4 Influence of Fly Ash Application on Heavy Metal Forms and Their Availability

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CONTENTS

4.1 INTRODUCTION

Despite continuing efforts to find alternative and environmentally safe energy sources, coal remains a major fuel used for production of electricity worldwide. In the world today, about 25% of the energy produced, or 38% of the total electricity consumed, is generated from coal. Although a declining trend of coal use was recorded recently [1], the forecast is that coal consumption for energy production will increase. This is because the energy requirements continue to increase in response to a steadily increasing world population and coal remains an abundant and relatively cheap natural energy source.

Countries substantially dependent on coal for electric power generation include the U.S. (56%), China (80%), and India (66%) [2]. Europe (EU-15) on average produces 25% of its electricity from coal, although in some member countries this percentage is over 50%. For example, electricity power in Poland is almost fully coal based and in countries like Denmark and Germany over 50% of the electricity consumed is generated from coal [2]. Greece produces the second largest amount of coal in Europe and the sixth largest in the world. The available coal deposits are estimated to be about 3.2 billion tons; this is considered adequate for the next 45 years [3]. Over 73% of the power requirements of Greece come from lignite and its annual consumption is estimated at about 64 Mt [4].

During combustion in a power plant, coal generates great quantities of residues known as coal combustion products (CCP). They include the noncombustible mineral components of coal that are partitioned into fly ash (FA), bottom ash (BA), boiler slag (BS), and flue gas desulfurization residue (FGD). Fly ash generally consists of fine particles that are not easily disposed

of. Most of this fraction of CCPs is captured by pollution control devices before release to the atmosphere. Mechanical collectors remove the coarser and predominantly sand-sized particles, and the finer silt-sized particles are removed by electrostatic precipitators. The amount of fly ash produced each year is enormous. For example, the total fly ash production in the U.S. was 63 million tons in 1998. The respective amount of fly ash produced annually in Greece is estimated to be nearly 13 million tons [5].

Knowledge of fly ash properties may provide insights for determining appropriate methods of treatment. The properties of fly ash are determined by the composition of the parent material (coal) and the conditions during coal combustion. Efficiency of emission control devices as well as storage and handling affect at large fly ash properties. Adriano et al. [7] and El-Mogazi et al. [8] provided excellent reviews of fly ash properties. They concluded that morphology of fly ash helps in understanding its physical properties and leaching behavior.

Fly ash is usually considered an amorphous ferro–aluminum silicate mineral [7] because a typical fly ash aggregate consists of spherical particles embedded in an amorphous matrix. Chang et al. [9] determined that fly ash is composed of approximately 63% silt-sized particles in the range of 2 to 50 μm; 33% of the particles had a diameter > 50 μm and the remainder had a diameter < 2 μm. The surface area varies between 0.46 and 1.27 $m^2\ g^{-1}$ and this influences the sorptivity of nutrients [10]. Chemically, fly ash contains almost all existing elements in nature. However, the major matrix elements are Si, Al, and Fe, as well as Ca, K, Na, and Ti.

Most of the fly ash produced is disposed of by landfilling, stockpiling, and storage in settling ponds. The remainder is used as cement, concrete, or ground material; raw feed for cement clinker; structural fill; road base; mineral filler; snow and ice control; mining applications; agricultural application; and so on. In 2000, from a total of 57.14 million tons of fly ash produced in the U.S., about 68% was disposed of; the remaining was recycled through the previously mentioned uses [6].

Nevertheless, fly ash has become an increasing disposal problem in many countries of the world. A sound alternative to fly ash recycling is its agronomic utilization. Research so far has shown many advantages of fly ash utilization as soil amendment, which brings about improvement of soil texture [11] and bulk density [12]; increase of water-holding capacity through increased porosity [12]; increase of soil pH in acid soils [13,14]; and increase of soil salinity, especially with unweathered fly ash, and of nutrient concentrations [13]. All these beneficial effects usually result in increased crop yield as has been reported by several workers [13,15–17]. However, fly ash addition to soils may also have adverse effects on crop growth, usually due to B, salt, and heavy metal toxicity. El-Mogazi et al. [8] summarized these adverse effects on several agricultural crops. In most cases, B and salt toxicity can be reduced if fly ash is preleached [18].

From an environmental point of view, the effect of fly ash on the concentration of heavy metals in soil is of special interest. Heavy metals of environmental significance in fly ash include As, Cd, Pb, Mo, Ni, Se, and Zn [8]. Relevant research has shown that application of fly ash to soil at various rates increases heavy metal content of some crops while others remain unaffected. In a pot experiment, Furr et al. [19] investigated the influence of fly ash application on the uptake of 42 elements by several crops. They found that fly ash application increased As, Mo, and Ni concentration in the edible parts of beans; As in cabbage; and As and Mo in carrots. However, fly ash application did not increase heavy metal concentration in onions, potatoes, and tomatoes.

In a similar study, Furr et al. [20] found that application of 50 tons/acre of fly ash increased As and Se concentration in several crops, including the edible parts of vegetables like beans, cabbage, carrots, potatoes, and tomatoes. Increased heavy metal uptake was also found for apple, millet, and vegetables [21] for the elements B, Co, Cu, and Mo and corn grain [22].

The main alternatives to the agronomic utilization of fly ash in Greece are cement additives and disposal in landfills. Research on the implications of application of domestic fly ash to soil is limited, although an increasing interest was recently expressed [13,23]. This chapter presents the

results of an experiment on the influence of fly ash and sewage sludge on soil quality and on wheat growth and heavy metal uptake.

4.2 MATERIALS AND METHODS USED

The influence of fly ash on soil properties and wheat characteristics was investigated in a greenhouse pot experiment in which an acidic soil classified as Typic Haploxeralf was used, and in a field experiment in an acid soil from Central Greece, classified also as Typic Haploxeralf. Some chemical properties of the soils used are presented in Table 4.1.

Fly ash was collected from the electrostatic precipitator of a lignite-fired electric power plant in Northern Greece and aged for 3 months by maintaining in open air and leaching periodically with deionized water. The material was strongly alkaline (pH 12.1); its heavy metal composition is shown in Table 4.2. Sewage sludge was the same for both experiments and it was collected from the waste water treatment plant of the city of Tirnavos (central Greece). Its composition determined according to Leschber et al. [24] is shown in Table 4.3.

In the greenhouse experiment, a completely randomized block design was composed of seven treatments with four replicates each (Table 4.4). The application rates of fly ash (fa1, fa2) were determined in a preliminary incubation experiment in which addition of 30 g fly ash/pot resulted in a

TABLE 4.1
Selected Properties of the Soils Used in the Experiments

Properties	Pot experiment soil	Field experiment soil
pH (water 1:1)	4.85	5.01
Clay content, %	15	13
Organic matter content, %	1.8	0.61
Cation exchange capacity, cmol(+) kg^{-1}	13	9.50
Base saturation, %	38	55
Electrical conductivity (1:5), mmhos cm^{-1}	0.11	0.05
Total Zn, mg kg^{-1}	42.3	29.86
Total Mn, mg kg^{-1}	275	254
Total Cu, mg kg^{-1}	38.7	24.20
Total Ni, mg kg^{-1}	34.65	12.23
Total Pb, mg kg^{-1}	49.52	11.93
Total Mo, mg kg^{-1}	—	11.43
Total Se, mg kg^{-1}	—	0.33
Total Cd, mg kg^{-1}	—	0.62
Total Co, mg kg^{-1}	—	5.82
Total As, mg kg^{-1}	—	1.68

TABLE 4.2
Heavy Metal Concentration (mg kg^{-1}) Extracted by DTPA and HNO_3 of the Fly Ash Used in the Experiments

Extraction method	As	Cd	Co	Cu	Mn	Mo	Ni	Pb	Se	Zn
DTPA	nd	nd	nd	0.8	nd	nd	0.5	0.5	nd	nd
HNO_3	17.2	3.2	10.7	28.1	135.1	35.9	170.6	36.5	3	18.5

nd: not detected.

TABLE 4.3
Some Characteristics of the Sewage Sludge Used in the Experiments

pH (H_2O 1:1)	$CaCO_3$ (%)	EC, mmhos/cm	Organic matter content (%)	Total N (%)	Zn (mg kg^{-1})
6.5	1.1	2.87	34.0	4.45	1320
Cu, mg kg^{-1}	Ni, mg kg^{-1}	Pb, mg kg^{-1}	Cd, mg kg^{-1}		
287	46.4	183.0	1.49		

TABLE 4.4
Treatments of the Pot Experiment

Codes	Treatments
c (control)	Soil without amendments
if	Soil plus inorganic fertilizers at 150 kg N/ha and 80 kg P_2O_5/ha
fa1	Soil plus 30 g fly ash/pot only
fa2	Soil plus 90 g fly ash/pot only
fass1	Soil plus 2.65 g sewage sludge/pot plus 30 g fly ash/pot
fass2	Soil plus 5.25 g sewage sludge/pot plus 30 g fly ash/pot
fass3	Soil plus 10.5 g sewage sludge/pot plus 30 g fly ash/pot

TABLE 4.5
Treatments of the Field Experiment

Codes	Treatments
C (control)	Soil without amendments and fertilizers
IF	Without amendments but 160 kg N/ha and 80 kg P_2O_5/ha
FA1	22.5 tons fly ash/ha plus the same amount of N and P
FA2	67.5 tons fly ash/ha plus the same amount of N and P
FASS1	22.5 tons fly ash/ha plus 6.3 tons/ha sewage sludge
FASS2	22.5 tons fly ash/ha plus 12.6 tons/ha sewage sludge

pH of 6.5 and addition of 90 g/pot further increased soil pH to 7.5. The mixtures of fly ash and sewage sludge with 2.5 kg of soil were wetted to field capacity and equilibrated in the pots for 1 month. Fifteen seeds/pot of durum wheat (*Triticum aestivum* L.) were planted in the pots and grown for 2 months in a nonheated greenhouse. The ground plant parts were then harvested, dried, and weighed. At the same time, soil samples from all pots were collected, air-dried, crushed, and sieved with a 2-mm sieve. Soil samples were analyzed for pH, and DTPA-extractable and total heavy metal content.

A 2-year field experiment was conducted near the city of Larissa in central Greece. The selected treatments in a completely randomized block design are presented in Table 4.5. Fly ash rates were selected after a preliminary incubation experiment. Each treatment was replicated four times in experimental plots of 16 m^2 each.

The amendments were applied in October and the field was planted with durum wheat (*Triticum aestivum* L.) in November. At the harvesting time in June, surface composite soil samples were taken in order to determine heavy metal content (As, Ni, Se, Mo, Cd, Co, Zn, and Pb). Heavy metal determination included extraction with DTPA [25]; digestion with 4 M HNO_3 at 80°C overnight [26]; and fractionation to exchangeable, organic matter and carbonate bound, and clay-associated forms according to Emmerich et al. [27]. Soil pH was measured in a water:soil 1:1 suspension according to McLean [28]. Plant samples were analyzed for heavy metal content after

dry ashing at 500°C and dialysis with dilute HNO_3. The same heavy metals were measured in wheat grain after the appropriate preparation. Heavy metal content in the extraction solutions was determined by atomic absorption spectrometry or inductively coupled plasma (ICP).

In addition to these analyses, soil samples taken from the field plots were sequentially extracted to determine the distribution of Cu, Ni, and Zn in the exchangeable, organic, carbonate, and residual pools. The exchangeable-associated metals were extracted with KNO_3; the organic-associated forms with NaOH; the carbonate-bound metals with EDTA; and the residual metal concentrations with 4 N HNO_3 digestion [27].

Grain yield and concentration of heavy metals in soil, plant, and wheat grain were evaluated using analyses of variance (ANOVA) procedures. To separate treatment means, the least significant difference (LSD) at $P < 0.05$ test was used. Regression analysis was performed when necessary. When differences between treatments are significant, they are indicated with 1 asterisk for a probability level of 95%, with 2 asterisks for a probability level of 99%, and with 3 asterisks for a probability of 99.9%.

4.3 RESULTS AND DISCUSSION

4.3.1 Pot Experiment

Fly ash application increased soil pH significantly. Soil pH progressively increased from 5.02 in the control to 6.62 in the low fly ash treatment to 7.48 in the high fly ash treatment (Table 4.6). The addition of sewage sludge to fly ash did not further increase soil pH because pH in the sewage sludge treatments was not greater than that in the fa1 treatment. This finding was expected because the initial pH of sludge was 6.5 (Table 4.1). The application of the inorganic fertilizer, however, decreased soil pH by about 0.2 units, probably due to nitrification of ammonium.

Fly ash and sewage sludge application significantly increased total heavy metal concentration in soil (Table 4.6). The addition of sludge also increased total metal concentration in soil. In contrast to total concentrations, the concentration of all DTPA-extracted metals was higher in the control treatment. The lowest DTPA (or available) concentrations were found in the high fly ash treatment (fa2) despite the increased total concentration of these metals. The reduced metal availability in the soil appears to be caused by the great pH increase due to fly ash addition.

The addition of sludge to fly ash progressively increased the available forms of the metals to levels similar to that of the control (Table 4.6). The increased metal extractability in the presence

TABLE 4.6
Effects of Fly Ash and Sewage Sludge Application on Soil pH, DTPA-Extractable and HNO_3-Digested Heavy Metals[a] in the Pot Experiment

		Treatment						
		CO	IF	FA1	FA2	FASS1	FASS2	FASS3
pH		5.02b[b]	4.81a	6.62e	7.48f	6.64d,e	6.39c	6.43c,d
DTPA	Cu	11.41c	9.36b	9.19b	7.84a	9.35b	9.49b	11.30c
	Pb	0.78b	0.42a	0.42a	0.39a	0.38a	0.80b	0.65a,b
	Cd	0.14d	0.10b	0.10b	0.07a	0.09b	0.09b	0.12c
	Zn	2.44d	1.71c	1.26a,b	1.09a	1.80c	1.64bc	2.65d
HNO_3	Cu	34.95a	75.31c	64.06b	74.67c	73.87c	76.69c	79.06c
	Pb	4.16a	7.87c	6.93bc	7.33b,c	7.31b,c	6.94b,c	6.62b
	Ni	88.95a	105.37c,d	91.03b	110.12c,d	106.23c	104.22c	118.12c
	Zn	63.95a	89.68c	74.84b	102.92c	98.12c	99.06c	95.94c

[a] mg kg^{-1}.

[b] Means within rows followed by different letter(s) are significantly different at probability level $P < 0.05$.

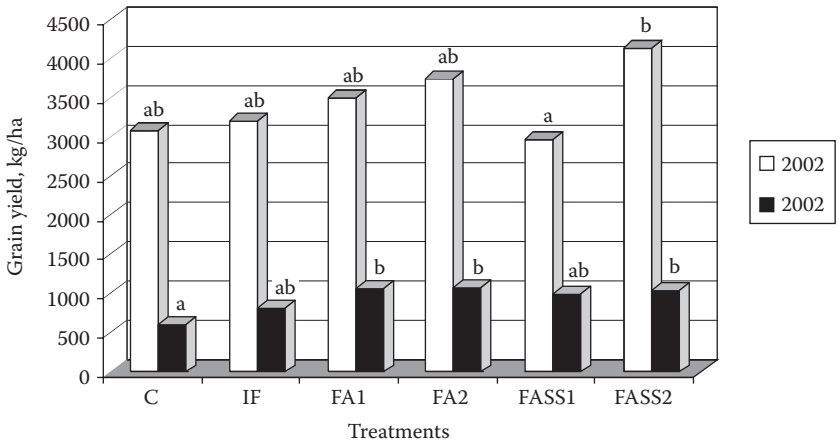

FIGURE 4.1 Influence of fly ash and sewage sludge application on wheat yield. (Bar means within years followed by different letter(s) are significantly different at $P < 0.05$.)

of sludge cannot be explained in terms of pH changes because soil pH did not increase after sludge addition. However, the increase in heavy metal availability after increased sewage sludge application to soil has been reported by many workers (for example, Antoniadis and Alloway [30]). The reduced availability of heavy metals due to fly ash application is a desirable property of this material that may prevent excessive uptake of heavy metals by crops. However, close monitoring is required in order to maintain an elevated soil pH (6.6 to 7.5 according to the data of this experiment), thus avoiding remobilization of heavy metals.

4.3.2 Field Experiment

Caution should be taken in the interpretation of the results because pot experiments have restricted value and may not be representative of field conditions. This is the reason that, in addition to the pot experiment, a field experiment was conducted, the results of which are presented below. A summary of the field treatments is shown in Table 4.5.

4.3.2.1 Influence of Fly Ash on Wheat Grain Yield

Fly ash application had no significant effect on grain yield the first year of the experiment (Figure 4.1). Significant difference in wheat yield occurred only between the two sludge-containing treatments. Yield was greatly reduced in the second year and this was attributed to adverse weather conditions. Even so, fly ash increased wheat yield when applied alone or in combination with sewage sludge (Figure 4.1). The only exception was the plant yield of the FASS1 treatment, in which it was significantly lower than in the rest of the treatments, even less than the control. This, however, should not be attributed to any toxicity effect because the trend was not consistent at FASS2 and was not recorded in the subsequent year.

The increased yield appears to be caused by a corresponding increase in soil pH due to fly ash application (Figure 4.2). Fly ash application increased soil pH from 4.61 in the control and 4.62 in the treatment with inorganic fertilizer to 5.32 at FA2 and 6.56 at FASS2. In contrast to the pot experiment, the addition of sludge to fly ash increased soil pH.

4.3.2.2 Influence of Fly Ash on Heavy Metal Content of Soil and Wheat

4.3.2.2.1 Total Heavy Metal Content in Soil

The total concentration of heavy metals in soil generally remained unchanged after application of fly ash or in combination with sewage sludge. This is indicated in Table 4.7 for the metals Cd, Co,

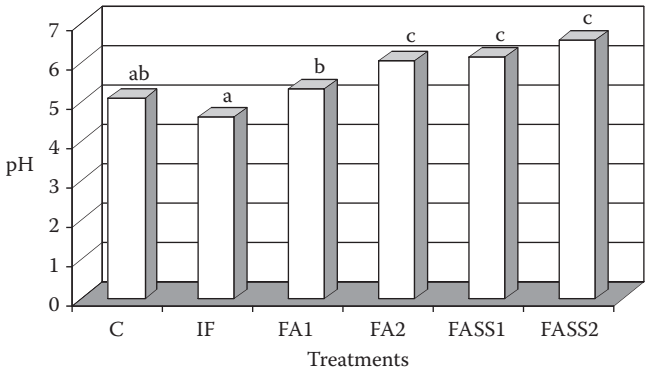

FIGURE 4.2 Influence of fly ash and sewage sludge on soil pH. (Different letters on bars show statistically significant differences at probability level $P < 0.05$.)

TABLE 4.7
Influence of Fly Ash and Sewage Sludge Application on Soil Heavy Metal Concentrations in the Field Experiment

Treatments	Metal concentration (mg kg^{-1})					
	Cd_{HNO3}	Cd_{DTPA}	Co_{HNO3}	Co_{DTPA}	As_{HNO3}	As_{DTPA}
C	0.575a[a]	nd	5.72a	0.175b,c	1.7a	0.12a
IF	0.525a	nd	5.77a	0.3d	1.8a	0.17a,b
FA1	0.575a	nd	5.82a	0.3c	1.85a	0.17a,b
FA2	0.6a	nd	5.75a	0.13b	1.7a	0.22b
FASS1	1.8a	nd	5.42a	0.10a	1.6a	0.3c
FASS2	0.6a	nd	5.45a	0.10a	1.77a	0.25b
	Mn_{HNO3}	Mn_{DTPA}	Mo_{HNO3}	Mo_{DTPA}	Ni_{HNO3}	Ni_{DTPA}
C	254a	20.78b	11.4b	0.125c	12.27a	0.95c
IF	248a	22.45b	9.22b	0.094b,c	11.7a	1.12d
FA1	250a	20.63b	2.55a	0.025b	12.37a	1cd
FA2	249a	13.38a	2.52a	0.028b	12.92a	0.8b
FASS1	242a	12.75a	2.37a	0.0002a	11.57a	0.65a,b
FASS2	245a	9.35a	9.68b	0.006a	12.1a	0.52a
	Zn_{HNO3}	Zn_{DTPA}	Se_{HNO3}	Se_{DTPA}	Pb_{HNO3}	Pb_{DTPA}
C	26.87a	0.62a	0.32c	nd	12.07a	0.57a,b
IF	24.7a	0.7a	0.32b,c	nd	11.42a	0.9b
FA1	16.75a	0.52a	0.25a	nd	11.92a	0.62a,b
FA2	16.65a	0.65a	0.3a,b,c	nd	11.9a	0.47a
FASS1	18.3a	0.87a	0.27a,b,c	nd	12.2a	0.5a
FASS2	26.4a	3b	0.35c	nd	12.6a	0.52a

[a] Values in the same columns followed by different letter(s) differ significantly at the probability level $p < 0.05$.

As, Mn, Ni, Zn, and Se and in Figure 4.3 for elements such as Mn, Zn, and Co. Total Mo concentration decreased in the treatments with fly ash compared to the control and inorganic fertilizer treatment. Only the high sludge application (FASS2) caused Mo concentration to increase to the level of the control treatment, possibly indicating that sewage sludge was enriched in Mo.

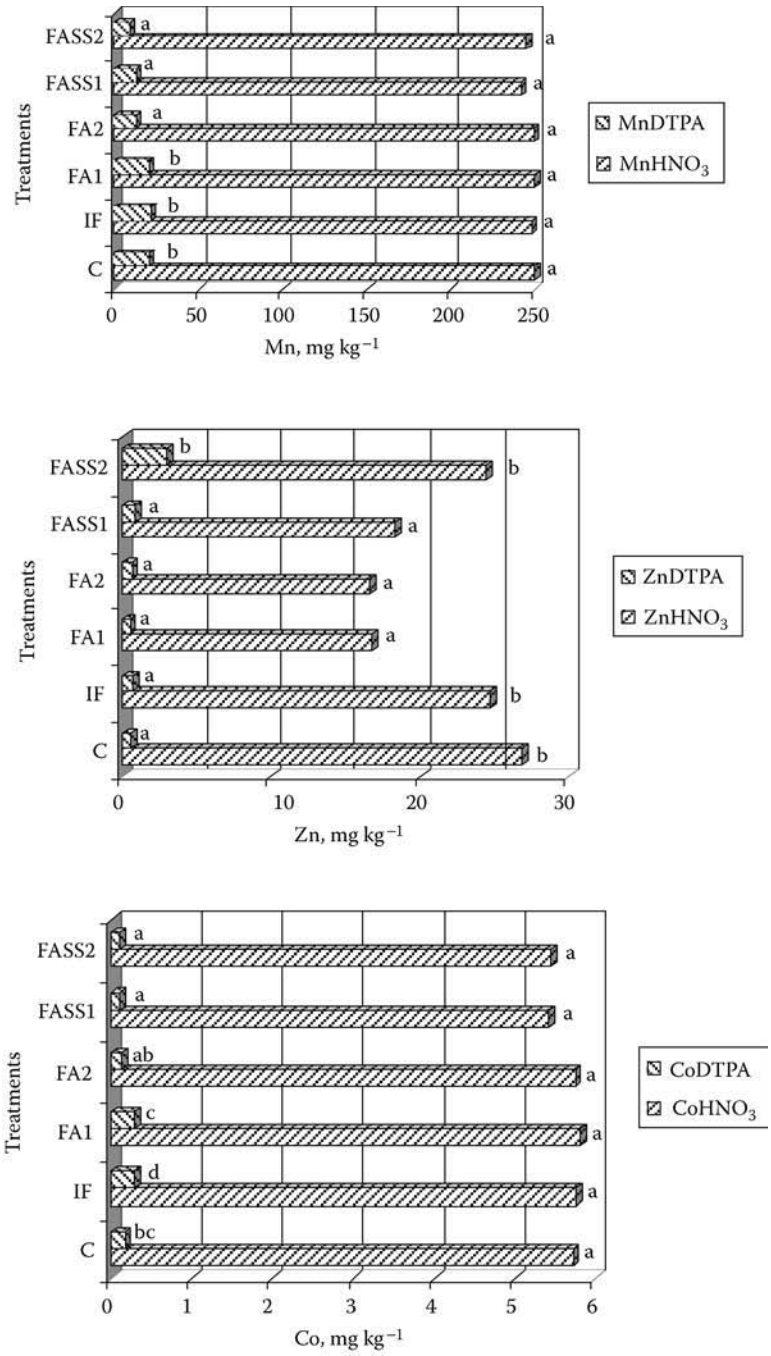

FIGURE 4.3 Influence of fly ash and sewage sludge application on total and DTPA extractable Mn (top), Zn (middle), and Co (bottom) in the field experiment. (Different letters on bars representing the same parameter indicate significant difference at probability level $P < 0.05$.)

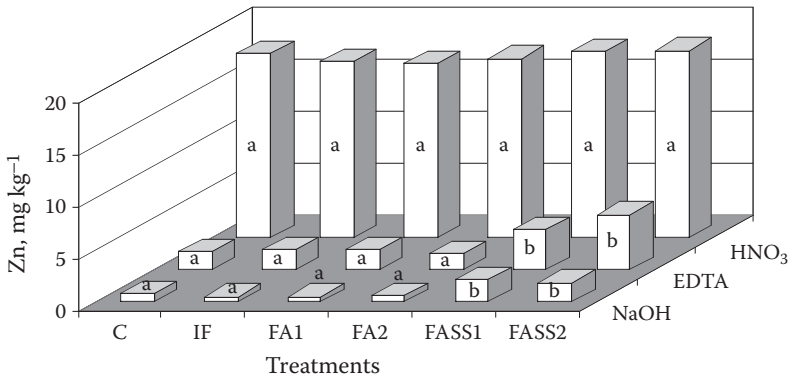

FIGURE 4.4 Influence of fly ash and sewage sludge on soil Zn fractions in the field experiment. (Different letters on bars representing the same fraction indicate significant difference at probability level $P < 0.05$.)

However, in the case of Ni, its concentration was higher in the treatment with the higher fly ash rate (FA2), probably due to the high Ni concentration in fly ash (170.6 mg kg^{-1}).

4.3.2.2.2 "Available" Heavy Metal Contents in Soil

The situation was different with the "available" forms of heavy metals, i.e., those extracted with DTPA. The "available" forms of heavy metals such as Co, Mn, Mo, Ni, and Pb decreased upon application of fly ash (Figure 4.3 and Table 4.7). Cadmium and Se concentrations extracted with DTPA were negligible. DTPA-extractable Zn and As concentration was higher in the sludge treatments; this should be attributed to the positive relationship of Zn and As with sewage sludge-borne organic matter. The fact that heavy metal availability decreased with fly ash application would be attributed to the pH effect as the significant negative correlations between soil pH and DTPA-extractable Co ($r = –0.74$***), Ni ($r = –0.74$***), and Pb ($r = –0.52$**) (data not shown) indicate. These correlations clearly show the effect of soil pH on metal availability, leading to the conclusion that fly ash application is a safe practice from the standpoint of reducing the availability of most metals in acid soils.

4.3.2.2.3 Heavy Metal Distribution in Soil

Three of the metals studied (Cu, Ni, and Zn) were fractionated into exchangeable-, organic- and carbonate-associated fractions. The changes in these fractions as a result of fly ash and sewage sludge application are presented in Figure 4.4 for Zn and in Figure 4.5 for Ni (data for Cu are not shown). The exchangeable fraction of Zn (KNO_3 extractable) was not affected by fly ash application. However, in the case of Ni, this fraction was negatively influenced by fly ash application. The organic-associated fraction (NaOH extractable) and the carbonate-bound fraction (EDTA extractable) were increased for Zn and Ni, but these fractions remained unaffected in the case of Cu.

The residual fraction (HNO_3 digested) remained unchanged in Zn and significantly increased in Ni. The implication of soil pH in determining the decrease in the exchangeable form is demonstrated by the significant correlations in Figure 4.6 for the exchangeable-, organic-, and carbonate-bound fractions of Ni and Cu. The data, therefore, indicate that fly ash provides metal forms that tend to diminish availability to plants.

4.3.2.2.4 Heavy Metal Concentrations in Wheat Grain

Heavy metal concentration was also measured in wheat grain. Cadmium and Co concentrations were at undetectable levels. Nickel and Se concentration in the treatments including fly ash and sewage sludge applications ranged between 3.52 and 7.20 and 1.13 and 2.14 mg kg^{-1}, respectively; this was not significantly different from that in the control and the inorganic fertilizer treatment

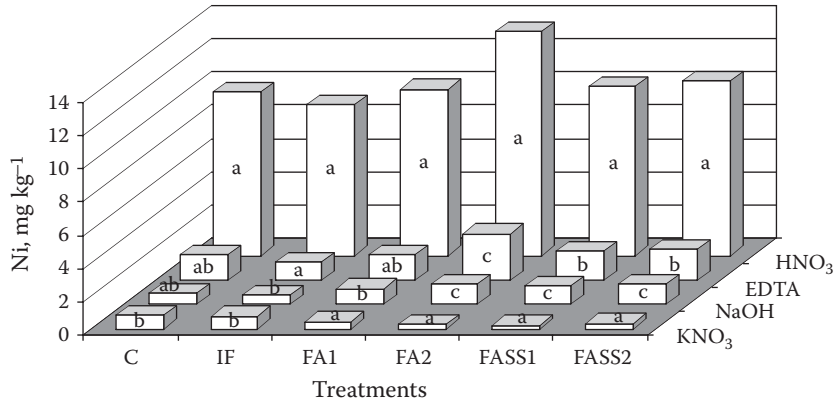

FIGURE 4.5 Fly ash and sewage sludge influence on Ni fractions in the field experiment. (Different letters on bars representing the same fraction indicate significant difference at probability level $P < 0.05$.)

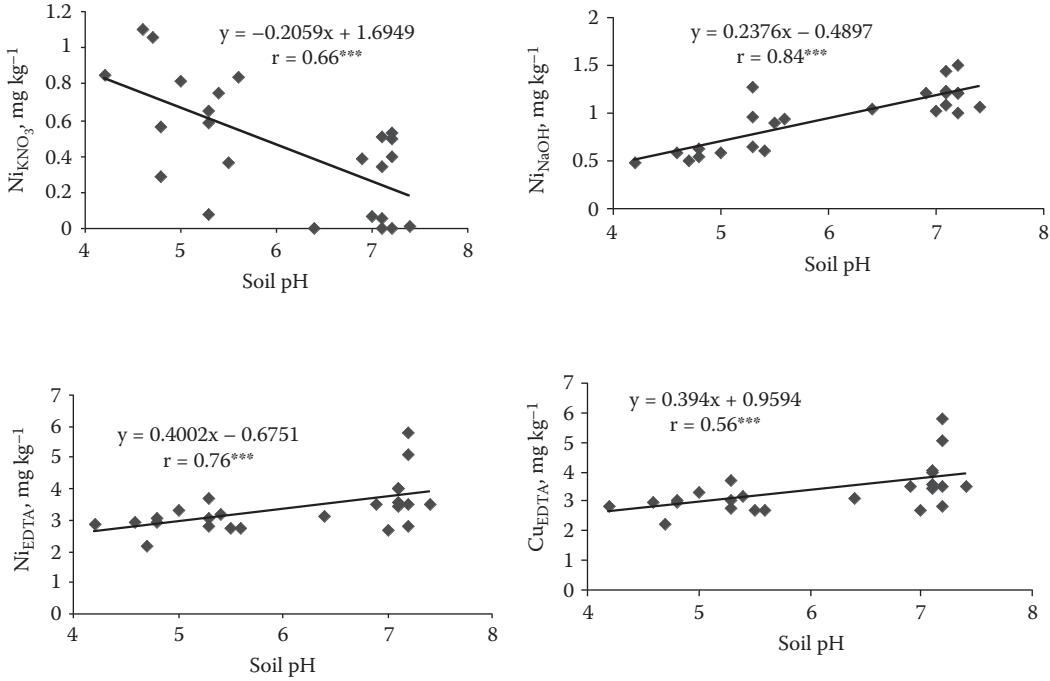

FIGURE 4.6 Relationship between soil pH and exchangeable Ni (top left), organic matter associated (top right), and carbonate bound fractions of Ni and Cu (bottom left and right, respectively).

(data not shown). Copper concentration in wheat seeds was significantly increased in all treatments containing fly ash and sewage sludge (Figure 4.7).

Molybdenum showed an unexpected trend in that its concentration was higher in the control (C) and the inorganic fertilizer treatment (IF) in which soil pH was lower, although one would expect the opposite behavior (Figure 4.7). Zinc, on the other hand, increased significantly from 20 mg kg^{-1} (in the control) to around 33 to 35 mg kg^{-1} (at FASS1 and FASS2 treatments) (Figure 4.8). Finally, Mn showed an unclear trend (Figure 4.8). Therefore, heavy metal accumulation in wheat

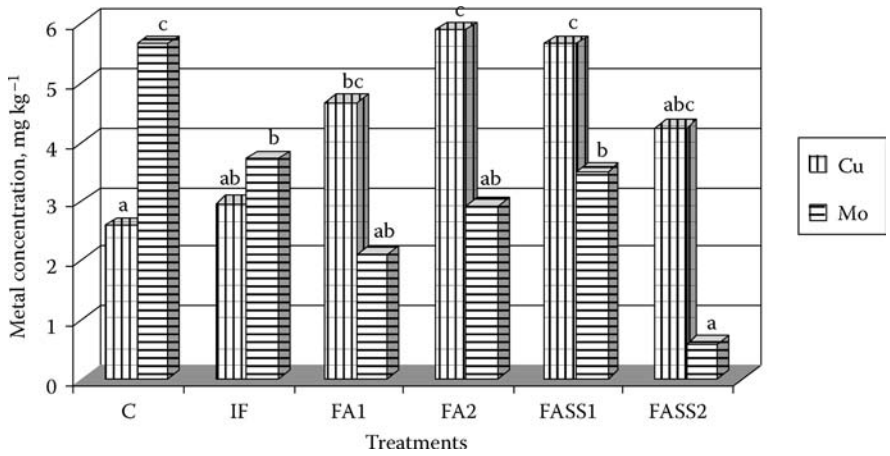

FIGURE 4.7 Influence of fly ash on the concentration of Cu and Mo in wheat grain. (Different letters on bars symbolizing the same parameter show significant difference at probability level $P < 0.05$.)

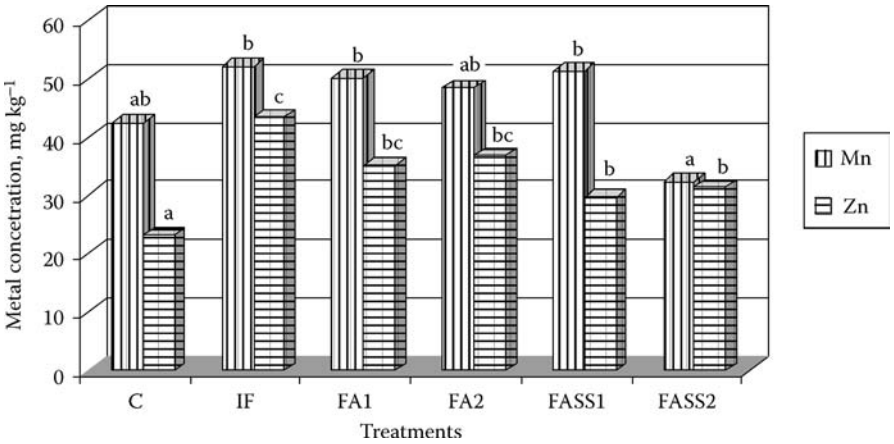

FIGURE 4.8 Influence of fly ash on the concentration of Mn and Zn in wheat grain. (Different letters on bars symbolizing the same parameter show significant difference at probability level $P < 0.05$.)

grain had no clear effect in all cases studied except for Zn and Cu, which clearly exhibited an increasing trend with increase in fly ash application rate.

4.4 CONCLUSIONS

The results of the present study showed that, although fly ash application to the soil along with sewage sludge increased total heavy metal content in soil (pot experiment), in general it decreased their availability to wheat plants, obviously due to pH increase. More specifically, total concentration of exchangeable fractions of Ni (readily available) in soil decreased with fly ash application (Cu- and Zn-exchangeable fractions were not detected). This was consistent with the decrease in DTPA-extractable heavy metals with fly ash addition. However, sewage sludge application increased DTPA-extractable As and Zn. Wheat grain concentration of heavy metals did not increase significantly except for Cu and Zn; however, both are essential to plant growth. Other potentially toxic elements such as Cd and Pb were completely excluded from plant uptake.

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