

DOE/SR/18047--3

DE92 013685

TECHNICAL TERMINAL REPORT

INVESTIGATION ON THE UTILIZATION OF COAL FLY ASH AS AMENDMENT TO
COMPOST FOR VEGETATION IN ACID SOIL

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Date Published: August 1, 1991

PREPARED FOR THE
U.S. DEPARTMENT OF ENERGY
UNDER GRANT No. DE-FG09-88SR18047

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PART I: INTRODUCTION

This technical terminal report prepared for the U.S. Department of Energy describes briefly the research work we have carried out on coal ash residues collected from coal-fired power plants at Savannah River Plant Site under a U.S. Department of Energy grant No. DE-FG09-88SR18047. The report gives a short discussion of the scientific background, experimental methods, results and significance of the findings. It lists the papers, resulted from this work, that are presented at various scientific meetings including three international conferences and also those published or submitted for publications in refereed journals. The report also includes the names of personnel including the students that participated in the project from time to time.

The principal objectives of the original project were (a) to collect coal fly ash samples from several coal-fired power plants at Savannah River Plant Site and compare the physico-chemical properties of water extracts from them by measuring pH, conductivity and concentration of selected cations and anions in the extracts, (b) to study the distribution of some of the elements among crude coal, slag(bottom ash), fresh fine ash, weathered ash and ash from lagoon, (c) to make fly ash-amended composts using commercial and/or "home-made" organic compost to be used as a manure for plant growth, (d) to determine the dry matter yield of four plants (corn, sorghum, collard green and mustard green) raised in soil treated with fly ash-amended compost under optimum conditions and (e) finally to develop correlation equations, if possible, between the metal(s) uptake by the plants and their concentrations in fly ash-amended composts.

As the investigation progressed some of the minor objectives such as the determination of U and Th content of the ash by the radiochemical measurement of their daughter products had to be given up because of the nonfeasibility of such studies. However, new objectives such as the optimization of various parameters to make a reasonably good manure, fractionation of nutrients according to particle size, downward mobility of nutrients in soil and the effect of the ash-amended manure on other plants had to be incorporated in the project. Furthermore, analysis of elements in water extracts were limited to 12 nutrients that are essential for plant growth. In addition to the analytical techniques discussed in the original proposal inductively coupled plasma (ICP) technique was also used to determine the nutrients in some of the plants.

The project that was originally planned to terminate by May 31, 1991 was extended for an additional period of 3 months to complete our work on all of the different phases of the project. The technical findings resulted from the project have been presented in several scientific meetings including three international conferences. One paper has been published and three are under review. A chapter entitled "Nutrients in coal and coal ash residues and their potential for agricultural crops" has been accepted for inclusion in a book entitled " Trace Metals, Coal and Coal Combustion Products", (eds.) K.S. Sajwan, D.C. Adriano and R.F. Keefer, 1991 (in press).

Several students majoring in chemistry and other disciplines have benefitted by their participation in this project at various times. Some of them have presented papers at scientific meetings and one has co-authored a paper. All students have received some training in research methodology and

the treatment of scientific data.

PART II: BRIEF DESCRIPTION OF RESEARCH

II.1. SCIENTIFIC BACKGROUND

It has been estimated that the production of coal in the United States alone will reach an all time high of 1.91×10^9 metric tons by the end of 2000 (1). Burning of coal in coal-fired power plants generates different types of ash residues and discharges significant quantities of particulate matter and vapors to the atmosphere (2,3). Fly ash is the most abundant of all residues that include slag (bottom ash), boiler ash and precipitated fine fly ash (4). In plants equipped with particulate emission control devices most of the elements are collected in the fly ash retained by such devices, electrostatic precipitators, with almost 99% efficiency (2). The fly ash is collected in dust collectors while the larger sized particles are recovered as boiler ash. The bottom ash and boiler ash are slurried with water and pumped into ash basins or lagoons. The fly ash is stacked in a nearby location for weathering and disposal by different means. Nondestructive neutron activation analysis (NAA) of ash samples have been performed by several scientists (2,4,5), but it will not furnish data on the elemental content of ash samples that is leachable by water.

The annual production of fly ash in U.S. alone, according to Adriano et al. (6) is about 58×10^6 metric tons. They have discussed the problem of utilization and disposal of fly ash and other coal residues in terrestrial

ecosystems. Longterm impacts on soil, surface- and ground water contamination resulting from the leaching of ash from ash ponds, landfills and other storage facilities have not been investigated in detail. Currently about 20% of fly ash is being utilized in industrial applications such as brick making, as a filler in asphalt mix, stabilizer in road bases, thermal insulation and deodorization of animal waste.

Fly ash is known to contain most of the essential nutrients for plant growth, except N and P, in varying amounts (7). Several investigators have attempted to use fly ash for direct treatment of soil as manure for raising agricultural crops (8-11) with varying degrees of success. Most of them found that direct application of fly ash to the soil did not increase the yield of most of the plants grown in ash-amended soil. More recently Adriano et al.(12) have used fly ash as an amendment to sludge for application as a fertilizer for vegetation. However, the presence of significant amounts of heavy metals such as Cd, Cu, Ni and Zn in sludge are harmful to plants (13, 14). Coal fly ash has never been used as an amendment to the easily available organic compost for vegetation in soil. This carbonaceous material will not only dilute the deleterious effects of fly ash but also enter into chemical reaction with the ash releasing more plant nutrients to the system.

II.2. EXPERIMENTAL METHODS

II.2.1. Collection and processing of ash samples

v Fly ash samples from five plant sites, SRS 484-D, SRS 784-A, SRS 184-K, SRS 105-P and SRS 200-H at Savannah River Plant site were supplied by Savannah

River Operation Office. Out of the above five, only SRS 484-D power plant was equipped with an electrostatic precipitator. A reference fly ash sample was also collected from SCE & G power plant. Only the fresh fly ash obtained from SRS 484-D was used for making composts. All coal ash samples including the bottom ash, boiler ash from vertical hoppers plant, weathered ash, fine fly ash and ash from lagoon used for the elemental distribution study were from SRS 484-D plant. The ash from lagoon may be mixed with discharge from other plants. The coarse ash from SRS 184-K was subjected to fractionation study. Leaf ash was made in the garden by burning dry leaves in order to compare its nutrient content with that of other ash residues for evaluating its usefulness as a manure. All samples used for this study were dried in an oven at 60° C. Three different types of organic manure were attempted for composting. Two of them, "Gotta Grow" (rich grade) and "Compost Toast" (low grade) were purchased from Bricker's farm, Augusta, GA and the third, "home-made", was composted at our site.

II.2.2. Extraction of nutrients from coal and coal ash residues.

We have used only water as extractant, except in the case of crude coal, for the release of nutrients in the system, because only water soluble nutrients will flow to the ecosystem as contaminants and also be available to plants when used with fly ash-amended compost as manure. Results of measurement of total content of elements in ash samples by NAA do not reveal how much of each contaminant will be released to the aquatic system through leachates. In this work analysis is limited to 12 nutrients, N, P, K, Ca, Mg, S, Fe, Zn, Mn, Cu, Mo and B that are essential for plant growth (15). Water extracts of ash, soil, organic compost and ash-amended composts were prepared

by hand-shaking 10 g of the dried sample with 100 ml of mega-pure water (specific conductance: 1.2 $\mu\text{mho/cm}$) for one minute and then agitating for an hour with a mechanical shaker. It was found that the extracts should be kept for at least 5 days for equilibration (7). The mixture was filtered through a Millipore filter paper (0.45 μm) into polyethylene bottles using suction. The pH and conductances of all water extracts were measured for comparison among different samples. One gram of dried coal was ashed in an electric furnace at 600° and the ash was digested with 1 N HCl, diluted with pure water, filtered and made up to 100 ml to prepare the stock solution for coal analysis.

II.2.3. Study of nutrient distribution among particles of different size

The coarse fly ash collected from SRS 184-K was fractionated using U.S.A. standard testing sieves of different openings. The separated fractions were treated with water as before and water extracts were prepared to measure pH, conductivity and concentration of nutrients. The results of the distribution of selected elements among the separated fractions have been reported elsewhere (7). In general, the fraction with particles greater than 500 μm in diameter yielded greatest concentrations of these elements in water extract in conformity with previously suggested mechanism of absorption and retention of elements by coal ash during coal burning process.

II.2.4. Preparation of fly ash-amended composts

In order to optimize various parameters such as type of compost, fly-ash to compost ratio, ash-amended compost to soil ratio for plant growth different experiments were performed the details of which are reported elsewhere (16). Three types of organic composts, "Gotta Grow"(rich), "Compost Toast"(low grade)(both commercial) and the inexpensive "home-made" composed were used for

amendment with fly ash. The rich manure was found to be ineffective to make use of the nutrients available in fly ash for vegetation. The "home-made" compost prepared at our site by composting grass clippings was found to be the best and most inexpensive to make fly ash-amended organic manure. The useful fly-ash to compost ratio was established by mixing fly ash with "home-made compost" in various proportions (10-60% FA) and testing the manure for plant growth. Plant yields as well as nutrient concentrations in fly ash-amended composts and in plants were considered to be the indicators of effective composition. The fly ash-amended compost to soil ratio was established using a fixed amount of "compost toast" mixed with 20% fly ash and varying amounts of soil in pots before plantation of seeds.

II.2.5 Greenhouse study of plant growth in soil treated with fly ash-amended compost

Seven plants, collard green and mustard green (fall crop) and corn, sorghum, bell pepper, string beans, and egg plant (spring crop) were chosen for the study. Plant seeds were sown in pots lined with plastic bag containing 1.75 kg of FA-amended compost of an assigned composition and 5.25 kg of sifted sandy loam soil (a predetermined ratio of 1:3) mixed thoroughly with a twin-shell standard solid-solid blender from Patterson and Kelly Co. Replicate pots for a given type of bed were used for each plant, including the control. The plants were thinned to three when they reached a height of about 7 cm, watered regularly with pure water and harvested at the end of 8 weeks. The plants were dried in the oven for 3-5 days depending on the type of plant and the weights of dry plant were measured.

The dry plants were ground and powdered in a motor-driven stainless steel

blender. A one gram sample of each plant from each pot was randomly picked and weighed in a quartz crucible and ashed at 500° C in an electric furnace. The ash was digested with 10 ml of 1 N HCl, diluted with water and filtered. The clear filtrate was diluted to 100 ml to perform the analyses.

II.2.6. Column experiments to measure the downward mobility of nutrients in soil

It is important to determine the downward transport of nutrients or a profile of their concentrations as a function of depth in soil to ensure that the nutrients are within the reach of plant roots. Two identical PVC columns (110 cm ht x 15 cm diam) filled with sandy loam soil and kept for several years were brought to our greenhouse from Savannah River ecology laboratory. The columns were provided with five outlets or ports (A-E) for water flow, on their side. The columns were extended by 45 cm by glueing similar PVC tubes at their tops to introduce fly ash-amended composts (See Figure 1). The columns were then equilibrated with Mega-pure water after checking the leaks and closing the ports with rubber corks. A blank or control run was made by collecting 100 ml of water from the bottom port E of each column keeping always the top surface wet. Two types of fly ashes (SRS 484-D fine fly ash) and (SRS 184-K (coarse fly ash) were used to make FA-amended composts (20% FA) with "home made" compost. Three kgs of FA-amended composts were placed in respective columns marked as 484-D and 184-K. A 500 ml of pure water was added to each column and mixed with the compost for a few minutes. One hundred ml fraction of the eluant were collected from three ports of each column. These effluents and the controls were analyzed for the nutrients. After several weeks both columns were cut axially with an electric saw and eight sections of

soil including the FA-compost section were removed for analysis. The soil samples were dried in the oven at 60° and water extracts were prepared from the dry samples as discussed before.

II.2.7. Chemical analysis

The concentrations of six metals, K, Ca, Mg, Zn, Mn and Cu in all water extracts and some of the plant samples reported in this work were measured by flame atomic absorption techniques. The concentrations of most of the elements including Fe, Mo and Sb in the rest of the plants were determined by inductively coupled plasma (ICP) analysis. Boron was determined in all samples using the improved azomethine-H method (17). Dissolved orthophosphate was measured by a spectrophotometric single reagent method (18). Sulphate was determined by a turbidometric method using a conditioning agent and precipitating as BaSO_4 with BaCl_2 (18). Nitrate was determined potentiometrically using Orion's digital ionanalyzer and a double junction electrode with 2 M $(\text{NH}_4)_2\text{SO}_4$ solution to adjust the ionic strength.

II.3. RESULTS AND DISCUSSION

II.3.1. Physical and chemical properties of coal and coal ash residues.

The nutrients that are available in fly ash for agricultural crops have no doubt their origin in crude coal no matter by what mechanism the fly ash absorbs them. Although the ranges of concentration of trace elements, based mostly on NAA, are the same among coals of different origin the sulfur content and fly ash generated from coal combustion are significantly different and they range from 0.4 to 4% and 4 to 26%, respectively (11). The results of the

analysis of water extracts of all fly ash samples collected from Savannah River Plant sites and SCE & G including the pH and conductance values were reported previously (Appendix I, Tables I & II). It was found that it takes at least five days for the water extract to reach equilibrium with the samples (7). The fly ash collected from power plants equipped with electrostatic precipitators was either neutral (SRS 484-D, pH = 6.96) or basic (SCE & G, pH = 8.37), while those from others were acidic. The results of distribution of selected elements among fractions of SRS 184-K fly ash sample separated according to particle size are presented in Table IV of Appendix I. The fraction with particles greater than 500 um in diameter yielded greater concentrations of the elements with the exception of Ca.

The concentrations of selected metals and nonmetals in water extracts of fly ash samples collected from different sources have been reported in Table II of Appendeix I. There is considerable difference in the concentration of some of the elements among ashes collected from different plants. Fly ash sample collected from SRS 184-K contains the largest amount of Mg, Zn, Mn, B and S.

II.3.2. Vertical deposition of nutrients in various coal ashes in 484-D plant

The results of analysis of various coal residues collected during the combustion of coal in SRS 484-D plant are presented in Table I. This Table also includes the analytical results of crude coal used for combustion. The elemental content of these residues is related to the percent of ash produced from the coal and also the efficiency of the removal of the element from the combusted product stream. It may be represented by the equation:

$$C_X(\text{ash}) = F_{\text{ash}} \cdot C_X(\text{coal}) \cdot \text{REF}_X \quad (1)$$

where $C_X(\text{ash})$ is the concentration of X in ash, $C_X(\text{coal})$ is that in coal, F_{ash} is the fraction of coal that produced the ash and REF_X is the removal efficiency factor for the element. In the absence of correct estimates of F values one can define a relative removal efficiency factor (RREF) for each element choosing a reference element for normalization. Using Mg as a reference element the RREF can be expressed by the equation:

$$\text{RREF}_X = \text{REF}_X / \text{REF}_{\text{Mg}} = C_X(\text{ash}) / C_X(\text{coal}) / C_{\text{Mg}}(\text{ash}) / C_{\text{Mg}}(\text{coal}) \quad (2)$$

The RREF value for any element can be calculated for the measured concentrations of element X and Mg in the ash and coal. Obviously its value for Mg will be equal to 1.0. The relative efficiency of the removal of Ca, K, S, N and B from the flue gas seems to be relatively much higher than others. The basic character of the ash residues collected from power plants equipped with electrostatic precipitators may be attributed to the efficient removal of base metals from the gas stream onto the residues.

II.3.3. Distribution of nutrients in coal and coal ashes accumulated in the environment.

Distribution of water-extractable nutrients in coal and coal ashes accumulated in the vicinity of SRS 484-D power plant is presented in Table II. It is interesting to note that K is enriched in bottom ash while Ca is enriched in ash from lagoon. The enrichment of Ca in the ash from lagoon may be due to the accumulation of the insoluble CaCO_3 and/or slightly soluble CaO . All of the three transition metals, Zn, Mn and Cu are much more concentrated in weathered ash than in others. Weathered ash and ash from lagoon have significant amount of S in the form of sulfate which can be leached to aquatic system.

II.3.4 Downward transport of nutrients in soil

Results of the column experiments are presented in Tables III and IV. Table III shows that the elution pattern of the nutrients are somewhat different from each other. Although concentrations of all metals, except Zn, are highest in the eluate from the bottom port, there is still the difference in the rates of their mobility. There is also some difference in the elution pattern of elements from two different columns loaded with two different fly ash-amended composts. This may be attributed to the difference in the texture of the fly ash used for amendment. It should also be pointed out that the rate of flow of water in column 184-K was much higher than that in column 484-D indicating that water retention capacity of the fine fly ash is much higher than "coarse" fly ash. This finding may have some application for the utilization of coal ash in landfills where fast drainage is required.

The first 0-15 cm section in Table IV represents the unused FA-amended compost, the second records the concentrations in the interphase between the first and third section and the rest different soil sections of the column. This Table reveals that the concentration of most of the nutrients decreases as a function of depth and probably levels off at a depth of about 80 cm. It appears that Mn is relatively more enriched in sections beyond 80 cm in depth in both columns indicating that Mn probably exists as Mn^{2+} and its rate of movement is larger than that of others.

II.3.5. Results of analysis of "home-made" compost and fly ash-amended compost

The results of analysis of "home-made" compost and of fly ash-amended composts of different compositions are shown in Table V. The results shown in this Table show that some of nutrients in fly ash are released to the system

During composting. Mass balance calculations using analytical data on 484-D fly ash, "home-made" compost and fly ash-amended compost (20% FA) reveal that the ash-amended compost is enriched by 12.1% in K, 61.5% in Mg, 45.7% in N and 4.8% in S. However, Ca, Zn and B were depleted by 12.9%, 63.1% and 36.7%, respectively. The percent enrichment or depletion was calculated using the following equation:

$$\%E = 100(C_X(\text{FA-Comp})_{\text{obs.}} - (C_X(\text{FA}) \cdot a_{\text{FA}} + C_X(\text{comp}) \cdot b_{\text{comp}}) / C_X(\text{FA-Comp})_{\text{obs.}}) \quad (3)$$

where %E is the percent enrichment or depletion, C_X s are concentrations in fly ash, compost or FA-amended composts and a_{FA} and b_{comp} are the proportions of FA and compost in FA-amended compost. Similar enrichment and depletion but of different magnitude were also observed in FA-amended composts of various compositions. This observation suggests that the chemical interaction between the fly ash and the organic compost does take place during composting the mixture.

The beneficial effects of the FA-amended composts on agricultural crops are derived because of the fact that organic compost can provide additional nutrients such as Mg, Zn, P, S, and N that are not available in adequate amounts in fly ash for plant nutrition. Optimization of various parameters for the application of amended compost to soil were established by planting corn and sorghum in pots lined with plastic bag. The range of compositions of FA-amended compost was established by raising both plants in pots containing soil treated with different fly ash/compost ratios and by measuring their dry yield after harvest. The FA-comp/soil ratio was established by planting corn in pots containing various proportions of FA-amended compost (20% FA) and soil. In all cases the total weight of the matrix was kept constant at 7 kg. It was

observed that the plants grown using FA-comp/soil ratio of 1:3 had the maximum yield and the range of composition of the FA-amended compost is 20-40% FA depending upon the nature of plant.

II.3.6. Effect of FA-amended compost as manure for agricultural crops.

We have investigated the effect of FA-amended composts on the yield and elemental uptake of seven plants, namely corn, sorghum, collard and mustard greens, string beans, egg plant, and bell pepper. The yields of the first four plants were examined using fly ash-amended compost of various composition, but the last three were tested using a single ash-amended composition (20% FA). In all cases control plants using soil as well as soil mixed with organic compost alone were raised for comparison. The total weight of the matrix in each case was 7 kg.

Photographs of the greenhouse and selected crops grown under different soil treatment with fly ash-amended composts including the controls are presented in Figures 1, 2 and 3. Corn in Figure 1 and mustard green in Figure 2 were raised using ash-amended compost of variable composition. Pepper in Figures 2 and 3 and the beans in Figure 3 were grown in soil, soil mixed with organic compost and soil treated with ash-amended compost (20% FA) for comparison. Figures 4 and 5 depict plots of dry shoot yield versus percent of fly ash in ash-amended composts for corn and sorghum and for mustard green and collard greens respectively. Table VI presents comparative data on the dry matter yield of all seven plants grown in bare soil, soil treated with organic compost and soil treated with ash-amended compost (20% FA). The figures show an increase in yield of 114% over that of control for corn and 106% for sorghum at 30% fly ash level while for collard greens and mustard greens the

increase is as much as 378% and 348%, respectively at 20% fly ash level. Table VI reveals that in all cases, except sorghum and collard greens, plants treated with organic compost alone have the highest yield. Fly ash-amended organic compost does not seem to be an effective manure for the string beans, egg plant and bell pepper although the last two show slight increase over their yields over the control. In agreement with the findings of Salter et al.(9) we have observed that soil treated with fly ash-amended compost also retains much more water than the soil alone and its capacity to hold water increases with an increase in ash content, a fact that will help farmers to manage their water resource if they use this manure.

II.3.7. Uptake of nutrients by plants.

The results of the measurement of concentrations of nutrients in the last five plants grown under different conditions are presented in Tables VII and VIII. Similar results for corn and sorghum have been reported elsewhere (16). Although Sb is not an essential nutrient its concentration was found to be almost constant regardless of the type of treatment and therefore, is also included in the Tables. For easy reference the concentrations of nutrients that are enriched in plants treated with ash amended compost are underlined. Each listed value is the average of triplicate measurements. It is interesting to note that K is much more elevated in all plants treated with ash-amended compost than in those treated otherwise. The plants may absorb larger amount of water soluble nutrients when they are available in soil fertilized with ash-amended compost or by commercial fertilizer. The boron content of string beans, egg plant and bell pepper is also very high when the plants are nourished with ash-amended compost. Poor growth and yield of these plants can

therefore, be attributed to the pytoxicity of boron which the plants assimilate in larger quantities. Calcium was enriched only in collard and mustard greens nourished by ash-amended compost.

In order to evaluate the plant capacity to absorb nutrients under different nurturing conditions an enrichment factor (EF) or a deficiency factor (DF) was defined as follows:

$$EF \text{ or } DF = \frac{C_{FA-Comp}(X) - C_{soil}(X) \text{ or } C_{org.Comp}(X)}{C_{Sb}(ave)} \quad (4)$$

where $C_{FA-Comp}(X)$ is the concentration of X in plants nourished by ash-amended compost, $C_{soil}(X)$ is its concentration in plant raised in soil, $C_{org-Comp}$ is its concentration in plant treated with organic compost only and C_{Sb} is the average content of Sb in these plants raised by the same soil treatment. Since the concentration of Sb is nearly constant in any plant irrespective of how it is raised it can be used as a reference element for normalization to account for the differences in the moisture content, uniformity of the bed and biomass production of the plant.

Two sets of factors for each element for each plant have been computed and they are listed in Table IX. Positive numbers indicate the enrichment and the negative show deficiency of that element in plants nourished by ash-amended compost relative to those raised in soil or soil treated with organic compost. It can be seen from this Table that except for egg plant nourished by ash-amended compost, there is nitrogen deficiency in all plants. Potassium is enriched in all plants treated with ash-amended compost, but there are deficiencies for Ca in beans, pepper and egg plant. The enrichment

factor for B is much higher in beans, egg plant and bell pepper relative to others. This suggests that the enrichment of B, a phytotoxic element and the deficiency of Ca in beans, egg plant and bell pepper may be responsible for their poor yield.

II.3.8. Correlation studies on elemental concentrations and crop yield.

Correlation studies were conducted to determine whether there is a linear dependence of the concentration of nutrient(s) in ash-amended compost and the dry matter yield of the plant. Figure 6 depicts the correlation plots of concentration of K in ash-amended compost (water soluble) versus the dry matter yield of mustard and of B concentration in compost versus the yield of collard green. The linear equations corresponding to these plots and the "r" values are given in the figure. It is obvious from this figure that the dry matter yield increases with an increase in concentration of K in compost while an increase in B content diminishes the yield. Figure 7 shows the linear relationships of P and S in sorghum plant versus their respective concentrations in the ash-amended composts. It can be seen from these plots that linear relations do exist, at least in some cases, between concentration of elements in plants and in the composts. No other element showed similar relationships with significant "r" values.

II.4. IMPORTANT FINDINGS AND CONCLUSIONS

Application of fly ash-amended composts as manure enhances the crop yield of certain plants like corn, sorghum, collard and mustard greens. Organic compost made out of grass and leaves (home-made) is better than the commercial

composts for amendment with fly ash. A 20-40% fly ash in the amended compost and a soil to ash-amended compost ratio of 3:1 are recommended for making bed for plantation. Organic compost mixed with fly ash, due to reduced porosity, will help the bed to retain water and conserve water supply to plants. Organic compost will release to the manure additional quantities of N, P, and S that are not substantially available in fly ash.

It appears that chemical reaction and/or mineralization occurs during composting of fly ash with organic manure to release more N, P, K and S to the system. Potassium is more elevated in all plants grown in potted soil treated with fly ash-amended compost than in those grown in soil or soil treated with organic manure. Contrary to expectation Ca in fly ash is not effectively used by plants as the latter treated with ash-amended compost is not rich in Ca. This suggests that Ca may be tied up as insoluble CaSO_4 in the manure so that it may not be bioavailable to the plant. Uptake of boron by bean, bell pepper and egg plant is considerably higher than that absorbed by corn, sorghum and greens resulting in poor yield for the former. There is some correlation between plant yield and concentrations of some nutrients in compost. Linear correlation was also observed between the elemental content of some nutrients in plants and in the compost.

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Table I

Vertical distribution and removal efficiency of coal ashes for nutrients
during coal combustion in SRS 484-D power plant*

Nutrient	Crude coal (conc.)	Bottom ash		Boiler(1-4) ash		Boiler(1-13) ash		Boiler(1-16) ash		Fresh fly ash	
		conc.	RREF	conc.	RREF	conc.	RREF	conc.	RREF	conc.	RREF
K	1,885 ± 126	15.8	0.88	261.4	2.7	1,152	3.54	1,164	3.54	138.3	1.44
Ca	405 ± 26	51.2	13.2	1,245	59.9	1,574	22.5	1,581	22.1	779.3	37.8
Mg	725 ± 21	6.9	1.0	37.2	1.0	125.5	1.0	128.3	1.0	36.9	1.0
Zn	26.3 ± 2	0.34	1.34	0.45	0.33	3.9	0.84	5.2	1.1	0.90	0.67
Mn	27.6 ± 4	0.30	1.1	1.26	0.88	4.7	0.96	4.7	0.96	0.82	0.58
Cu	35.8 ± 4	0.71	2.1	0.50	0.27	5.5	0.88	5.9	0.93	0.43	0.23
B	62.3 ± 6	8.3	13.9	298.5	93.4	823.5	76.4	842.5	76.5	69.4	21.9
S	3,445 ± 751	895.8	37.6	0.0	0.0	3,854	0.33	3,906	0.33	999.8	0.29
N	93 ± 22	296.8	333.8	80.4	16.9	14.2	0.88	5.4	0.33	108.3	22.9

*: Conc. expressed in mg/kg; P was not detected, Fe and Mo were not measured

Table II

Distribution of nutrients in coal and coal ashes accumulated
in the vicinity of SRS 484-D power plant[#] *

Nutrient	Crude coal	Weathered ash	Bottom ash	Ash from lagoon
K	1,883	5.0	15.8	9.6
Ca	405	114.0	51.2	346.4
Mg	725	109.4	6.9	16.2
Zn	26.3	4.5	0.34	0.39
Mn	27.6	16.1	0.30	0.30
Cu	35.8	3.7	0.71	0.43
B	62.3	31.9	8.3	40.3
S	3,445	4166.8	895.8	958.5
N	93.0	33.4	296.8	85.3

#: Water soluble nutrients; *: conc. is in mg/kg, P was not detected, Fe and Mo were not measured.

Table III

Concentrations of Selected nutrients in eluates from column experiments
using fly ash-amended "home-made" compost^{*}

Nutrients	Column 1: Covered with 484-D FA-amended					Column 2: Covered with 184-K FA-amended				
	Compost					Compost				
	Control	Port B	Port D	Port E		Control	Port A	Port C	Port E	
K	2.18	1.15	1.48	2.25		1.03	10.51	1.98	2.18	
Mg	6.19	1.44	1.73	2.73		0.47	10.66	1.50	2.30	
Ca	27.48	3.67	6.76	25.10		1.93	32.40	4.25	21.00	
Zn	0.04	0.05	0.12	0.04		0.01	0.32	0.24	0.05	
Mn	0.08	0.12	0.39	0.40		0.02	4.24	0.12	0.44	

^{*}: Only 5 metallic nutrients were measured; Conc. expressed in mg/kg in 100 ml of the eluant.

Table IV

Results of elution experiments on downward movement of nutrients in soil

Column	Localized concentrations (mg/kg)									
section	K	Ca	Mg	zn	Mn	Cu	B	P	S	N
Column #1: Filled with sandy loam soil covered with 484-D FA-amended compost										
0-15 cm	402	332	121	0.75	3.63	0.38	33.7	12.1	708	140
15-20 cm	102	128	58	0.40	0.42	0.25	6.5	1.78	250	136
20-40 cm	29	62	32	0.47	1.56	0.17	2.4	0.30	167	72
40-60 cm	24	24	12	0.31	3.97	0.21	5.5	1.50	242	40
60-80 cm	12	27	10	0.35	1.28	0.25	2.4	2.70	275	38
80-100 cm	19	37	16	0.53	10.7	0.03	14.4	0.90	267	47
100-115cm	14	38	6	0.23	2.75	0.04	7.4	1.50	275	45
115-125cm	5	11	7	0.23	5.97	0.08	1.7	0.0	242	42
Column #2: Filled with sandy loam soil covered with 184-K FA-amended compost										
0-15 cm	286	92	58	0.85	2.00	0.28	11.4	18.7	258	92
15-20 cm	57	24	16	0.30	0.22	0.17	2.4	8.9	133	149
20-40 cm	35	36	12	0.91	2.22	0.25	12.2	0.0	200	157
40-60 cm	12	40	10	0.52	1.75	0.38	12.0	2.4	300	29
60-80 cm	16	37	10	0.56	2.89	0.04	0.0	1.5	184	138
80-100 cm	17	33	10	0.46	4.11	0.17	2.0	0.0	133	174
100-115 cm	18	32	2	0.19	3.31	0.10	1.7	1.2	92	127
115-125 cm	8	8	1	0.53	2.91	0.03	1.7	0.6	133	87

Table V

Results of Analysis of "Home-made" Compost and Coal Fly Ash Amended Compost

Element	SRS 484-D	Fly Ash	comp.(1)	0% FA	Comp.(2)	15% FA	Comp.(3)	20% FA	Comp.(4)	30% FA	Comp.(5)	40% FA	Comp.(6)	50% FA	Comp.(7)	60% FA	F values	F ₁	F ₂
K	184		3197		2575		2952		2059		1501		1501		1189		21.2*	25.8*	
Na	145		2199		1162		1404		1586		1299		852		2033		79.4*	8.1*	
Ca	1895		294		274		544		343		347		363		528		17.6*	19.5*	
Mg	41		175		159		385		187		155		163		157		88.1*	79.3*	
Zn	0.2		2.6		1.9		1.3		0.7		0.6		0.5		0.2		15.6*	15.4*	
B	29.3		23.3		29.1		18.1		32.4		30.9		40.3		41.5		11.7*	11.1*	
P	ND		560		269		367		133		69		73		24		85.9*	69.7*	
S	683		4951		3986		4308		4044		3469		3760		3292		33.8*	38.5*	
N	7.9		893		913		1320		761		1238		1624		1077		18.2*	16.7*	

*: Significant at p 0.01; \$: One and two way analysis of variance(ANOVA) in the elemental content of composts; F₁ values are indicators of the differences between the mean values of element content of composts of different composition and F₂ values include the interactive aspects of the replicate samples of all the groups. Variance "within" 4 replicates for each treatment was found to be not significant in each case.

Table VI

Dry matter yield of plants grown in bare soil, soil treated with organic compost
fly ash-amended compost *

Plant	bare soil	soil treated with organic compost	soil treated with fly ash- amended compost(20% FA)
Corn	21.0 g	46.0 g	38.0 g
Sorghum	16.0 g	27.0 g	31.0 g
Collard greens	43.0 g	172.3 g	205.7 g
Mustard greens	53.8 g	284.6 g	237.8 g
Beans	12.2 g	25.8 g	5.3 g
Egg plant	7.0 g	22.7 g	11.9 g
Bell pepper	6.0 g	17.6 g	9.9 g

*: Average of triplicate samples

Table VII

Concentration of nutrients in mustard and collard greens grown in potted soil under different

conditions

Element	Collard green				Mustard green		
	bare soil	Organic compost	FA-amended compost (20% FA)	bare soil	Organic compost	FA-amended compost (20% FA)	
Mg element/kg dry matter							
* N	2750	3500	2240	2950	3440	2430	
P	4476	4834	4824	3493	4213	<u>4382</u>	
K	19171	39978	<u>48563</u>	21669	63497	<u>70836</u>	
Ca	36300	34536	<u>37985</u>	27055	19417	<u>23970</u>	
Mg	1964	3381	<u>4079</u>	1107	2037	<u>2172</u>	
S [#]	8470	10280	<u>19037</u>	8330	8060	5830	
Zn ^{\$}	17.4	51.0	<u>65.9</u>	25.3	40.9	<u>52.4</u>	
Mn ^{\$}	13.3	22.7	13.5	10.7	12.7	8.7	
Cu	6.3	6.8	1.0	18.5	15.8	13.3	
B	19.3	8.0	<u>27.8</u>	17.3	6.3	<u>18.6</u>	
Fe	55.2	72.5	67.5	62.4	63.1	64.7	
Mo	8.8	1.3	4.3	5.2	0.0	1.6	
Sb	<u>11.9</u>	<u>12.9</u>	<u>13.0</u>	<u>11.7</u>	<u>12.0</u>	<u>15.9</u>	

*: Potentiometric; #: Turbidometric; \$: Atomic Absorption; All the rest by ICP.

Concentration of nutrients in beans, pepper and egg plant grown in potted soil under different

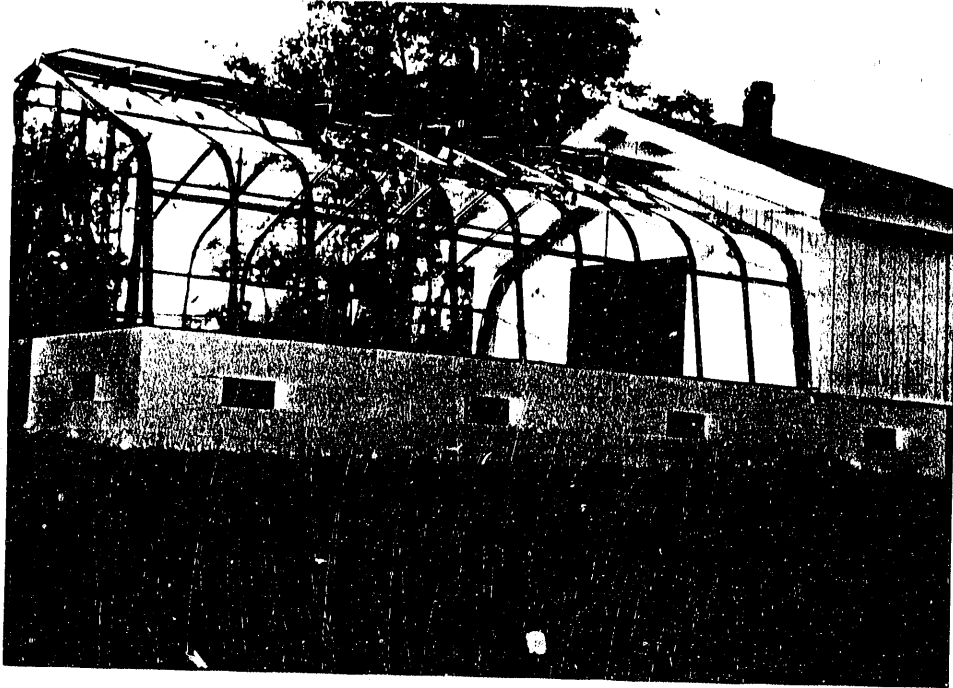
-28-

*: Potentiometric, #: Turbidometric, The rest by ICP, No Mo was foundEbp

Table IX

Enrichment(EF) or deficiency(DF) factors for major and macro nutrients including toxic boron in different plants

Elements	Collard Vs		Mustard Vs		Beans Vs		Pepper Vs		Egg plant Vs	
	Soil	O.Compost	Soil	O.Compost	Soil	O.Compost	Soil	O.Compost	Soil	O. Compost
Ave. Sb Conc.	12.6 + 0.6	13.2 + 2.3	16.2 + 0.4	14.4 + 0.8	12.5 + 0.1 mg/kg					
for 3 treatments										
N	-40.0	-100	-39.0	-76.5	-307	-248	-9.0	-18.0	-117	42.4
P	27.6	0.8	67.3	12.8	39.0	11.7	98.0	76.3	187	155
K	2333	681	3725	556	2220	1001	2337	602	2369	185
Ca	134	274	-234	345	-680	-1097	-109	-110	-95	-458
Mg	168	55	81	10.2	-66	-113	14.0	-7.8	42.4	13.0
S	638	694	-189	-184	20.4	93.2	-33.0	68.0	311	327
B	0.67	1.6	0.1	0.93	6.9	6.3	13.3	13.3	8.6	8.5

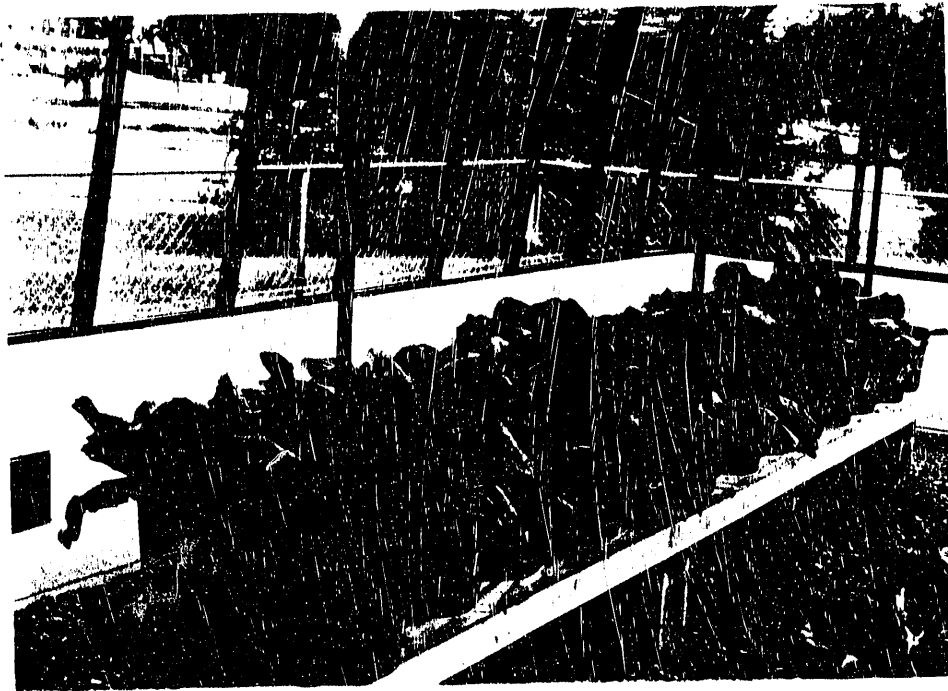


(a)

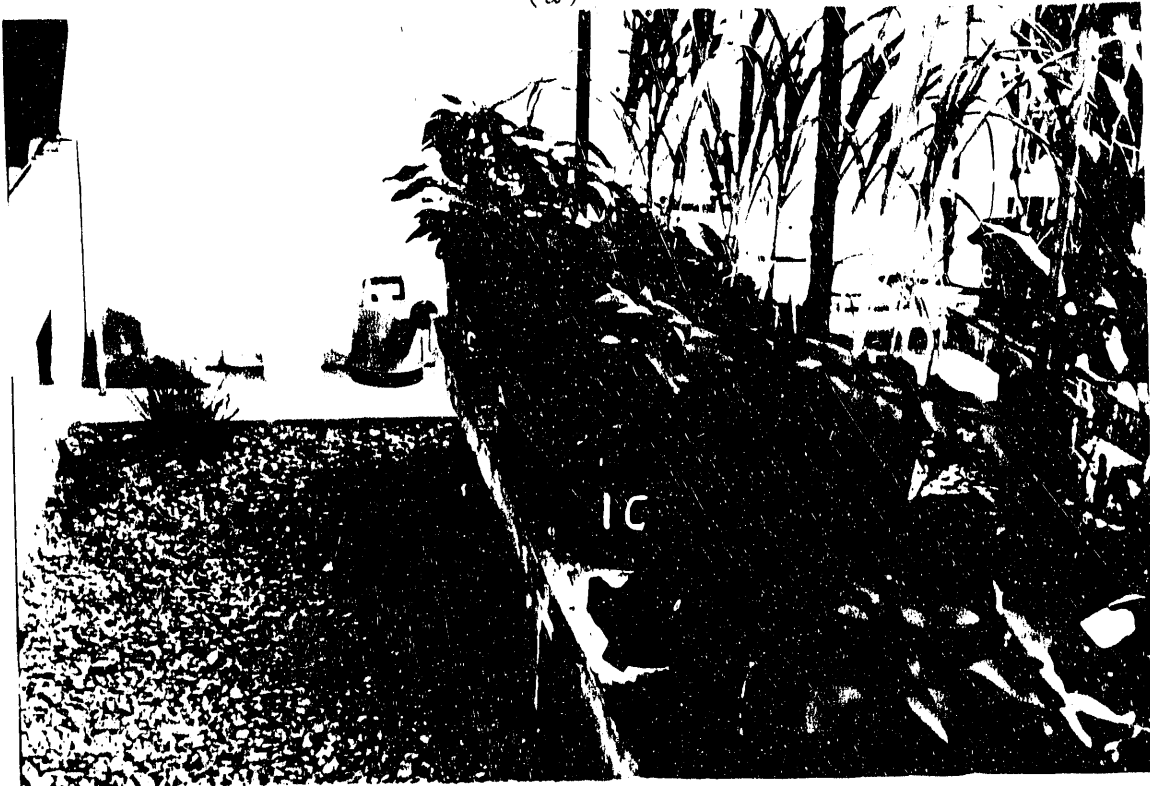


(b)

Figure 1. (a) Photograph of the greenhouse
(b) Corn crop before harvest



(a)



(b)

Figure 2. (a) Crop of mustard greens before harvest

(b) Crop of bell peppers before harvest

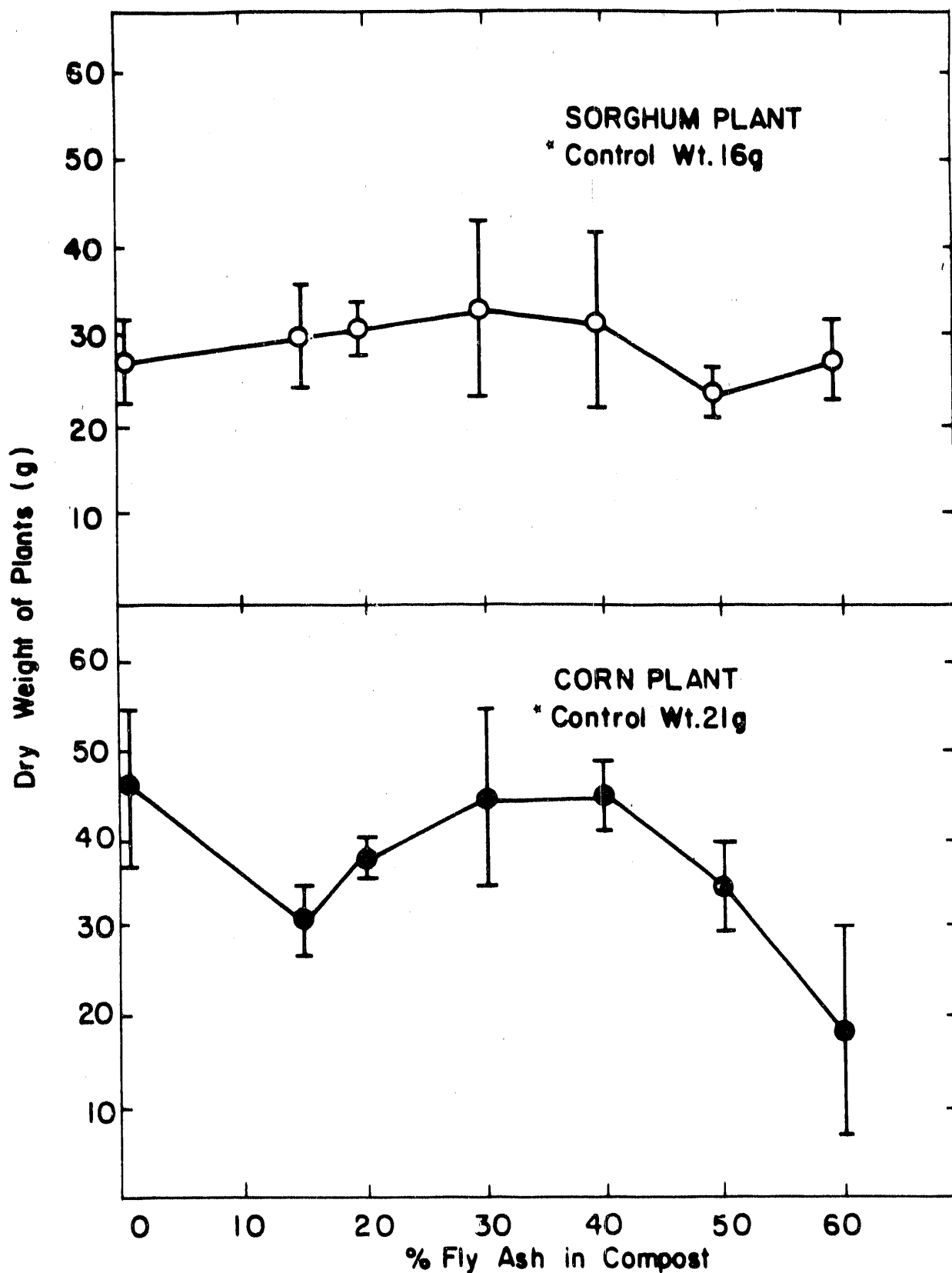


(a)



(b)

Figure 3. (a) Bell pepper crop under three different treatments
(b) String bean crop under three different treatments



FA-Compost/Soil Ratio = 1:3; * : Control; "Home-made" Compost

Figure 4. Plots of the yields of corn and sorghum as a function of percent of fly ash in compost

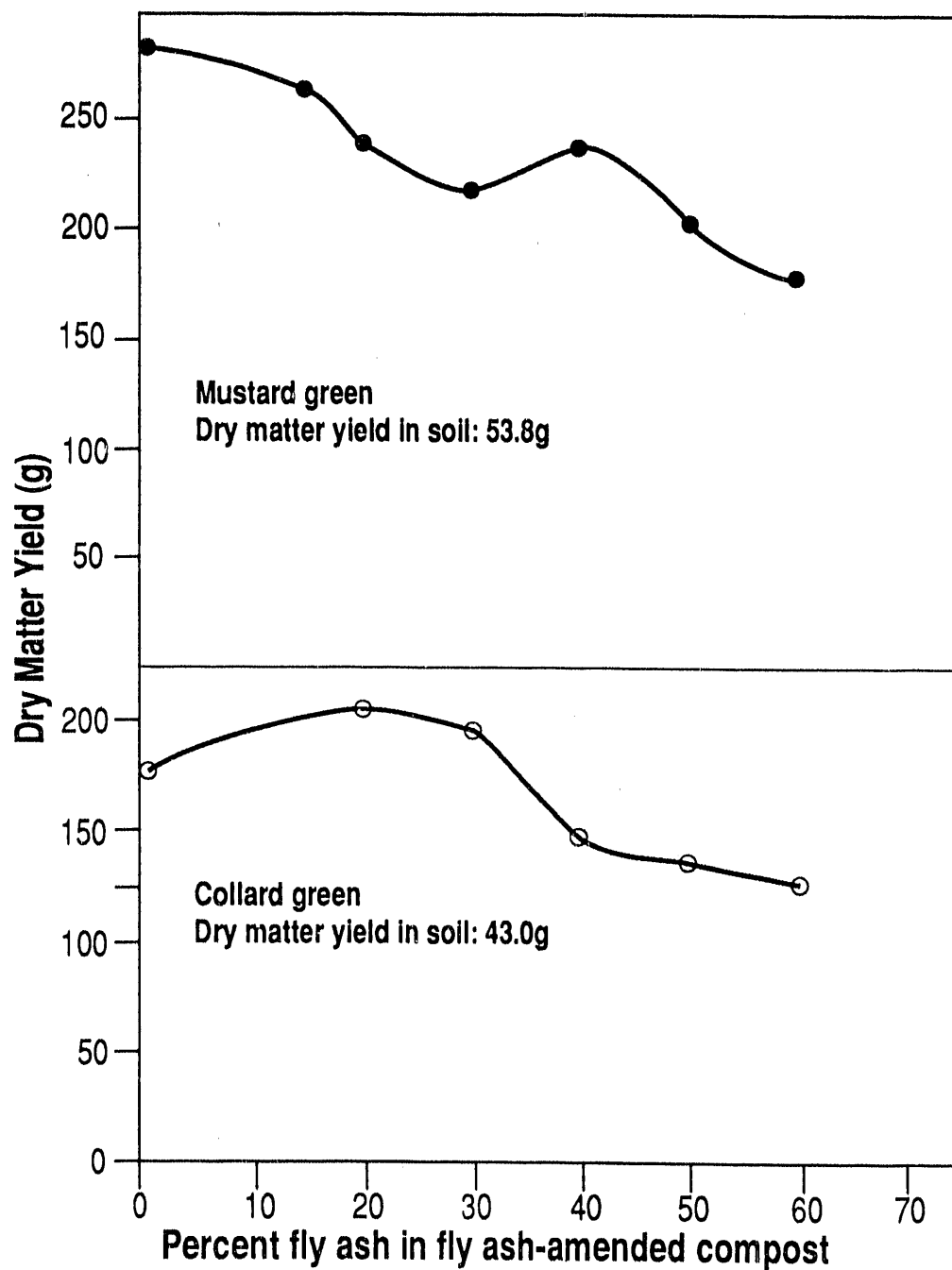


Figure 5. Plots of dry matter yields of mustard greens and collard greens as a function of percent fly ash in compost

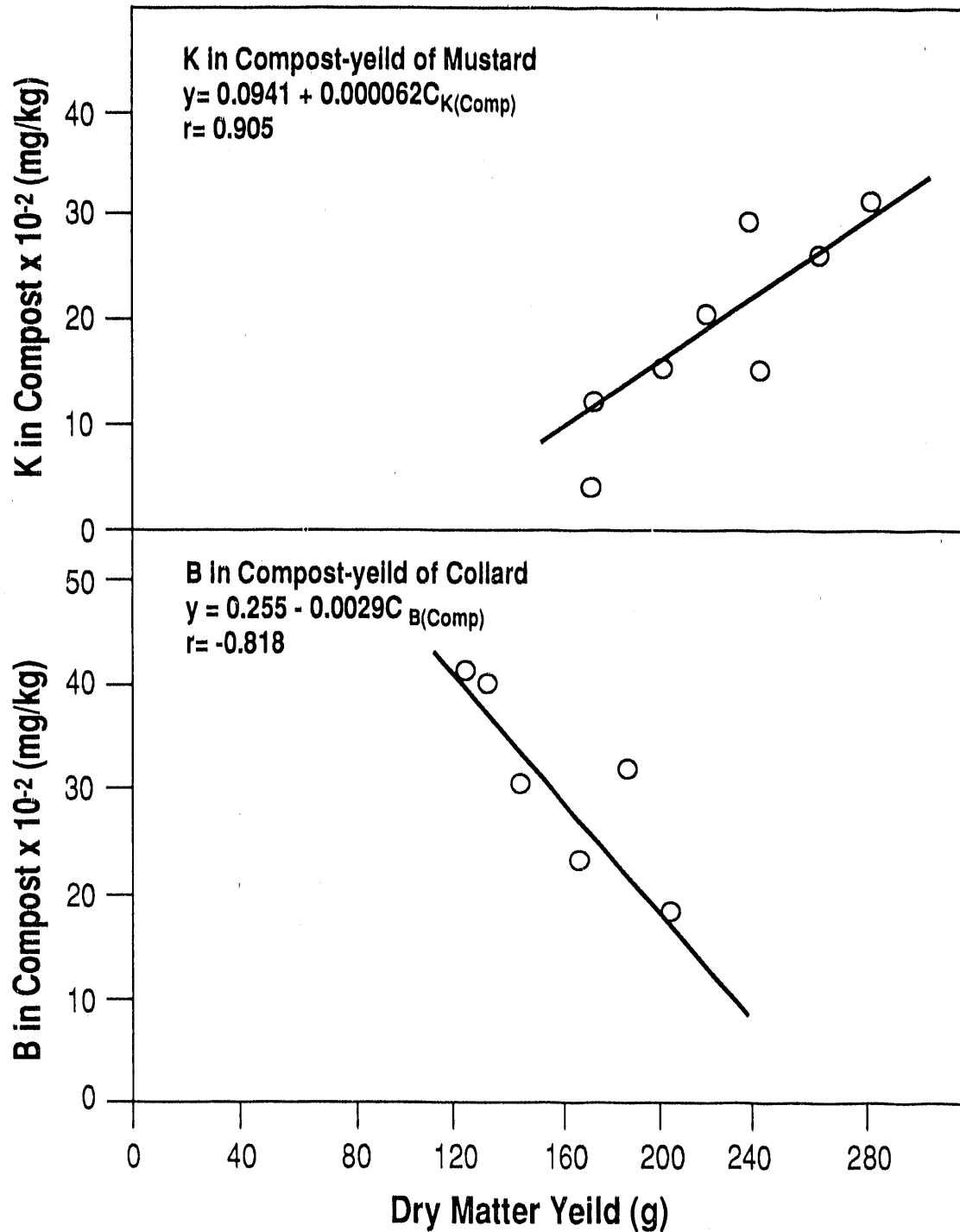


Figure 6. Correlations between elements in compost and dry matter yield.

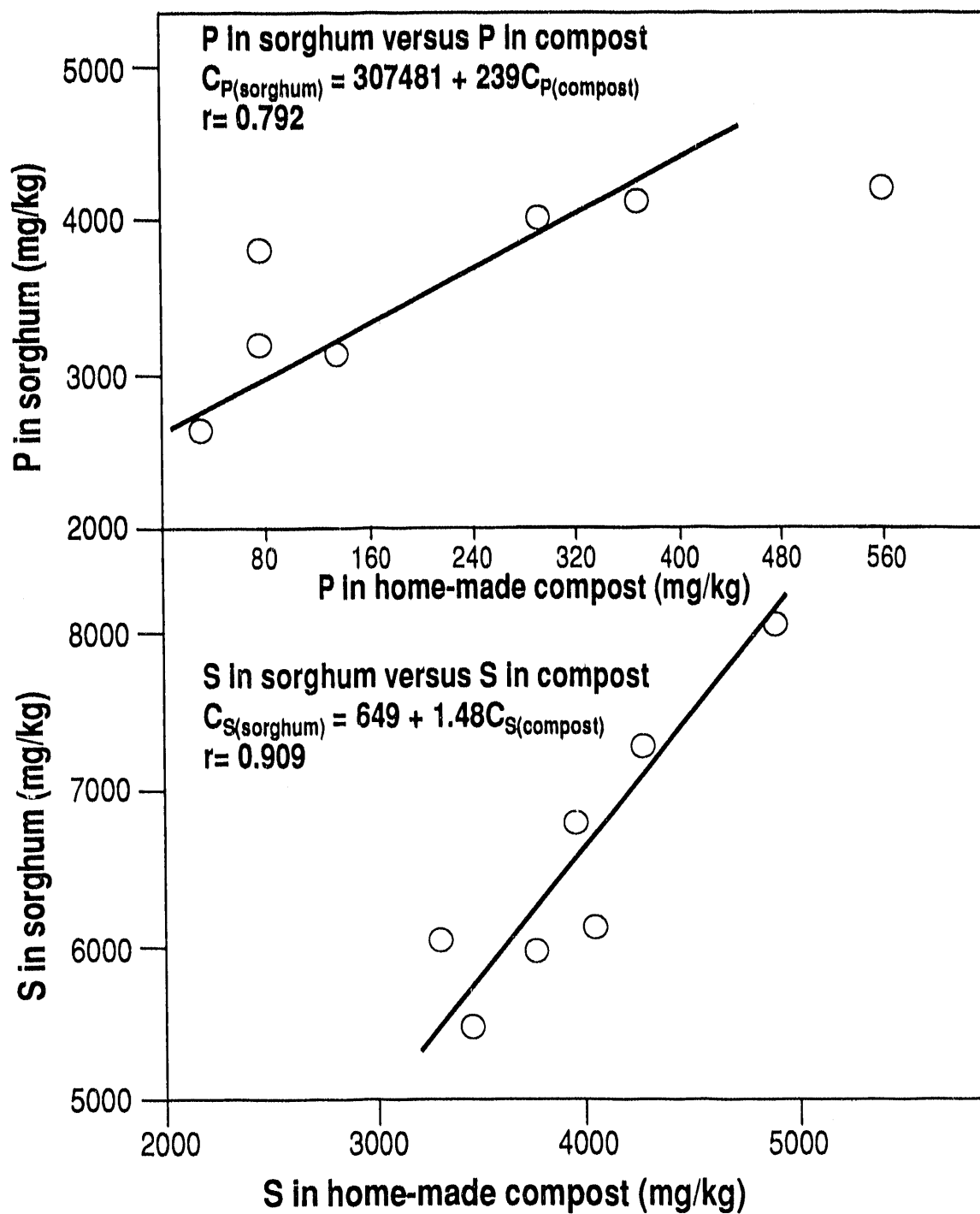


Figure 7. Correlations between S and P in sorghum plant and their respective concentrations in compost.

PART III: PERSONNEL PARTICIPATED IN THE PROJECT

<u>Name</u>	<u>Research Title</u>	<u>Current status</u>
<u>Senior Personnel</u>		
Manchery P. Menon	Principal Investigator	Professor at SSC
Gian S. Ghuman	Co-investigator	Professor at SSC
J. James	Co-investigator	Professor at SSC
Kailas Chandra	Co-investigator	Professor at SSC
Kenneth Sajwan	Participant (nonremunerative)	Research Scientist at SREL, Aiken, S.C.
<u>Student Participants</u>		
Delwin Jackson	Research Assistant	Graduated, accepted at Georgia Tech.
Vicorine McDonald	Research Assistant	Graduated, went to Graduate school
David Wright	Research Assistant	Graduated, working in a laboratory
Lemile D. Chandler	Research Assistant	Graduated, 1991
Ruby D. Reed	Research Assistant	Prospective Graduate, Aug. 1991
Tracy Anderson	Research Assistant	Senior at SSC
McDonald Collette	Research Assitant	Senior at SSC

Benjamin Bacon	Research Assistant	Senior at SSC
Venu Bhatanagar	Research Assistant	studying for MBA at SSC
Katrina Robinson	Research Assistant	Junior at SSC
Leon Banks	Research Assistant	Junior at SSC
Lashawn Brisbon	Research Assistant	senior at SSC
Malay Kumar	Research Assistant	studying for MBA at SSC
Hamid Raza	Research Assistant	Senior at SSC
Senobia Y. Owen	Research Assistant	Graduated, working in a Company.

PART IV: PAPERS PRESENTED IN SCIENTIFIC MEETINGS

1. M.P. Menon, G.S. Ghuman, J. James, K. Chandra and D.C. Adriano. Physical and Chemical Characteristics of Water Extracts of Different Coal Fly Ashes and Fly Ash-amended Composts. Sixty-Sixth Georgia Academy of Science Meeting, Valdosta State College, Valdosta, GA, April 28-29, 1989.
2. G.S. Ghuman, M.P. Menon, K. Chandra, J. James and D.C. Adriano. Dissolution of Metals from Fly Ash in Aqueous Systems. Sixty-Sixth Georgia Academy of Science Meeting, Valdosta State College, Valdosta, GA, April 28-29, 1989.
3. M.P. Menon, G.S. Ghuman, J. James, K. Chandra and D.C. Adriano. Effects of Coal Fly ash-amended Composts on the Yield and Elemental Uptake of Plants. International Conference on Metals in Soils, Waters, Plants and Animals, Orlando, FA, April 30-May 3, 1990.
4. G.S. Ghuman, M.P. Menon, D.C. Adriano, K. Chandra and J. James. Uptake of Metals by Corn from Fly ash-compost amended soil. International Conference on Metals in Soils, Waters, Plants and Animals, Orlando, FA, April 30-May 3, 1990.
5. B.B. Bacon^{*}, M.P. Menon, G.S. Ghuman, J. James, D.C. Adriano and K. Chandra. Optimization of Treatment Parameters for the Use of Fly ash-amended Composts for Plant Growth. Sixty-Seventh Georgia Academy of Science Meeting, Mercer University, Macon, GA May 4-5, 1990.

6. G.S. Ghuman, M.P. Menon, J. James, K. Chandra and K. Sajwan. Effect of Coal Fly Ash-amended Organic Compost as a Manure for Agricultural Crops. Sixty-Eighth Georgia Academy of Science Meeting, Fort Gordon, Augusta, GA, April 26-27, 1991.
7. M.P. Menon, G.S. Ghuman, J. James, K. Chandra and K. Sajwan. Fractionation and Transport of Nutrients among Coal Fly Ash Residues and in Soil covered with Fly Ash-amended Organic composts. Twentyfirst International Symposium on Environmental Analytical Chemistry, Holiday Inn, Jekyll Island, GA, May 20-22, 1991.
8. M.P. Menon, G.S. Ghuman, J. James, K. Sajwan and K. Chandra. Environmental Impact and Beneficial Effects of Coal Fly Ash on Soil and Agricultural Crops. ISEP International Symposium on Environmental Pollution. Bond Place Hotel, Toronto, Canada, June 6-7, 1991.

* Student authors

PART V: PUBLICATIONS

A. Papers either published or those in press

1. M.P. Menon, G.S. Ghuman, J. James, K. Chandra and D.C. Adriano. Physico-chemical Characterization of Water Extracts of Different Coal Fly Ashes and Fly Ash-amended Composts. Water, Air, and Soil Pollut. 50: 343-353, 1990.
2. M.P. Menon, G.S. Ghuman, J. James and K. Chandra. Effects of Coal Fly Ash-Amended Composts on the Yield and Elemental Uptake by Plants. J Environmental Science and Health. 1991 (in press).
3. M.P. Menon, G.S. Ghuman, J. James, K. Chandra, K.S. Sajwan and D.C. Adriano. Nutrients in Coal and Coal Ash Residues and their Potential for Agricultural Crops. A chapter in "Trace Metals, Coal and Coal combustion Products (eds.) K.S. Sajwan, D.C. Adriano and R.F. Keefer. 1991 (in press).

B. Manuscripts under Review

1. M.P. Menon, G.S. Ghuman, J. James, K. Chandra and K. Sajwan. Environmental Impact and Beneficial Effects of Coal Fly Ash on Soil and Agricultural Crops. J Agricul. Food Chem.
2. M.P. Menon, G.S. Ghuman, J. James, K. Chandra, B. Bacon^{*} and K. Sajwan. Fractionation and Transport of Nutrients among Coal Ash Residues and in

Soil covered with Fly Ash-amended Organic Compost. Water, Air, and Soil
Pollution.

PART VI: APPENDIXES

- A. Copies of Reprints of Published Paper(s).
- B. Copies of Abstracts of Paper(s) in Press.
- C. Copies of the Abstracts of Paper(s) under Review

APPENDIX A: COPIES OF REPRINTS OF PUBLISHED PAPER(S)

PHYSICO-CHEMICAL CHARACTERIZATION OF WATER EXTRACTS OF DIFFERENT COAL FLY ASHES AND FLY ASH- AMENDED COMPOSTS*

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(Received September 7, 1989; revised February 12, 1990)

Abstract. The pH, conductivity and the concentration of 15 selected elements were measured in the water extracts of five coal fly ash samples collected from Savannah River Site (SRS) and one from South Carolina Electric and Gas (SCE & G) power plant. This work was intended to study the differences in the physico-chemical properties of SRS fly ash samples relative to those of a reference sample (SCE & G) and to make fly ash-amended composts for agricultural use. Similar analyses were also performed in water extracts of a commercial organic manure, 'Gotta Grow', that was composted with one of the fly ash samples (SRS 484-D) in different proportions. Our results show that fly ash samples used in this study differ considerably in pH, conductivity, and elemental composition and that transition metals appear to bind more tightly on smaller particles than on larger ones. The elementally rich manure, 'Gotta Grow', is not suitable to study the effects of fly ash on the elemental release from fly ash-amended composts. Low grade or home-made organic composts are being investigated as possible choice for making fly ash-amended composts.

1. Introduction

Out of all naturally available resources coal plays a dominant role as a source of energy. According to the President's national energy plan the production of coal in United States alone will reach an all time high of 1.91×10^9 t by the year 2000 (Gordon, 1978). The coal excavated from different parts of the country or of the world such as bituminous, sub-bituminous, lignite and Australian hard and soft brown coals are different in their chemical composition and physical characteristics (Brown and Swaine, 1964; Yudovich *et al.*, 1972). Burning of coal in power plants results in the accumulation and emission of a variety of by-products, the most important of which is the fly ash. Depending upon the geological history of the coal the ash yield can vary anywhere from 4 to 30% of the crude coal (Bolch, 1980).

Considerable amount of work has been carried out in the United States and other countries on the utilization and disposal of fly ash, the major waste product of coal-fired power plants (Adriano *et al.*, 1980; Phung *et al.*, 1978; Martens and

* paper presented at sixty-sixth annual meeting of the Georgia Academy of Science, Valdosta State College, Valdosta, Ga, April 28-29, 1989

Plank, 1974; Salter *et al.*, 1971). The fly ash is currently used, with no regard to its chemical composition, in land-filling, in construction industry, as a filler in asphalt mix, stabilizer for road bases, thermal insulation, and deodorization of animal wastes (Bolch, 1980). Large fly ash particles are removed by dust collectors while the smaller particles are collected by electrostatic precipitators. The physical, mineralogical and chemical properties of fly ash depend on the composition of the parent coal, coal burning conditions and emission control devices (Adriano *et al.*, 1980). Fly ash consists of particles of all sizes ranging from 2 to 1000 μm in diameter. There have been reports that the elements present in crude coal are partitioned not only among the different types of coal ash residues but also among particles of different size in fly ash (Page *et al.*, 1979; Davison *et al.*, 1974).

Most of the work carried out so far to utilize fly ash for vegetation centered on efforts to amend the soil characteristics with the addition of fly ash. Our research, on the other hand, is aimed at the utilization of fly ash to amend the characteristics of organic compost for agricultural use in acidic soil. In this paper we report the results of the analysis of six different fly ash samples (five from Savannah River Site (SRS) and one from South Carolina Electric and Gas (SCE & G) power plant and of fly ash amended organic composts.

2. Materials and Methods

2.1. COLLECTION AND PROCESSING OF FLY ASH SAMPLES

Four drums (208 L) full of fly ash was collected from SRS 484-D power plant which is equipped with an electrostatic precipitator. This was very fine fly ash ($< 500 \mu\text{m}$ in diam.) which was later used for making fly ash amended composts. Several kilogram quantities of coal ash were also collected from the plants: SRS 784-A, SRS 184-K, SRS 105-P and SRS 200-H being operated at different locations within the Savannah River operation facilities. Since none of these plants is provided with an electrostatic precipitator the ash samples contained both coarse and fine particles. One fly ash sample (SRS 184-K) which showed marked difference in concentration of elements than the rest was separated into three fractions according to particle size, using U.S.A. standard testing sieves, for elemental distribution studies. All of these samples were collected in plastic bags. For comparison of the results of analysis of SRS fly ash samples with those from a reference sample, coal fly ash was also obtained from the SCE & G power plant. All fly ash samples were dried in an air-oven at 50°C for 24 hr before preparing water extracts.

2.2. STUDY OF THE EQUILIBRATION PROCESS OF SUSPENDED FLY ASH IN WATER

Ten grams of the dried fly ash samples (SRS 484-D and SCE & G) were mixed separately with 100 mL of distilled-deionized (DD) water in 250 mL Erlenmeyer flasks and shaken for 1 min. The mixture was then agitated on an Eberbach top-loading shaker for 1 hr except for samples with a waiting time of 30 min. The

mixture was filtered through a Millipore filter paper (0.45 μm pores) into polyethylene bottles using suction. The experiment was repeated several times changing the waiting time before filtration from 0.5 hr to 7 days. For each waiting time three identical samples were processed in the same manner. The pH, conductivity, total weight of the solids and the concentration of a few selected metals were measured in each of the filtered samples. These experiments demonstrated that it takes at least five days for the fly ash to reach equilibrium with its dissolved components to show nearly constant values. The extraction time for all water extracts of all fly ash samples for detailed analysis was therefore, chosen as 5 days.

To determine the extent of extractability of water soluble salts by the first and subsequent extractions, the residue from the 5-day extract of SRS 484-D and SCE & G ash samples was equilibrated with the same volume of DD water, agitated and left for 5 d as before. The pH and conductivity of the filtrate from this extract were measured. Residue from this extract as well as that from the third extract were also processed in a similar manner.

2.3. PREPARATION OF FLY ASH AMENDED COMPOSTS

Fly ash collected from SRS 484-D and the organic manure, 'Gotta Grow', purchased from Bricker's farm, Augusta, Ga were mixed in six different proportions (5, 10, 20, 30, 40 and 50% by weight FA) to make composts of six different compositions. The total weight of the fly ash and organic manure was 1 kg in each case. The fly ash and organic manure were mixed thoroughly in polyethylene containers and moistened with DD water. The containers were covered partially with lids and left for six weeks so that the components could react with each other and decompose. At least once in a week the compost was turned over and mixed again adding more water, if needed, to keep them moist. During decomposition evolution of ammonia gas was evident by its strong smell.

2.4. CHEMICAL ANALYSIS OF FLY ASH SAMPLES AND FLY ASH-AMENDED COMPOST

All fly ash samples were equilibrated with DD water for 5 days in the same manner as described before and filtered through the Millipore filter paper. The filtrates from all samples were stored at 4 °C in a refrigerator until the time of analysis. All of the ten metals (K, Na, Ca, Mg, Zn, Mn, Cu, Cd, Mo, and Ni) reported in this work were determined by Perkin-Elmer's flame-atomic absorption spectrometer, model 306, using air-acetylene flame. Commercially available atomic absorption standards (Fisher Scientific) with appropriate dilution with DD water were employed for the construction of the calibration curves for the analysis of each metal. To improve the sensitivity of detection only single-element cathode tubes were used with the spectrometer for the determination of trace metals. Water extracts from fly ash amended composts after equilibration for 5 days (10 g of wet compost with 100 mL of DD water) were also analyzed for all the above metals except Mo which was below detection level, using the same technique. The water content of each compost was determined by weighing about 10 g of the wet compost in

a pre-weighed china dish and reweighing after it was dried in an air-oven at 55 °C overnight.

Boron was determined in both types of samples spectrophotometrically using the improved azomethine-H method (John *et al.*, 1975). Dissolved orthophosphate in each of the samples was also measured by a spectrophotometric method as P using a combined reagent consisting of 5 N H_2SO_4 , antimony potassium tartrate, ammonium molybdate and ascorbic acid (EMSL, 1979). Sulfate was measured as S by the turbidometric method using a conditioning agent that consists of ethanol, NaCl and glycerol with BaCl_2 as precipitating agent (EMSL, 1979). Perkin-Elmer model Lambda 3 spectrophotometer and the spectronic 20 colorimeter were used for the analysis of the above nonmetals. Chloride was determined as Cl and nitrate as N using the respective specific ion electrodes and Orion model 920 E expandable and digital ionanalyzer. In both cases, a double junction reference (Orion) electrode with appropriate outer chamber solutions were used to make EMF measurements. A constant volume of the ionic strength adjustment buffer (ISAB) was added to the standards and samples before analysis.

3. Results and Discussion

Results of the studies on the equilibration of two fly ash samples collected from SRS 484-D and SCE & G plant sites, as depicted in Figures 1 and 2, show that

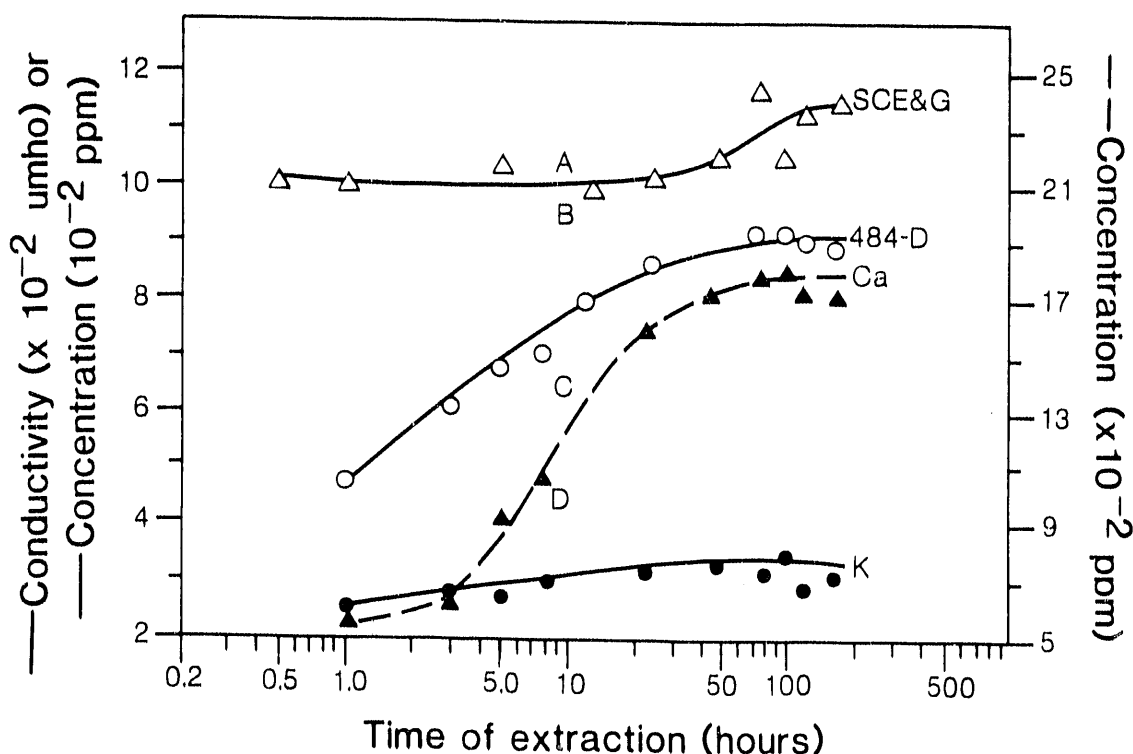


Fig. 1. Measured conductivity and the concentration of K and Ca vs extraction time (A: Conductivity (SCE & G sample); B: Conductivity (SRS 484-D sample); C: Conc. of Ca (SRS 484-D sample); D: Conc. of K (SRS 484-D sample)).

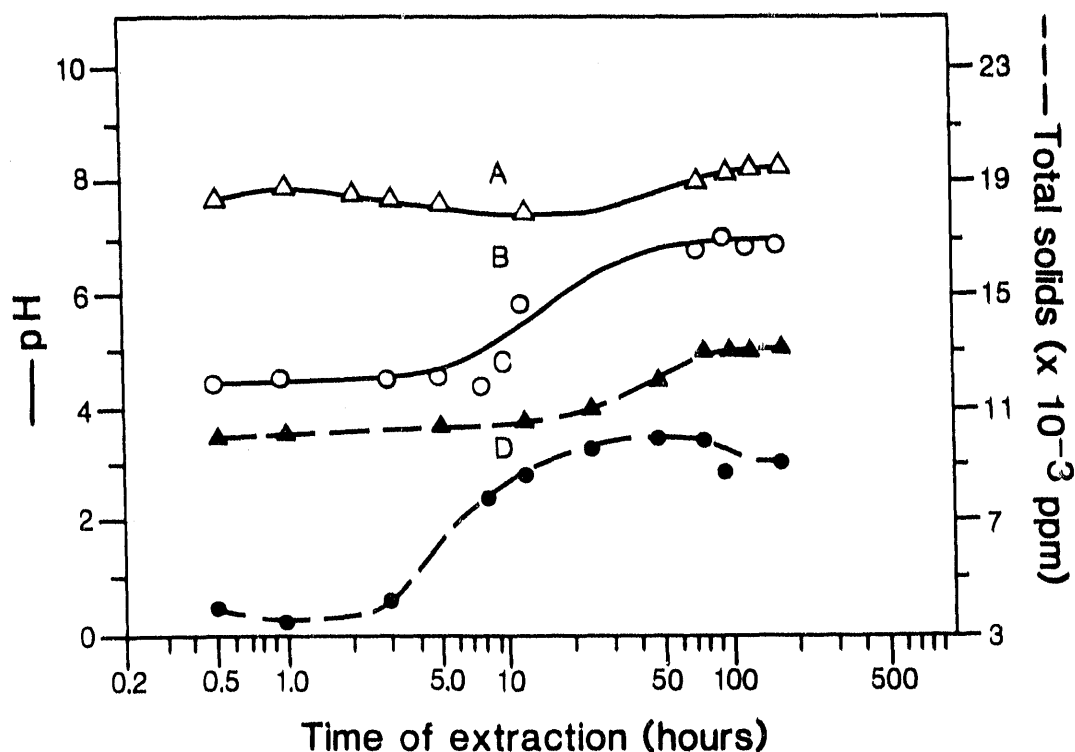


Fig. 2. pH and concentration of total solids vs extraction time (A: pH (SCE & G sample); B: pH (SRS 484-D sample); C: Total solids (SCE & G sample); (D) Total solids (SRS 484-D sample)).

the pH, conductivity and the concentration of two selected metals (Ca and K) increased with extraction time and reached a plateau after 4 to 5 days. This indicates that for the analysis of water soluble cations and anions in fly ashes, the samples should be equilibrated with water for at least 5 days. All fly ash samples were therefore, equilibrated with water in 1:10 ratio for a period of five days before

TABLE I

Conductivities and pH of water extracts from fly ash and fly ash amended compost

Water extracts of fly ashes

Measured quantity	SRS 484-D	SRS 784-A	SRS 184-K	SRS 105-P	SRS 200-H	SCE & G
Conductivity (μmho)	927	1199	1816	973	999	1095
pH	6.96	4.25	3.94	4.47	4.58	8.37

Water extracts of fly ash amended composts

Measured quantity	Comp.(1) 0% FA	Comp.(2) 5% FA	Comp.(3) 10% FA	Comp.(4) 20% FA	Comp.(5) 30% FA	Comp.(6) 40% FA	Comp.(7) 50% FA
Conductivity (μmho)	9050	6510	5530	5350	4690	4400	5230
pH	8.51	8.49	8.03	8.08	7.60	7.43	8.62

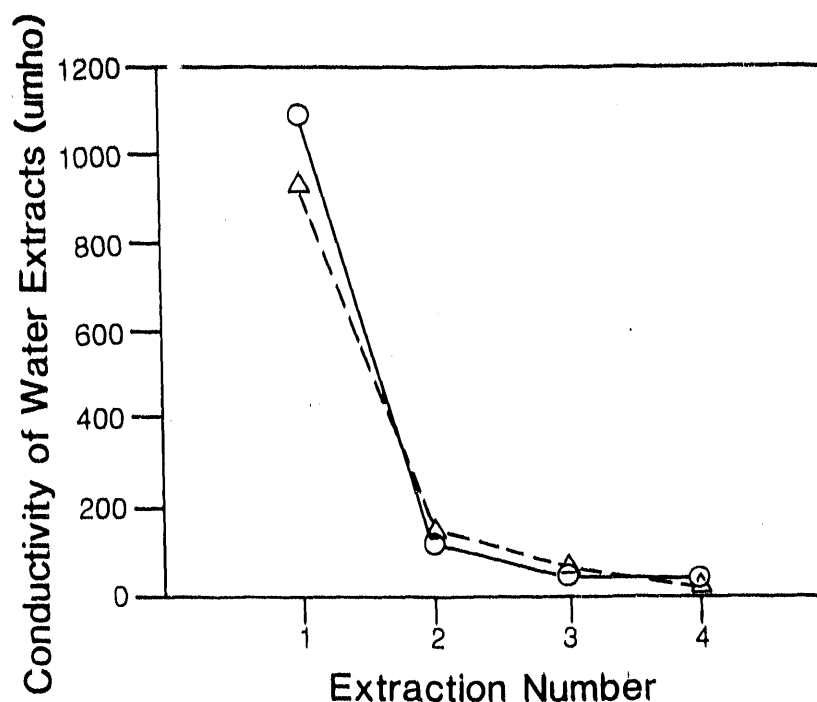


Fig. 3. Conductivity of fly ash extracts vs extraction number (O): Water extracts from SCE & G samples; (Δ): water extracts from SRS 484-D samples).

analysis. The pH and conductivity of water extracts of fly ash samples and of fly ash-amended composts equilibrated for 5 days are shown in Table I. It is obvious from this table that ashes collected from four plants (SRS 784-A, SRS 184-K, SRS 105-P and SRS 200-H) are acidic while fly ash from SRP 484-D is neutral and that from SCE & G plant is basic. The decrease of conductivity with repeated extractions (Figure 3) suggests that water soluble nutrients from fly ash are available to the plants, if it is used as an amendment to compost, for a period of ten days. Table I also reveals that the pH and conductivity of water extracts of fly ash amended composts are very different from those obtained for the water extracts of SRS 484-D ash.

The analytical results of the measured concentrations of selected metals and nonmetals in the fly ash extracts are presented in Table II. There is considerable difference in the concentration of some of the elements among ashes collected from different plants. Fly ash sample collected from SRS 184-K contains the largest amount of Mg, Zn, Mn, and B. This sample which contains particles of different size was therefore, chosen for fractionation and elemental distribution studies. It can also be seen from this Table that SRS 484-D fly ash is relatively rich in Ca, but contains smaller quantities of transition metals (Zn, Mn, Cd, Cu, and Ni). The amount of B and S that are detrimental to plant growth are also relatively small in this sample. It is possible that the transition metals have been bound very strongly with the very fine ash (particle size: $< 500 \mu\text{m}$ in diam.) generated by this plant because of the operation of the electrostatic precipitator so that these

TABLE II

Results of analysis of coal fly ash collected from coal-fired plants at and near Savannah River plant facilities

Element	SRS 484-D	SRS 784-A	SRS 184-K	SRS 105-P	SRS 200-H	SCE & G ^a
	ppm					
K	184 (7) ^b	510 (18)	124 (16)	150 (14)	461 (7)	449 (16)
Na	145 (18)	329 (8)	553 (15)	214 (33)	334 (32)	540 (30)
Ca	1895 (69)	875 (50)	1517 (63)	1867 (14)	1443 (16)	1942 (58)
Mg	40.6(1.9)	97.4(7.9)	240 (5.8)	107 (3.6)	85.8(3.4)	109 (6)
Zn	0.2(.1)	39.3(2.9)	47.2(4.1)	5.3(.7)	29.8(1.0)	0.3(0.1)
Mn	4.6(2.1)	34.6(.9)	724 (16)	63 (5)	53 (6)	7.5(1.8)
Cd	0.2(.1)	0.5(.1)	0.5(.1)	0.1(.1)	0.3(.1)	0.4(.2)
Mo	ND	ND	ND	ND	2.8(.3)	5.7(2.3)
Ni	3.0(.8)	6.7(.2)	20.5(.4)	2.3(.5)	6.4(.4)	2.7(.5)
B	29.3(.3)	35.3(.5)	65 (0.8)	33 (.8)	27 (.5)	48 (2)
Cl	83 (.9)	124 (15)	83 (.9)	85 (2)	71 (.3)	124 (3)
P	ND	0.2(.1)	2.2(.1)	ND	ND	1.8(.2)
S	683 (52)	1833 (5.3)	3667 (37)	1117 (10.1)	1217 (8)	1517 (21)
	7.9(.9)	6.6(.7)	5.1(.4)	7.5(1.1)	6.3(.3)	6.9(.2)

a: 5 d old equilibrated water extract.

^a SCE & G Plant away from SRP.^b () Standard Deviation.

metals are not extracted significantly with water. This hypothesis is supported by our findings from elemental distribution studies on fractionated ash samples from SRS 184-K. It has been suggested that a high temperature volatilization of species containing the trace elements and preferential adsorption onto smaller particles during coal burning are factors that contribute to the high concentration (not necessarily water extractable) of these elements in smaller particles (Davison *et al.*, 1974). Most of the values reported in Table II are within the reported range of concentration of elements in fly ash (Elseewi *et al.*, 1980).

Table III lists the results of analyses of fly ash amended composts of different compositions. All of these values have been normalized to dry compost or corrected for their water content. The first column of table III reveals that the commercially purchased organic manure itself, when composted without any fly ash, releases significant amounts of ionic species of all elements that are extractable with water. This suggests that the added fly ash may not be that much beneficial in enriching the organic manure, 'Gotta Grow', with significant amounts of the nutrients. It was later recognized that 'Gotta Grow' is the richest organic manure that Bricker's farm sells. Use of low grade or home-made organic manure may be a better choice for making fly ash amended composts.

In order to ascertain the effect of fly ash on composted material, the analytical data for selected elements were treated as follows: The amount of an elemental species released during composting was computed from the difference between the amount measured in the composted material ($X_{el,(comp.)}$) and the total amount ($X_{el,(i)}$)

TABLE III
Results of analysis of coal fly ash amended compost made with organic manure

Element	Comp.(1) 0% FA	Comp.(2) 5% FA	Comp.(3) 10% FA	Comp.(4) 20% FA	Comp.(5) 30% FA	Comp.(6) 40% FA	Comp.(7) 50% FA
ppm of elements normalized to dry compost							
K	23,026	26,672	24,657	22,709	20,409	17,204	11,183
Na	8,670	7,952	8,140	4,941	4,299	3,280	2,212
Ca	1,352	2,232	1,452	1,915	1,753	1,214	1,100
Mg	436 (103) ^a	419 (61)	214 (11)	228 (27)	613 (18)	557 (16)	168 (14)
Zn	69 (7)	77 (10)	65 (5)	53 (2)	42 (4)	27 (2)	25 (4)
Mn	6.2(3.1)	6.7(0)	5.7(0)	8.2(1.6)	4.8(0)	3.3(1.1)	1.5(1.1)
Cu	17 (3)	24 (3)	17 (6)	14 (0)	18 (2)	24 (3)	18 (2)
Cd	0.8(3)	0.4(2)	0.4(1)	0.0	0.2(1)	0.3(1)	0.3(1)
Ni	32 (2)	29 (1)	33 (5)	24 (5)	16 (8)	11 (1)	8 (1)
B	80 (5)	46 (2)	22 (4)	33 (6)	31 (1)	25 (1)	36 (4)
P	316 (21)	295 (76)	362 (13)	324 (11)	307 (7)	282 (9)	372 (26)
S	2,550 (22)	2,906 (32)	2,578 (71)	2,185 (52)	1,970 (53)	1,879 (37)	1,792 (27)
N	939 (109)	754 (60)	677 (69)	692 (49)	524 (39)	429 (48)	497 (45)
Cl	32,589	33,675	29,572	19,831	17,344	12,226	11,949

^a () Standard Deviation; in the case of major elements the deviation is, in general, less than 5%.

initially present in the mixture using the equations:

$$X_{el.(i)} = a_M \cdot X_{el.(M)} + b_{F.A.} \cdot X_{el.(F.A.)} \quad (1)$$

and

$$X_{el.(rel.)} = X_{el.(comp.)} - X_{el.(i)}, \quad (2)$$

where $X_{el.(M)}$ and $X_{el.(F.A.)}$ are the concentrations of the element in the water extracts of the manure (not shown) and fly ash, respectively, a_M and $b_{F.A.}$ are the fractions of manure and fly ash used for compost and $X_{el.(rel.)}$ is the amount that was released during composting. Plots of $X_{el.(rel.)}$ vs $b_{F.A.}/a_M$ are shown in Figure 4 for four elements. The observed logarithmic relations can be expressed by the equation:

$$X_{el.(rel.)} = X_{el.(0)} e^{-k(b_{F.A.}/a_M)} \quad (3)$$

where k may be regarded as a dilution constant for the manure. Since the slopes of the straight lines are almost the same within the experimental errors one can

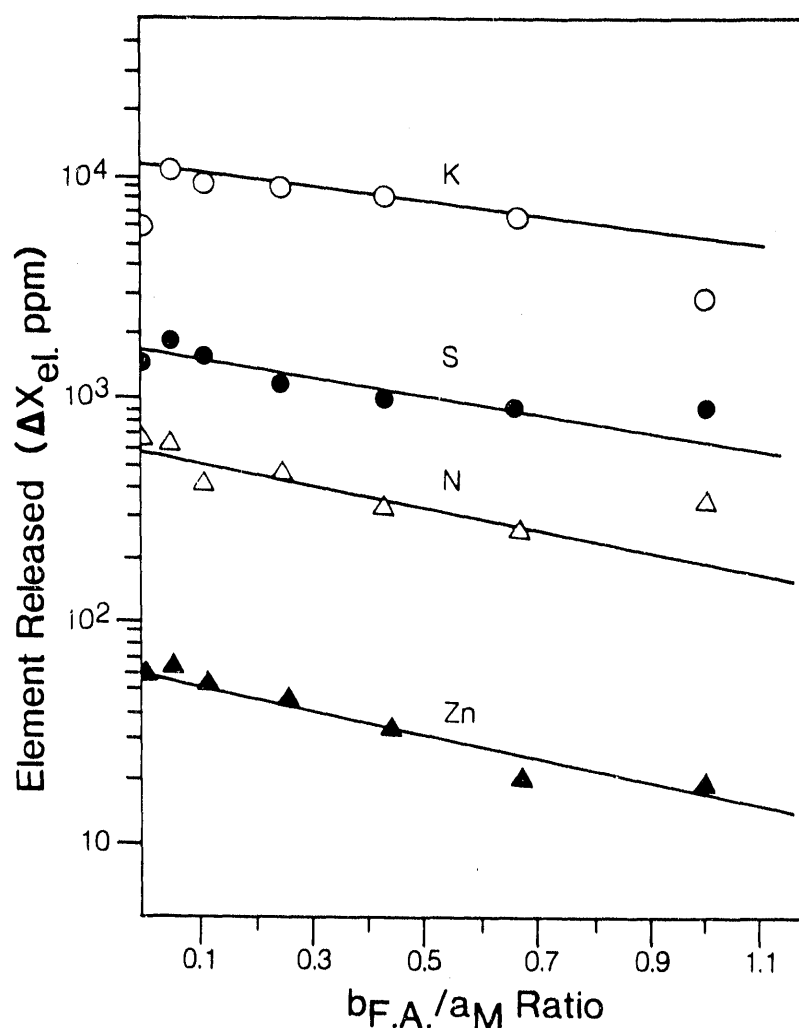


Fig. 4. A plot of element released during composting against fly ash to organic manure ratio.

TABLE IV
Distribution of selected elements among fractionated SRP 184-K fly ash samples^a

Measured quantity	Fraction (1)	Fraction (2)	Fraction (3)
Size	<180 μm	<500 μm	>500 μm
Percentage	70.2	20.4	9.4
Conductivity (μmho)	1609 \pm 2.8	1142 \pm 83	1438 \pm 35
pH	3.98	3.98	3.86
	ppm		
Na	733.4 \pm 42	542.1 \pm 22	904.8 \pm 16.4
K	135.2 \pm 40.3	91.8 \pm 33.3	156.1 \pm 43.7
Ca	1715.0 \pm 212	517.0 \pm 58	411.0 \pm 100
Mg	291.0 \pm 29	244.0 \pm 6	352.0 \pm 8
Zn	28.4 \pm 0.4	25.2 \pm 0.7	36.2 \pm 1.7
Mn	46.6 \pm 0.7	44.2 \pm 1.6	67.6 \pm 3.9
Cu	0.6 \pm 0.3	3.1 \pm 0.5	4.5 \pm 2.6
Ni	12.7 \pm 0.5	9.7 \pm 0.5	18.5 \pm 2.1
B	66.2 \pm 2.8	76.8 \pm 5.0	76.9 \pm 4.3
S	3562.0 \pm 309	2960.0 \pm 375	3260.0 \pm 227

^a Equilibrated water extracts were analyzed.

conclude that in each case only the dilution effect of the manure was observed in composts of various composition.

The results of the distribution of selected elements among fractions of SRS 184-K fly ash sample separated according to particle size are presented in Table IV. Analysis was performed on the water extracts of the separated fractions as described before. In general, the fraction with particles greater than 500 μm in diameter yielded greatest concentrations of these elements in water extract in conformity with the suggested mechanism of absorption and retention of elements by coal ash during coal burning process. There are also differences in pH and conductivities of water extracts of these fractions.

4. Conclusion

There is considerable difference in pH, conductivity and elemental concentrations in water extracts of fly ashes collected from different coal-fired power plants. The concentration of water extractable transition metals such as Zn, Mn, Cd, Cu, and Ni as well as the B and S content of fine fly ash collected from SRS 484-D which is equipped with an electrostatic precipitator are smaller than the concentrations of the respective elements in water extracts of other ashes. The 'Gotta Grow', the rich organic manure purchased from Bricker's farm is not suitable to study the effects of fly ash on the elemental release from fly ash amended composts. Low grade or home-made organic compost may be a better choice for making fly ash amended organic composts. A logarithmic correlation between the concentration

of the elements released during composting and the fly ash-to-manure ratio in the compost has been observed with the manure we used for the study. Fractionation studies show that there are variations in the concentrations of elements in water extracts of fractions of SRS 184-K ash separated on the basis of particle size.

Acknowledgments

The financial support provided by the U.S. Department of Energy through their grant No. DE-FG09-88SR18047 for this work is gratefully acknowledged. The laboratory assistance rendered by the students, Benjamin Bacon and Hamid Raza is also appreciated.

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APPENDIX B: COPIES OF ABSTRACTS OF PAPER(S) IN PRESS

EFFECTS OF COAL FLY ASH-AMENDED COMPOSTS ON THE YIELD AND ELEMENTAL
UPTAKE BY PLANTS

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ABSTRACT

The objective of this study was to determine the feasibility of coal fly ash-amended composts for use as an alternate manure for agricultural crops. "Home-made" organic compost was mixed with fine fly ash collected from Savannah River Site (SRS 484-D), in various proportions and allowed to decompose for two weeks, keeping the mixture wet. Water extracts from the amended composts were analyzed for selected major and trace elements. These amended composts were mixed with sifted sandy loam soil in a predetermined optimum ratio of 1:3 and used to grow corn and sorghum plants. It was shown that "home-made" compost could be used for efficient utilization of nutrients in fly ash by plants at 20-40% fly ash in compost when applied to the soil. The maximum dry shoot yields of both corn and sorghum were obtained with the application of amended compost containing 25% of fly ash. The maximum shoot yields correlated with the higher concentrations of K, Ca and N and lower concentration of B at 20-40% fly ash in the amended compost treatment.

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NUTRIENTS IN COAL AND COAL ASH RESIDUES AND THEIR POTENTIAL FOR
AGRICULTURAL CROPS

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A chapter

in "Trace Metals, Coal and Coal combustion Products (eds.) K.S. Sajwan, D.C.
Adriano and R.F. Keefer, 1991 (in press)

APPENDIX C: COPIES OF THE ABSTRACTS OF PAPER(S) UNDER REVIEW

ENVIRONMENTAL IMPACT AND BENEFICIAL EFFECTS OF COAL FLY ASH ON SOIL
AND AGRICULTURAL CROPS

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ABSTRACT

Organic compost (Home-made) prepared from grass clippings was amended with fine fly ash collected from a coal-fired power plant (SRS 484-D) at Savannah River Plant site, Aiken, S.C. to investigate its usefulness as a manure for agricultural crops. Direct application of fly ash to soil for plant growth resulted in poor yield due to high salinity, pH, deficiency for N and P and the toxicity of B. Composting of fly ash with carbonaceous material will not only reduce the deleterious effects of fly ash but also release additional nutrients required for plant growth. Fly ash-amended compost containing 20-40% fly ash was found to be effective in enhancing the dry matter yield of collard greens and mustard greens by 378% and 348%, respectively over the control. In earlier study the increase in yield for corn was found to be 114% and for sorghum 106%. However, string beans, bell pepper and egg plant did not show any significant increase in dry matter yield by the application of this manure. Analysis of the above ground biomass showed a large amount of boron uptake by the last three plants, which may be the reason for poor growth.

FRACTIONATION AND TRANSPORT OF NUTRIENTS AMONG COAL ASH RESIDUES AND IN
SOIL COVERED WITH ASH-AMENDED ORGANIC COMPOST

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Abstract

Burning of coals in coal-fired power plants generates different types of ash residues and discharges small particles and vapors to the atmosphere. The ash residues which account for the major part of the byproducts are collected and stored as bottom ash, boiler ash, fly ash, weathered ash and ash in lagoon. Analysis of water extracts of these residues will reveal how the nutrients are distributed in these residues and transported to aquatic systems. Equally interesting is the study of the downward movement of nutrients in soil treated with fly ash-amended organic compost when used as a manure for agricultural crops. In this work water extracts of different types of ash residues and eluates from descending ports of an experimental column of soil treated with fly ash-amended compost at the top, were analyzed for selected nutrients. In addition, sections of column soil at different depths were also analyzed. Our results showed that there is considerable difference in the efficiency of removal and deposition of nutrients on different residues collected from the power plant and stored outside. Bottom ash was

found to accumulate K, N, and S while Ca is enriched in ash from lagoon. Transition metals such as Zn, Mn and Cu are concentrated in weathered ash. The concentration of most of the nutrients was found to decrease, in column experiments, as a function of depth and levels of at a depth of 80 cm.

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