, 2000). Only the control and the 25% treatment of both hybrid poplar clones had tissue Fe/Mn ratios > 1. This indicates a nutrient imbalance in plants from the 5% and 10% treatments.

As with the corn tissues, strong negative correlations ($p < 0.01$) were obtained for some constituents. Shoot dry masses of both clones increased with increasing K and P concentrations, however increasing tissue concentrations of Ca and S appear to influence shoot mass negatively.

The uptake of metals and other pollutants (e.g., fluoride) by plants is influenced by a number of edaphic factors including redox potential, salinity, pH, and the presence of organic and inorganic substances. These factors are crucial to chemical speciation and therefore, availability to plants. The lack of a positive correlation between plant tissue concentrations of some metals and increasing scrubber by-product application suggests that these metals were unavailable for uptake from the growing substrate or their uptake was prevented by plant exclusion mechanisms. In view of the fact that HF reacts with lime to give calcium fluoride, a very insoluble form that reduces the availability of fluoride for plant uptake (Amalan Stanley et al., 2002; Kolkmeier, 1991), and the fact that there are many factors that influence the amount of fluoride emissions from brick kilns (e.g., firing method, water vapor content, raw materials, firing temperature, etc.), we did not attempt a fluoride chemical analysis. Although most studies have focused on the phytotoxic effects of fluoride gas emissions, studies by Kolkmeier (1986) and Schlandt (1985) report that the non-gaseous forms of fluoride, if present in our scrubber by-product, cause no damage to fluorine gas sensitive plants. In fact, it may be due to the ability of plants to adapt to pollutant stress through several mechanisms including selective ion uptake, ion immobilization in roots and foliage, selective membrane permeability, sequestration of ions into organs or organelles, adaptation to metal replacement in enzymes, and release of ions through leaf shedding and excretion from roots (Baker, 1987; Jones, 1998).

4. Conclusions

The study shows that application rates up to 12.5% scrubber by-product w:w had no adverse effect on corn seedling emergence. Also, shoot heights and the status of the photosynthetic apparatus of the seedlings was not severely impaired at applications below this level. Tissue concentrations of Ca and S were higher than normal even in plants from treatments below 12.5% with Cr concentrations exceeding maximum safe ranges for corn. Biomass production and leaf area of hybrid poplar plants were not affected by scrubber by-product applications of up to 5% w:w, however the photosynthetic apparatus of clone OP367 plants was more sensitive to the scrubber by-product than that of clone 15–29 plants. Plant tissues of both clones were deficient in N and plants from treatments above 5% w:w had excess sulfur.

The scrubber by-product is capable of providing elements essential for plant growth but also introduces nonessential trace elements to the growing substrate, which must be managed so as to prevent phytotoxic responses. Additionally, excess of an essential element can interfere with the normal metabolic processes of the plant as well as create ionic imbalances such as the deficiencies of other essential elements. Overall, we found that the product could be used up to a level of 12.5% without deleterious effects.

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