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INFLUENCE OF COAL COMBUSTION FLUE GAS DESULFURIZATION WASTE ON ELEMENT UPTAKE BY MAIZE (*Zea Mays L.)*

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ABSTRACT

A greenhouse study was conducted to determine the effect of coal combustion flue gas desulfurization (FGD) waste from a coal combustion electric power facility, located in Cope, SC on elemental uptake by maize (*Zea mays L.*). Unweathered FGD was applied to an Orangeburg series soil (Typic Paleudult) with an initial soil pH_{salt} of 4.90. The FGD was added at 0, 1, 2, 4, 6, 8, and 10% by weight. The test plant, maize, was harvested after 6 weeks of growth. Within 56 days of the FGD application, all rates of FGD significantly increased pH in the soil and the soil leachate above 6.0. The elemental concentration of the maize tissues indicated a characteristic elevation of B, Se, Mo, and As. However, no visual symptoms of toxicity of B or other elements in plants were observed. Increasing level of FGD caused a steady decline in biomass dry weight, with the highest treatment producing plants, which had approximately half the biomass of the control plants. Due to elevated concentrations of B and other elements (Se, Mo, and As) and due to adverse yield effects measured on plants, we do not recommend using FGD materials as a soil amendment for the purpose of growing agronomic and horticultural crops until sufficient time is allowed to substantially leach soluble salts including B and Se. This will necessitate monitoring the electrical conductivity and B and Se contents of the FGD waste to acceptable levels.

1. INTRODUCTION

According to the American Coal Ash Association, 105 million metric tons of coal combustion by-products (CCBs) were produced in the United States by the power generating utilities in 1997. Of that total, 1.68 million tons were applied on lands affected by mining operations.[1] The CCBs can be used in mine reclamation for acid mine drainage (AMD) prevention and treatment, subsidence control and surface restoration.[2] Class C Fly ash and Class F fly ash mixed with lime exhibit self-cementing properties and can be used to cap surfaces, line pavements and isolate acidic materials in the backfill to prevent AMD formation. In addition, highly alkaline CCBs, such as FGD and FBC residues, are used to directly neutralize acidic materials.

In the United States combustion of more than 800 million metric tons of coal annually results in approximately 75 million tons of solid residues. Even though these solid waste residues represent only about 2% of all the solid by-products now being produced in the US, these combustion residues are the sixth most abundant material for resource recovery. In addition, coal combustion residues account for about 90% of all fuel combustion wastes produced in the USA. Presently, only about 20% of these wastes are utilized, with the remainder deposited in landfills or surface impoundments.[3] Landfills designed for disposing of these wastes will be costly. Therefore major uses for these residues need to be discovered to abate the potential environmental consequences of storage and its associated cost.

Combustion of coal produces a variety of residues, including fly ash, bottom ash, flue gas desulfurization waste (scrubber sludge), fluidized bed boiler waste, and coal gasification ash.[4] Fly ash is the residue from coal combustion that enters the flue gas stream. Bottom ash is the residue from coal combustion that remains in the boiler. Flue gas desulfurization (FGD) waste, often called as scrubber sludge, results from the addition of limestone and/or dolomite to the coal either before (in the case of fluidized bed combustion) or after (in the case of flue gas desulfurization) combustion. These wastes are typically a combination of ash and various Ca, Mg, and S compounds.[5, 6]

In order to meet air pollution control laws, the industry has to either retrofit existing facilities or install desulfurization devices to capture SO_x compounds from the flue gas, which otherwise would enter the atmosphere and contribute to the acid precipitation.

Because of the large amounts of coal ash generated each year, a great deal of research has been conducted to identify and determine the feasibility of utilizing these wastes in agriculture, road and building construction, and industry. The majority of this research has concentrated on the potential for using ash as an amendment to agricultural soils due to its potential to improve the physical and chemical properties of, infertile, degraded soils.[7] Amendment of agricultural soils with fly ash can improve soil tilt and texture, increase pH (i.e., for acidic soils) and elevate the concentrations of some macro- and micronutrients. [7, 8] However, this amendment may also result in excessive soluble salt concentrations, excessive B, and increased concentrations of other potentially toxic trace elements, reduction in the availability of soil N and P, and elemental imbalances due to excessively high pH. Because of inconsistent chemical properties of fly ash and other residues, farmers are shunning these products as an amendment. But the most limiting factor in inhibiting greater usage of this product on land is the economics of transportation and application.

To meet air pollution regulations, a facility of the South Carolina Electric and Gas Co. installed a flue gas desulfurization (FGD) facility at their Cope Plant, near Orangeburg, SC. The environmental impacts associated with the disposal of FGD waste are similar in many ways to those associated with ordinary fly ash. Particle sizes of FGD waste are generally in the range of 5 to 50 • m.[9] Trace elements are present in these wastes as well, primarily in the ash component of the waste.[9, 10] Like fly ash, FGD sludge contains high concentrations of soluble salts (Miller, 1987) and is characterized by high pH. As with fly ash, the principal concerns with scrubber sludge disposal include groundwater contamination from leachate, and elevated concentrations of trace elements in plants and animals in the vicinity of the disposal area.[9] An additional problem, unique to FGD waste, is the presence of high concentrations of sulfite, a phytotoxic compound. Under anoxic conditions, this can result in the production of H_2S gas.[11]Under aerobic conditions, high levels of sulfite can substantially increase the oxygen demand, due to the oxidation of sulfite to sulfate, in surface and groundwater systems affected by these wastes. [9] Several investigators have suggested that FGD waste could be used as a source of essential nutrients, including B and Se, for soils deficient in these elements.[12] Because of the lack of data, few conclusions can be drawn concerning the potential impact of FGD waste on the environment; however, it is evident that more research is needed in this area.

This study investigated the influence of flue gas desulfurization (FGD) waste from Cope Plant, (South Carolina Electric and Gas Co.) as a soil amendment and with the following objectives: i). To evaluate the feasibility of unweathered (fresh) FGD residue on plant growth and elemental uptake; ii). To evaluate the effects of FGD waste on the soil solution chemistry, and iii) to delineate the more potentially toxic and deleterious elements that can cause direct phytotoxicity or in soil the quality of food chain.

2. MATERIALS AND METHODS

The Ap horizon of an Orangeburg Series-Typic Paledult soil was collected from Jim Traywick's farm, Cope, South Carolina. The soil was air dried, passed through a 2-mm sieve to remove gravel and coarse debris. The flue gas desulfurization (FGD) material was collected from Cope Coal Fired Power, Cope, South Carolina (Figure 1). Polyethylene pots were used for this study. Drainage holes were drilled in the bottom of each polyethylene pot, and the pots were lined with permeable nylon fabric. The pots were the filled with 7 kg soil blended with FGD material treated soil and placed in a 2.5-cm high plastic plate to collect drainage water (leachate). The experiment had seven treatments, which included the following rates of FGD: 0% (control), 1%, 2%, 4%, 6%, 8% and 10% by weight added to soil separately. The pots were arranged in a completely randomized design with each rate of application replicated four times. Five maize (*Zea Mays*, var. Pioneer 3165*)* seeds were sown in each pot and thinned to one after a week of germination. Maize plants were grown for six weeks. The plants were grown in a greenhouse under fluorescent lighting programmed to provide 16 hours of daylight. The day and night temperatures of the greenhouse were maintained at 30 ± 3^0C, respectively. All the plants were watered daily and moisture content was maintained approximately to field capacity through the growing period. Throughout the equilibration periods of eight weeks the leachate from each treatment was collected in collection plates six times and was analyzed for pH, EC (electrical conductivity), and elemental concentrations. Plants were harvested at the end of six week. The harvest tissues from each pot were carefully rinsed in four successive deionized distilled water baths, oven dried to 60^0C to constant weight, weighed to the nearest 0.01g for biomass production, and ground in Wiley Mill to pass a 22-mesh (841µm) sieve. The dried plant samples were wet ashed in a nitric-perchloric acid mixture, and analyzed for elemental concentrations. Soil cores were also collected from each pot at the time of plant harvest. The soil samples were air dried, sieved to pass a 2-mm screen, and digested with HF + Aqua Regia and extractable with 0.1 *M* HNO_3 for elemental analysis. For quality control, National Bureau of Standards tomato leaves (NBS, Washington, DC, NBS No. 15730) and spiked soil samples were used through all analysis. Both pants and soil-digested samples were analyzed through inductively coupled plasma optical emission spectrophotometer (ICP-OES) for elemental concentrations.

3. RESULTS AND DISCUSION

3.1. Effect of FGD on soil leachate property

Almost all doses of added FGD to the soil resulted in increased pH and EC values of the leachate. Pots were leached 6 times in total. Addition of 1% of FGD was the only treatment where the pH values of leachate did not change significantly over a period of 8 weeks (Table 1). For all FGD treatments EC values were elevated above the 0% FGD addition, indicating a proportional relationship between FGD application and increase in leachate salinity (Table 2). Progressive leaching demonstrated in this case that recovery of the background EC values accrued faster in comparison to pH. Also the characteristic increase in soluble salts followed by a gradual decline is indicative of unweathered ash.[7]

Concentration of tested elements in leachates from FGD amended soil increased progressively with FGD addition, and the highest concentrations were obtained in the 10% FGD treatment. For example, As increased from 0.0055 to 3.93 µg/g, respectively, for control and 10%FGD. Selenium concentrations increased by a factor of 22, in 10%FGD soils compared to control soil (Table 3). Elemental composition of the leachate also indicates a high soluble Ca concentration; Ca concentration increased a hundred fold following the addition of 10% FGD material.

Addition of FGD to the soil not only increased total concentration of elements but also the bioavailable pool of these elements. For example, the extractable As and Se levels were significantly higher in the treatment with 10% of FGD than in the untreated soil (Figure 2 and 3, respectively).

3.2. Effect of FGD on maize growth and element uptake

The influence of FGD waste on plants is indicated by maize yield and element concentrations in plant tissues. Yield of six-week-old maize started to decrease with the second dose of FGD and the lowest yield was obtained in treatment with the highest dose of FGD (i.e., 10%) (Figure 3). Increasing level of FGD caused a steady decline in biomass dry weight, with the highest treatment producing plants that had approximately half the biomass of the control plants. However, no visual symptoms of metal toxicity in plants were observed (Figure 4). Other pot studies using cola combustion products (CCPs) amendments have shown a similar reduction in overall biomass.[7, 13]

From the twenty studied elements in maize tissues (Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, Na, Pb, Sb, Se, Tl, and Zn) only five elements (Cd, Cr, Cu, Pb, and Sb) were not significantly influenced by FGD material (Table 4). Arsenic, B, Mo and Se are the elements of the greatest concern in this study because the excess of these elements can cause severe soil contamination resulting in plant toxicity and potential detrimental effects to l ive stock. Trace amounts of arsenic is essential for animal nutrition, but not for plant growth.[14] Molybdenum is essential for both plant and animal nutrition, while Se is essential only for animal growth. The concentrations of these elements were significantly elevated by each addition of FGD (Figures 5, 6, 7 and 8). Arsenic in maize tissues increased 5 times in treatment with 10% FGD, compared to the control treatment (Figure 5). Kabata-Pendias[15] reported that sufficient and normal As concentrations in mature leaf tissue for various species (in mg/kg DW) are between 1 and 1.7 mg/kg, however, a tolerable level of As in agronomic crops is 0.2 mg/kg. The tolerable level of As in agronomic crops was exceeded with the first FGD rate (1%). Boron concentrations in maize tissues increased significantly with each dose of FGD, and in the treatment with 10% FGD plants had concentrations (155 mg/kg) considered to be toxic for maize (Figure 6). According to Kabata-Pendias[15], the sufficient or normal B concentration in mature leaf tissues range from 10 to 100 mg/kg, and this level was exceeded with 8%FGD addition. Kukier and Sumner[16] also found excessive rate of fly ash increased B in corn (*Zea mays* L.) tissue to phytotoxic levels. Molybdenum concentration in plants in the control treatment was 0.279 mg/kg but in the treatment with the highest dose of FGD the concentration of this element increased to 3.48 mg/kg (Figure 7). Addition of each dose of FGD to the soil significantly increased the uptake of some macronutrients by the plant (Figure 9), for example, Ca concentration in maize tissues increased from 4975 mg/kg (control soil) to 8340 mg/kg (treatment 10% of FGD). It is a common belied that fly ash is rich Ca and Mg and therefore, can be used as a soil amendment for liming purpose and enhance the bioavailability of Ca and Mg. While it has been generally observed that fly ash application, including eastern U.S. ashes, improves the extractable Ca level in soil and plants[7, 8], this study indicates that that may not be true for Mg nutrition. Applications of FGD can create an imbalance in Ca/Mg nutrition, inducing Mg deficiency and perhaps K deficiency (Figure 9). Some micronutrients such as Mn and Zn concentrations in maize tissues decreased with increasing dose of FGD (Figure 10).

Application of FGD to agricultural lands could have both advantages and disadvantages. The pH enhancement may cause plant nutrient imbalance, particulary P and Mg deficiency and antagonistic reactions among elements because of excessive Ca, K, and S. Some other researchers observed similar antagonistic reaction among elements.[7, 16]

SUMMARY AND CONCLUSIONS

From the twenty studied elements only concentrations of 5 elements (Cd, Cr, Cu, Pb, and Sb) in maize tissues were not influenced by the FGD addition. All rates of FGD increased uptake of some macronutrients (Ca, Mg, and K) by 6 week-old maize plants. Concentration of some micronutrients (Mn and Zn) in maize leaves decreased with increasing dose of FGD, very likely due to antagonistic reactions with other elements such as Ca or Fe. FGD can serve as a supplementary source of certain essential elements for plants, such as B, Se, and Mo. However, these micronutrients could be phytotoxic when at high levels in soils. Although, for example B in soil is fairly soluble and leachable, this phytotoxic effect is only temporary in unweathered ash. Boron and soluble salts in unweathered ash by-products might restrict seed germination and establishment of plants especially at high rates of application, unweathered materials should be allowed to “weather” to enable leaching these harmful constituents. This implies that the timing of planting is important to avoid potential salt-related problems. Soil tests for electrical conductivity and metal level (e.g., B) can be conducted to determine when to plant. This study suggest that because of elevated concentrations of B and other elements and due to adverse yield effects measured on plants, unweathered FGD would not be a suitable amendment for 6-week old maize on this soil.

ACKNOWLEDGEMENT

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Table 1. Effect of FGD on pH of soil leachate over a period of 8 weeks.

Treatments	Week 1	Week 2	Week 3	Week 5	Week 7	Week 8
0% FGD	5.65	5.42	5.5	5.49	5.52	5.64
1% FGD	5.89	5.85	5.89	5.85	5.94	6
2% FGD	6.28	6.37	6.39	6.37	6.27	6.31
4 % FGD	7.05	6.9	7.33	7.15	7.03	7.21
6% FGD	7.37	7.43	7.55	7.62	7.53	7.57
8% FGD	7.5	7.57	7.68	7.7	7.64	7.65
10% FGD	7.74	7.74	7.77	7.86	7.75	7.83

Table 2. Effect of FGD on Electric Conductivity (mS/cm) of soil leachate over a period of 8 weeks.

Treatments	Week 2	Week 3	Week 5	Week 7	Week 8
0% FGD	0.28	0.235	0.217	0.195	0.19
1% FGD	2.41	1.045	1.132	1.25	0.935
2% FGD	3.27	1.45	1.47	1.66	0.97
4% FGD	4.38	1.57	1.95	1.92	1.7
6% FGD	4.72	1.91	1.99	2.15	1.98
8% FGD	5.47	2.05	2	2.1	2.01
10% FGD	5.33	1.95	2.11	2.16	2.02

Table 3. Concentrations of elements in leachate from soil treated with FGD (mg/kg or µg/kg*) over an eight-week equilibrium period.

Treatment	B	Na	Mg	K	Ca	As*	Se*	Mo*	Sb*	Hg*	Cd*
0%FGD	4.06	2.04	0.74	2.82	1.8	0.055	0.505	0.055	0.01	0.108	0.092
1%FGD	4.41	2.43	5.75	4.44	59.7	0.313	1.44	0.497	0.142	0.122	0.44
2% FGD	4.52	2.36	6.62	4.04	86.5	0.78	2.61	1.515	0.503	0.152	0.464
4% FGD	4.95	2.67	7.02	4.52	95.7	0.756	3.85	4.179	0.769	0.134	0.546
6% FGD	5.78	3.26	8.05	5.36	97.2	1.5	7.51	6.182	1.47	0.15	0.489
8% FGD	5.81	3.22	9.21	6.17	99.5	2.54	7.84	16.33	1.962	0.206	0.523
10% FGD	7.52	4.76	10.9	7.22	111	3.93	11.28	31.06	3.99	0.48	0.58

Table 4. Effect of FGD application on the concentrations of Cd, Cr, Ni, Pb and Sb in maize leaves.

Element (mg/ kg)	**0%**	**1%**	**2%**	**4%**	**6%**	**8%**	**10%**
Cd	0.168a*	0.214a	0.208a	0.217a	0.196a	0.198a	0.220a
Cr	0.382a	0.457a	0.465a	0.360a	0.491a	0.409a	0.465a
Ni	1.14a	1.20a	0.916a	0.698b	1.027a	0.899b	1.027a
Pb	0.526a	0.630a	0.480a	0.455a	0.638a	0.681a	0.694a
Sb	0.016a	0.006a	0.013a	0.009a	0.016a	0.012a	0.025a

* Means followed by letters a and b are significantly different between doses of FGD at $P<0.05$.

Figure 1. Flue gas desulfurization (FGD) waste was received from Cope Plant, (South Carolina Electric and Gas Co.) Orangeburg, SC.

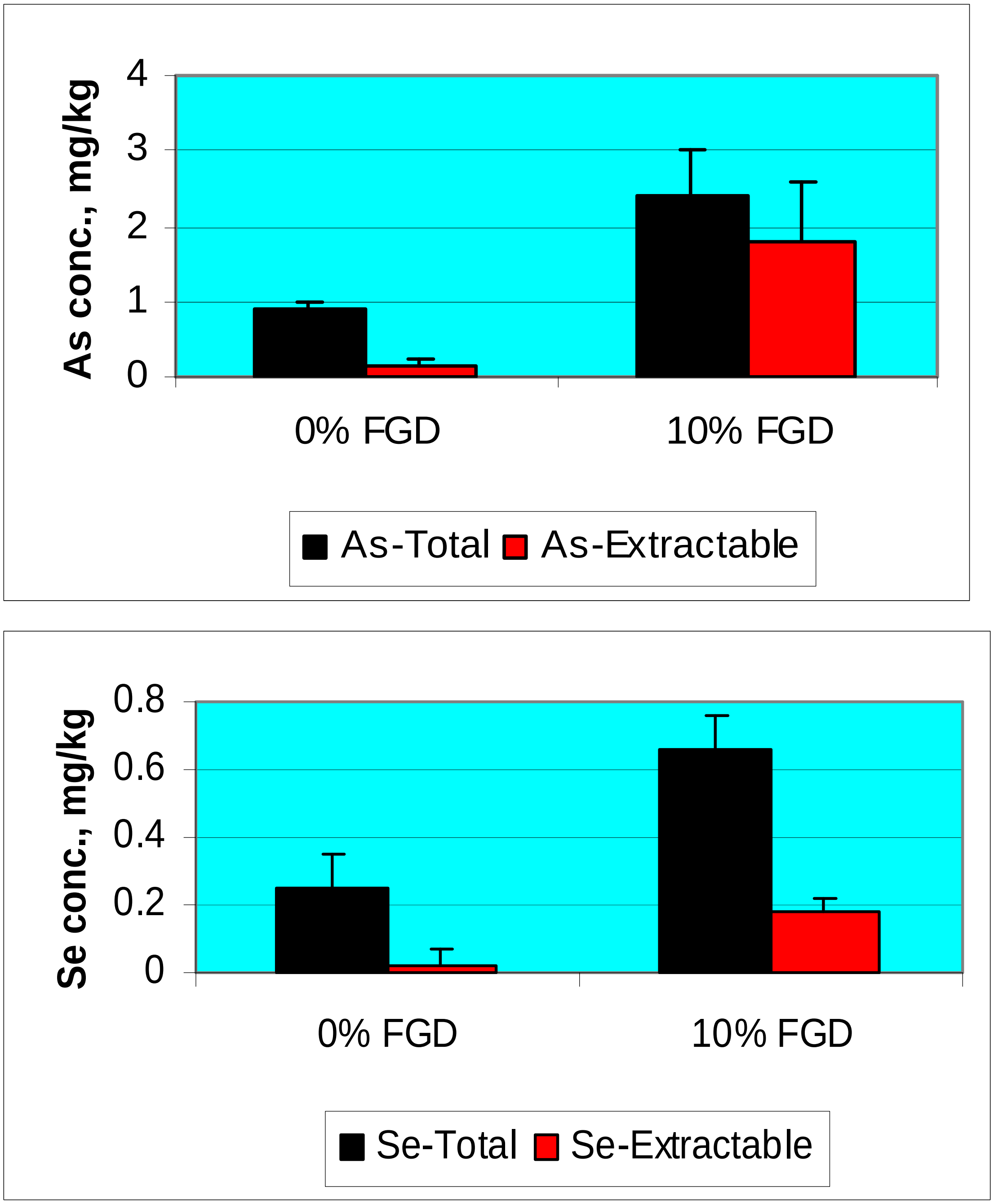

Figure 2 Total and extractable concentration of As and Se in soil with 0 and 10% of FGD. Soil was analyzed immediately after maize harvest (total –HF and aqua regia and extractable with 0.1 *M* HNO_3).

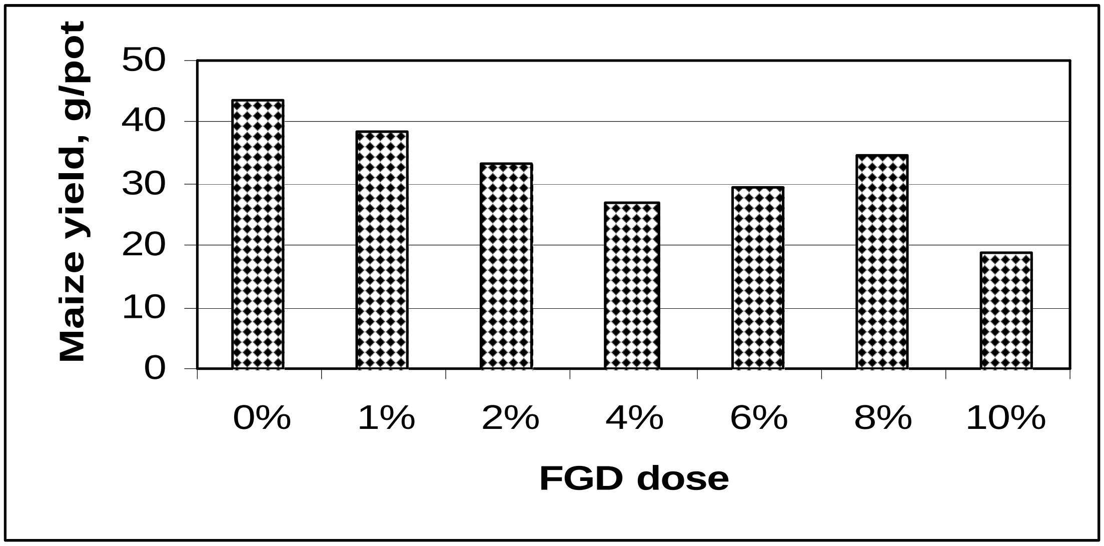

Figure 3. Effect of FGD on maize yield (g/pot).

Figure 4. Effect of FGD on maize growth.

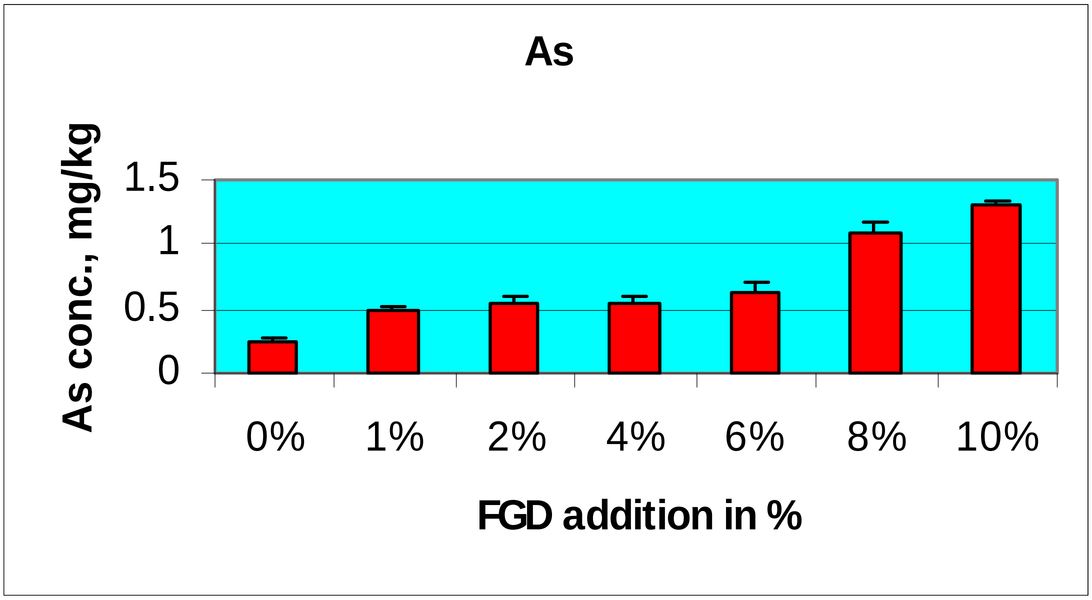

Figure 5. Effect of FGD on As concentration in maize leaves

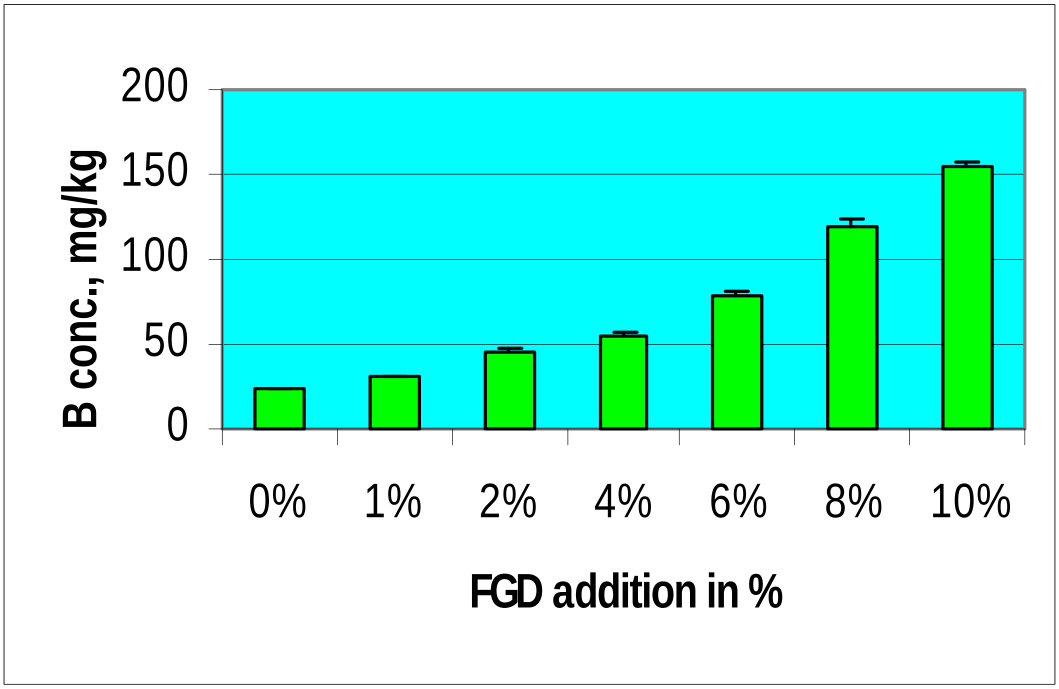

Figure 6. Effect of FGD on B concentration in maize leaves

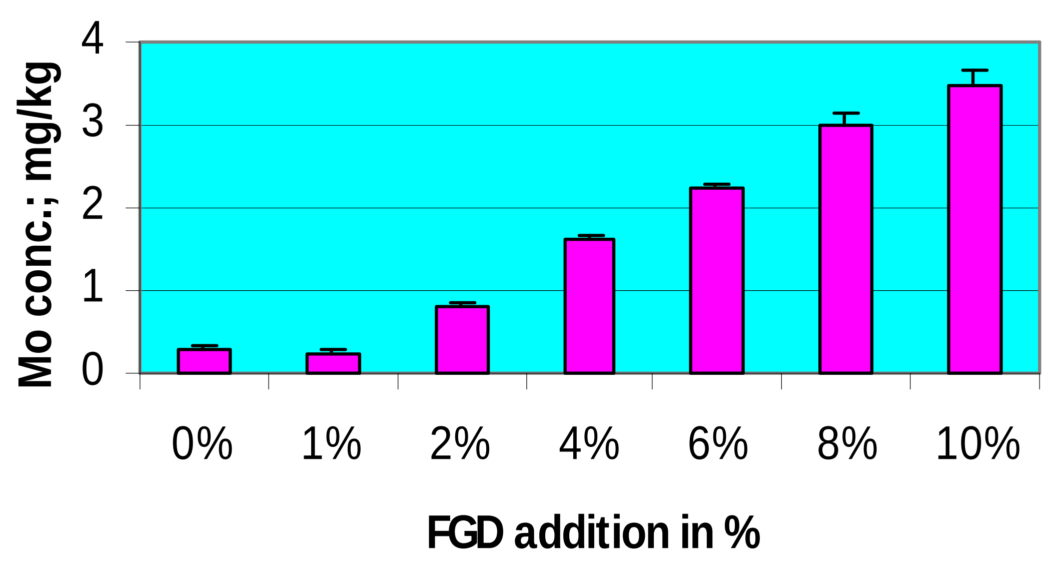

Figure 7. Effect of FGD on Mo concentration in maize leaves

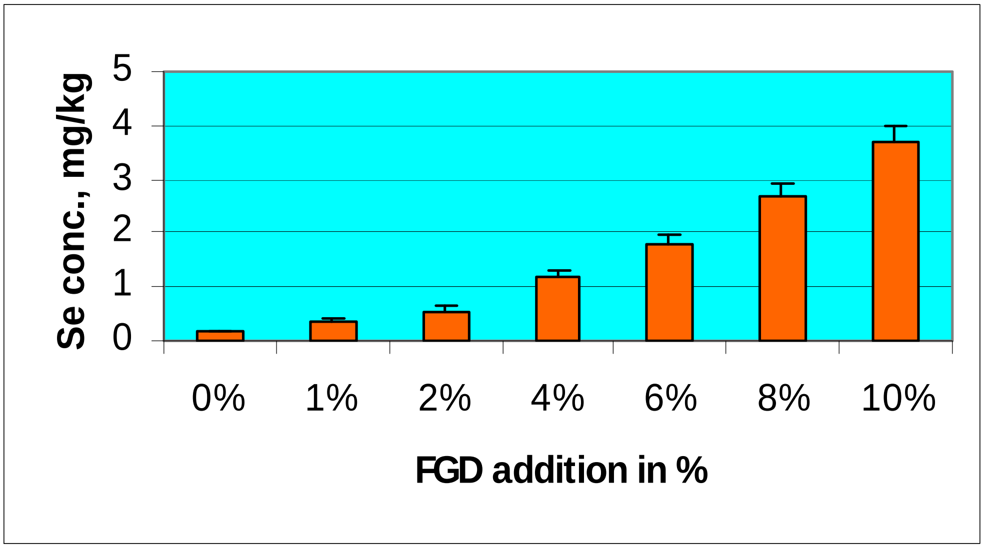

Figure 8. Effect of FGD on Se concentration in maize leaves

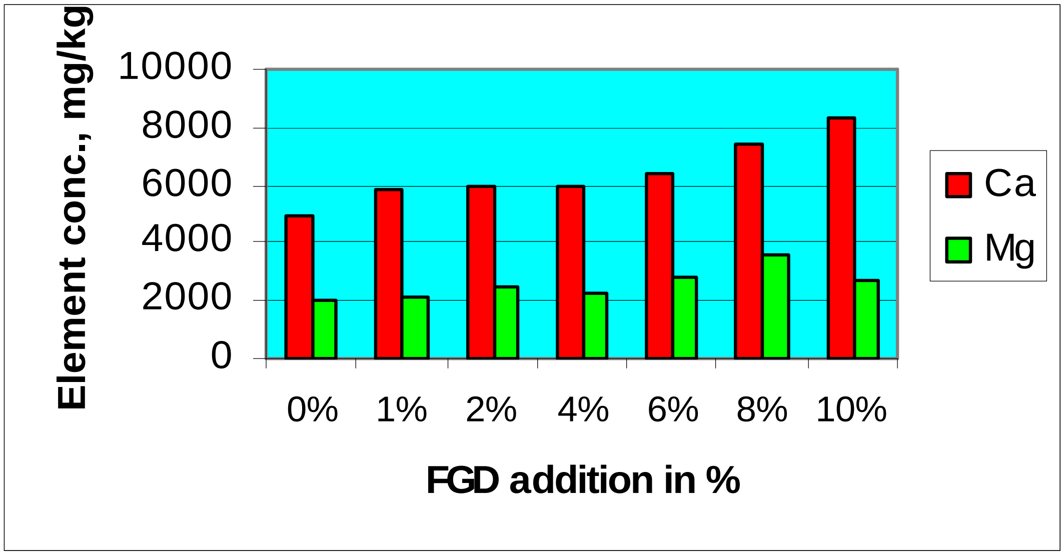

Figure 9. Effect of FGD on Ca and Mg concentrations in maize leaves

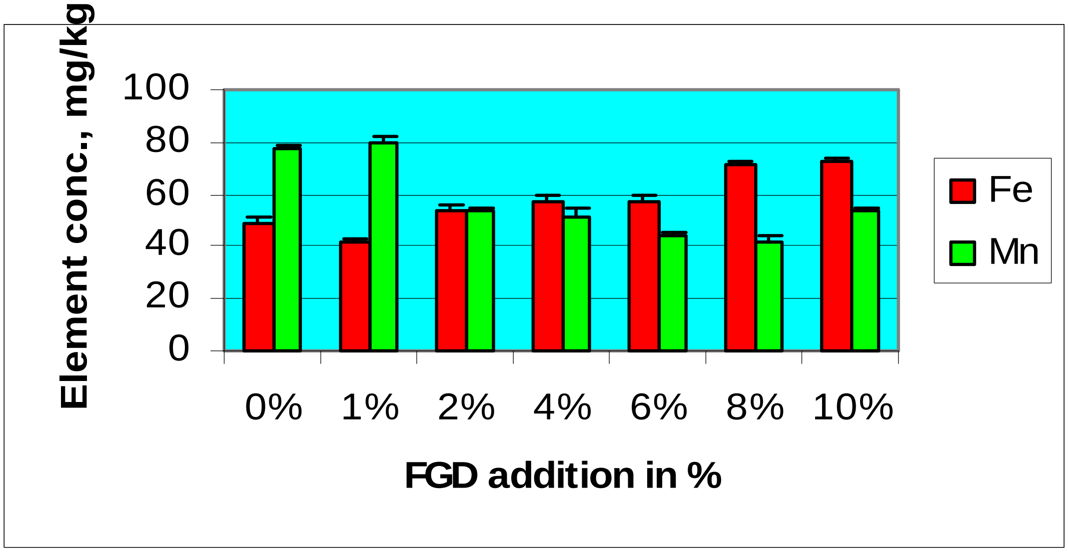

Figure 10. Effect of FGD on Fe and Mn concentrations in maize leaves