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STUDY OF THE EFFECTS OF CHEMICAL FERTILIZERS AND HERBICIDES ON THE LEVELS OF SOME HEAVY METALS AND ANIONS IN SOILS AND CORN (*ZEA MAYS*) GROWN IN SELECTED PARTS OF BENUE STATE, NIGERIA

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ABSTRACT
This study employed standard laboratory procedures to determine the effects of the uncontrolled applications of chemical fertilizers and herbicides on the levels of some heavy metals and anions in soils and corns (*Zea mays*) grown in some farms in Otukpo, Ohimini and Katsina-Ala Local Government Areas of Benue State, Nigeria between April and August, 2010. Levels of the heavy metals and anions in the samples were determined using an SP Pye (1900) Unicam Atomic Absorption Spectrophotometer equipped with air–acetylene burner and UV-Visible Smart Spectrophotometer (2000) respectively. Results of the concentrations of heavy metals in the corns of white maize varied between 0.016±0.001μg/g Co to 1.613±0.810μg/g Fe while a record of 0.019±0.003μg/g Co to 1.420±0.150μg/g Fe was obtained in the corns of yellow maize. The concentrations of the anions ranged from 30.18±3.91μg/g NO_2^- to 2511.18±1.03μg/g PO_4^{3-} in white maize corns and 28.45±1.35μg/g NO_2^- to 2705.03±5.01μg/g PO_4^{3-} in corns of yellow maize. Within 0-10cm of the soil depth, the heavy metals concentrations varied between 0.061±0.002μg/g Cr to 4.780±0.410μg/g Pb while the anions levels varied between 25.09±1.82μg/g NO_2^- to 400.83±1.16μg/g PO_4^{3-}. 10-20cm soil depth recorded higher concentrations of the heavy metals and anions. Both the levels of the heavy metals and anions were significantly ($P < 0.05$) higher in corns and soils obtained from farmers' fields than the values recorded in samples from the control farms cultivated in each of the sample locations. However, these concentrations were lower than the WHO/FAO's dietary permissible limits. The elevated levels of the heavy metals and anions in farmers' fields suggest that the farmers should be trained to adopt better management of the applications of these agrochemicals in maize cultivation.
Key words: Corns, Agrochemicals, Heavy metals, Anions, Farmers' Fields.

INTRODUCTION
The wrong usage of agrochemicals (chemical fertilizers, herbicides and pesticides) in crop cultivations as practiced by majority of the rural farmers portend great dangers to the qualities and yield potentials of crops (Abah *et al.*, 2009). Reports have shown that heavy applications of chemical fertilizers, pesticides and herbicides in crop cultivation can lead to the buildup of residual chemicals in soils, plants and crops (Radojevic and Bashkin, 1999), and the effects of these practices may extend beyond agricultural system. Omoloye (2009), while investigating field accumulation risks and the uptake effects of selected heavy metals noted that excessive accumulations of soil heavy metals present the risks of elevated heavy metal uptake by crops which could affect food quality and safety. Reports have also shown that the side effects of agrochemicals are often the result of improper usage or improper

choice of products in relation to the local conditions (UNEP, 1992). Several human health effects have been reported following excess dietary contents of residual chemicals such as heavy metals, anions and free radicals. It is suspected that in most cases, heavy metals in soils are taken up by plants via the roots and later accumulated in the stem and other edible portions of plants which eventually lead to poisoning when consumed (Nieboer & Yassi, 1998). Omoloye (2009), reported various negative impacts of heavy metals on the development, distribution and diversity of insect pest of maize and this is indicative of the potential danger to biodiversity and ecosystem management. Heavy metals accumulation in agricultural soils posed long-term problem of up-take accumulation. However, there is paucity of information on the extent of these contaminations and their effects on biodiversity and bioavailability in Benue State. Balk and Koeman (1984), noted that risks due to chemical contaminants in the terrestrial environment are often assessed by comparing current concentrations against reference concentrations above which adverse effects are considered likely to occur. Since, risk assessments cannot be extrapolated from one location to another, it becomes pertinent for localised risk assessment with a view to determining the impact of anthropogenic activities on the environment.

UNEP (1992), calculated that 2 billion hectares of land that was once biologically productive has been irreversibly degraded in the past 100 years due to contamination and inaccessibility. Land contamination/degradation is a threat to sustainable agricultural development and food security in the developing countries. Among all the degraded lands, those contaminated with heavy metals are largely irreversible and where reversibility is attempted, it is at high cost (Oldema, 1994). It has therefore become imperative that the environment and its resources should be managed judiciously to enhance sustainable national and socio- economic development. This study was therefore, designed to study the effects of chemical fertilizers and herbicides on the levels of some heavy metals and anions in soil and corn of maize grown in some farms in three Local Government Areas of Benue State, Nigeria.

MATERIALS AND METHODS

Study Area

The study area consists of Otukpo, Ohimini and Kastina-Ala Local Government Areas of Benue State (located between latitude $7^{o}30^{l}$N and $9^{o}45^{1}$N and longitude $6^{o}45^{l}$E and $8^{o}15^{l}$E in the north central geographical zone of Nigeria) (GNL, 2001). Recently, maize (*Zea mays*) cultivations in the these LGAs and Benue State as a whole have witnessed high applications of chemical fertilizers and herbicides to improve soil fertility and control weeds respectively. The wrong applications of these dangerous agrochemicals to crops have been reported in some farms in Benue State (Abah *et al*., 2009). This suggests the needs to carry out relevant studies of the environmental effects of usage of chemical fertilizers and herbicides in crop cultivations.

Sample Collection

Samples of maize (*Zea mays*) and soils were randomly collected using standard procedures described by Radojevic and Bashkin (1999). Bulk soil samples were collected at depths of 0-

10cm and 10-20cm using an auger. Samples were collected from farmers' fields where chemical fertilizers (NPK 15:15:15) and herbicides (roundup and forceup) were applied to maize to enhance soil fertility and control weeds respectively and the experimental farms cultivated without the usage of fertilizers and herbicides in each of the sample locations to serve as control. The maize corn were harvested four months after planting (4MAP) (April, 2010 to August, 2010) from three farms each in Otukpo, Ohimini and Kastina-Ala Local Government Areas of Benue State.

Determination of Heavy Metals
Samples Preparation and Analysis
Standard extraction methods of Radojevic and Bashkin (1999), AOAC (1984) and USEPA (1996) were employed to prepare the samples. 2.0g each of air-dried, ground and sieved (< 1mm) powder of the maize corn and 1.0g each of air – dried, ground and sieved (< 2mm) soil were used respectively. Five serial calibration standards were prepared for all the metals by diluting aliquots of the working metal solutions with 0.25M HNO_3 and the calibration standards were made to cover the optimum absorbance range of 0.2-10mg/l for the standard calibration curves. The samples extracts were analyzed for the levels of chromium (Cr), lead (Pb), cobalt (Co), nickel (Ni), copper (Cu), cadmium (Cd), iron (Fe) and zinc (Zn) using an SP Pye (1900) Unicam Atomic Absorption Spectrophotometer equipped with air – acetylene burner.

Determination of Nitrate and Nitrite Levels
Samples Preparation and Analysis
Standard aqueous extraction method of Radojevic and Bashkin (1999) was used to prepare the samples. 1.0g each of air-dried, ground and sieved (< 1mm) powder of the maize corn and 2.0g each of air-dried, ground and sieved (< 2mm) soil sample were used respectively. Levels of nitrate and nitrite in the extracts were determined using Smart spectrophotometer (2000) according to Smart Spectro test procedures (LaMottee, 2000). Levels of nitrate were determined by standard cadmium reduction method 3649-SC while nitrite levels were determined using standard diatotization method 3650-SC.

Determination of Phosphate and Sulphate Levels in the Maize Corn
Sample Preparations and Analysis
Standard extraction methods of Radojevic and Bashkin (1999) and AOAC (1984) were used to prepare the samples. 1.0g each of air-dried, ground and sieved (< 2mm) maize corn powder was used. To prevent loss of phosphate and sulphate during ashing, 5cm^3 of 20% (w/v) magnesium acetate were added to samples extracted for the determination of phosphate levels, while 5cm^3 of magnesium nitrate solution were added to samples extracted for the determination of sulphate levels (Radojevic and Bashkin, 1999). Phosphate levels were determined using HACH Direct Reading (DR) spectrophotometer (44800-00) according to the reactive phosphorous-amino acid (also called orthophosphate) method at 530nm while sulphate levels were determined using Smart Spectrophotometer (2000) according to standard barium method at 420nm.

Determinations of Phosphate Levels in the Soils
Samples Preparation and Analysis
Standard aqueous extraction method of Radojevic and Bashkin (1999) was used. 5.0g each of air-dried, homogenized and sieved (< 2mm) soil was weighed into polyethylene bottle and 50cm^3 of distilled water was added and shaken continuously for 5mins. This was filtered repeatedly through a Whatman No.42 filter paper until a clear extract was obtained. Then, 10cm^3 of the soil extract was pipette into 50cm^3 volumetric flask followed by the addition of 8cm^3 of colour developing reagent and the volume was made up to the mark with distilled water. The extracts were analyzed for the levels of soil phosphate as in the maize corn above.

Determinations of Sulphate Levels in the Soils
Samples Preparation and Analysis
Standard aqueous extraction method of Radojevic and Bashkin (1999) was also used. 2.0g each of the air-dried, homogenized and sieved (< 2mm) soils was weighed into a 100cm^3 flask followed by the addition of 40cm^3 water. Then, the flask was stoppered and shaken on a magnetic shaker for 1hr. Thereafter, the solution was filtered through a Whatman No.42 filter paper into another 100cm^3 volumetric flask and the volume was made up to mark with distilled water. The extracts were analyzed for the levels of soil sulphate as in the maize corn above.

RESULTS AND DISCUSSION
Figure I presents the concentrations (µg/g) of some heavy metals in the corn of yellow maize grown in some farms in Otukpo, Ohimini and Katsina-Ala Local Government Areas (LGAs) of Benue State, Nigeria between the period of April, 2010 and August, 2010. In the farmers' fields where chemical fertilizers (NPK 15:15:15) and herbicides (roundup and forceup) were applied to enhance soil fertility and control weeds respectively, higher concentrations of the heavy metals were recorded in the corn. The results varied between 0.019±0.003µg/g Co to 1.420±0.150µg/g Fe. Lower concentrations of 0.014±0.005µg/g Co to 0.688±0.200µg/g Pb were recorded in the corn of yellow maize grown in the control farms cultivated across the sample locations. Concentrations of the heavy metals in the corn of white maize (Figure 2) revealed 0.016±0.001µg/g Co to 1.613±0.810µg/g Fe in the farmers' field and 0.012±0.003µg/g Co to 0.881±0.210µg/g Fe in the control farms. Samples obtained from the farmers' fields across the sample locations recorded significantly higher levels of the heavy metals. This condition may be attributed to anthropogenically induced source. This finding colloborates the report of Omoloye (2009), who in his investigation of field accumulation risks of selected heavy metals noted that the concentrations of toxic metals were comparatively higher in contaminated urban soil than the control by up to 100 percent. The analyses of variance of the levels of the heavy metals were statistically significant ($p < 0.05$) between sample farms and locations. Figure 3 presents the concentrations (µg/g) of some anions in the corn of yellow maize grown in the studied areas. The results varied between 28.45±1.35µg/g NO_2^- to 2705.03±5.01µg/g PO_4^{3-} in the corn of yellow maize obtained from the farmers' fields whereas, the concentrations varied between 11.00±3.51µg/g NO_2^- to

2240.24±3.01µg/g PO_4^{3-} in the samples grown in the control farms. White maize corn recorded 30.18±3.91µg/g NO_2^- to 2511.18±1.03µg/g PO_4^{3-} in the farmers' fields while a mean concentration of 12.63±4.20µg/g NO_2^- to 2250.17±3.18µg/g PO_4^{3-} were obtained in the samples cultivated in the control farms (Figure 4). Generally, the levels of heavy metals and anions recorded in maize corn obtained from the farmers' fields were significantly higher than the levels recorded in the corn obtained from the control farms. This development may be due to the high usage of chemical fertilizers and herbicides by the farmers.

Figure 5 presents the concentrations (µg/g) of the heavy metals in the farms soils. In the farmers' fields, the results varied between 0.061±0.002µg/g Co to 4.780±0.410µg/g Pb within 0-20cm soil depth and 0.078±0.007µg/g Co to 6.600±0.190µg/g Pb within 20-40cm soil depth. In the control farms, the soils' contents of the heavy metals varied between 0.040±0.005µg/g Ni to 2.320±0.210µg/g Pb and 0.062±0.008µg/g Co to 4.800±0.920µg/g Pb within 0-10cm and 10-20cm soil depth respectively. These results differed significantly ($p < 0.05$) between the farmers' fields and the control farms. The soils from the farmers' fields recorded higher contents of both the heavy metals and anions (Figure 6). These conditions may not be unconnected with the usage of chemical fertilizers and herbicides in the farmers' fields. The soil mean transfer factors of the heavy metals (Figure 7) revealed that both the yellow and white maize recorded very high absorption of nickel (Ni). This suggests that Ni post the highest pollution threat to maize growers in the studied areas. The corn also showed high absorption of cadmium (Cd), iron (Fe) and zinc (Zn) but these were generally higher in the corn of white maize. This therefore, present the study area as prone to contamination by these elements. Generally, the levels of the heavy metals recorded in this study were below some established critical limits of 10-20.00mg/kg Fe, 0.5-10.00mg/kg Cr, 3-20.00mg/kg Pb, and 60-400.00mg/kg Zn which cause phytotoxicity in plants (FAO/WHO, 1976) and 200.00mg/day Fe, 200.00mg/day Cr, 1.00mg/day Pb 150-600.00mg/day Zn body weight which cause toxicity in humans (FAO/WHO, 1976).

Figure 8 presents the soil mean transfer factors of the anions in the maize corn. The sequence of the absorption and bio-accumulation of the anions revealed that $PO_4^{3-} > SO_4^{2-} > NO_3^- > NO_2^-$. The results revealed that maize absorptions of sulphate (SO_4^{2-}) and phosphate (PO_4^{3-}) were higher with mean transfer factors of 4.98 and 6.67 (white maize) and 5.13 and 7.33 (yellow maize) respectively. Sulphate and phosphate were reported to be more stable in soils than nitrate and nitrite radicals (Abah *et al*., 2007). Manahan (2005) also reported that sulphate and phosphate are resistant to leaching and this enhances their continued accumulation in the soil. Thus, they are readily available for absorption by crops and plants grown on soils rich in the anions. Generally, the anions contents of the maize corns were lower than the permissible dietary contents of 3.65mg/kg NO_3^- (WHO/FAO, 1985), 0.2mg/kg NO_2^- (WHO/FAO, 1985), 70.0mg/kg PO_4^{3-} (WHO, 1987) and 500mg/kg SO_4^{2-} (WHO, 2003) body weight respectively.

CONCLUSION

The results of this study revealed that the uncontrolled applications of chemical fertilizers and herbicides in maize cultivation may lead to anthropogenic build up of residual chemicals in soils and maize corn. Exposure of consumers to excess dietary (corn) contents of heavy metals and anions may lead to risk of food poison. Therefore, proper agronomic practices should be adopted to minimize the uncontrolled usage of agrochemicals in maize production and limit consumers' exposure to chemical contaminants.

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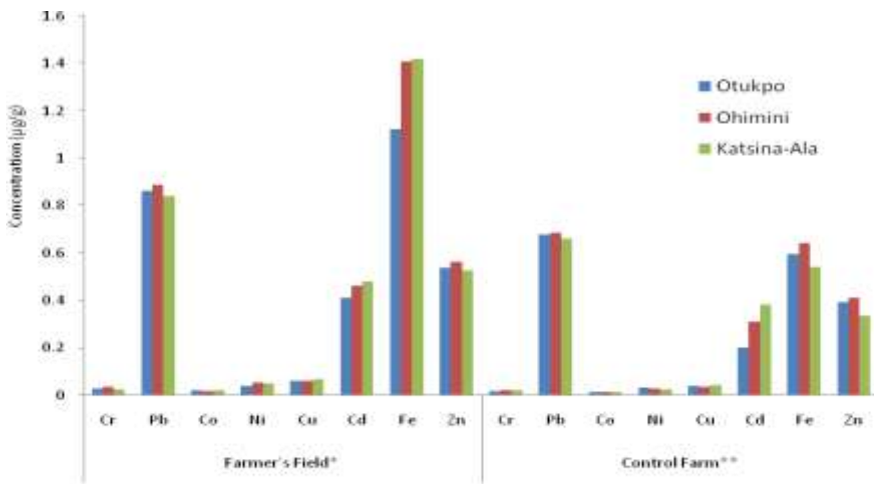

Figure 1. Concentrations (µg/g) of Some Heavy Metals in the corns of Yellow Maize Grown in Three L.G.A of Benue State, Nigeria (April, 2009 to August, 2009)

Different asterisk (*) on the Farmer's Field and Control Farm indicated that the heavy metals concentrations are statistically significant (P < 0.05)

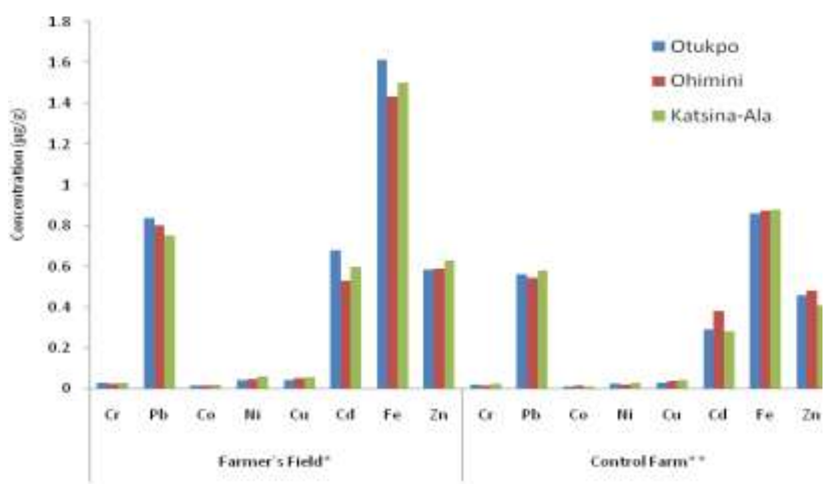

Figure 2. Concentrations (µg/g) of Some Heavy Metals in the corns of White Maize Grown in Three L.G.A of Benue State, Nigeria (April, 2009 to August, 2009)

Different asterisk (*) on the Farmer's Field and Control Farm indicated that the heavy metals concentrations are statistically significant (P < 0.05)

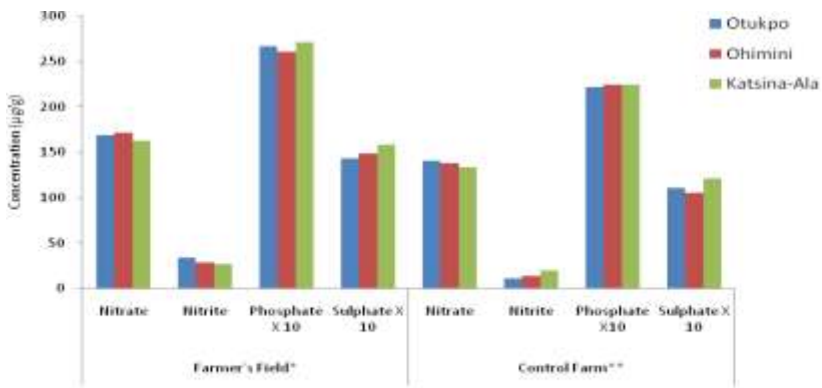

Figure 3. Concentrations (µg/g) of Some Anions in the corns of Yellow Maize Grown in Three L.G.A of Benue State, Nigeria (April, 2009 to August, 2009)

Different asterisk (*) on the Farmer's Field and Control Farm indicated that the anions concentrations are statistically significant ($P < 0.05$)

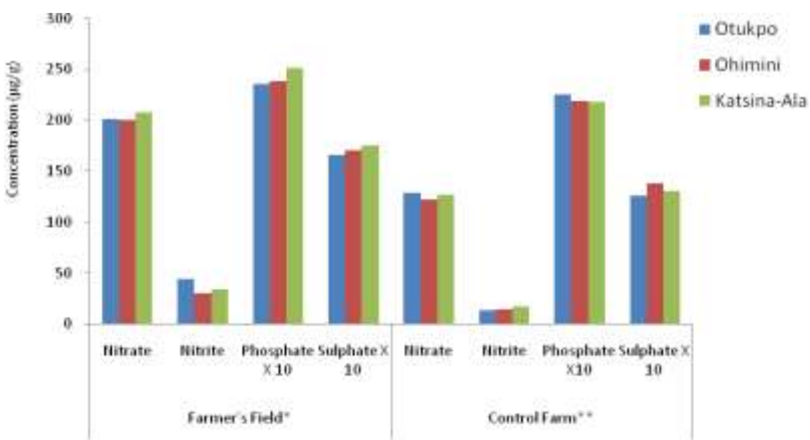

Figure 4. Concentrations (µg/g) of Some Anions in the corns of White Maize Grown in Three L.G.A of Benue State, Nigeria (April, 2009 to August, 2009)

Different asterisk (*) on the Farmer's Field and Control Farm indicated that the anions concentrations are statistically significant ($P < 0.05$)

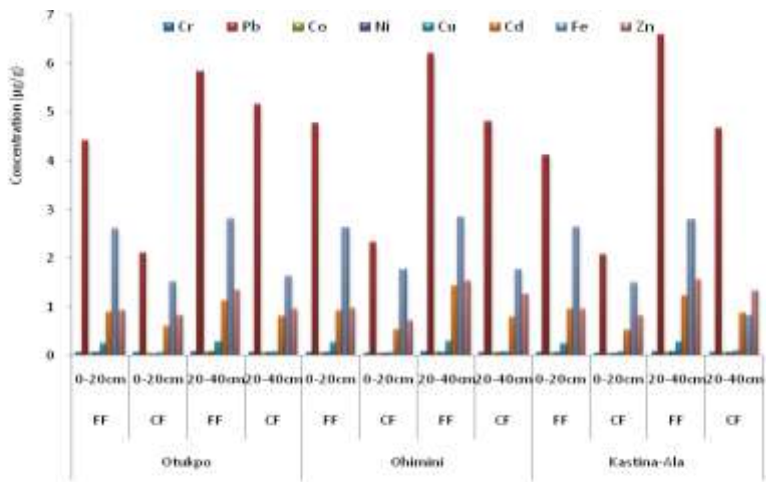

Figure 5. Concentrations (µg/g) of the Heavy Metals in the Farm Soils

Key: FF = Farmer's Field, CF = Control Farm

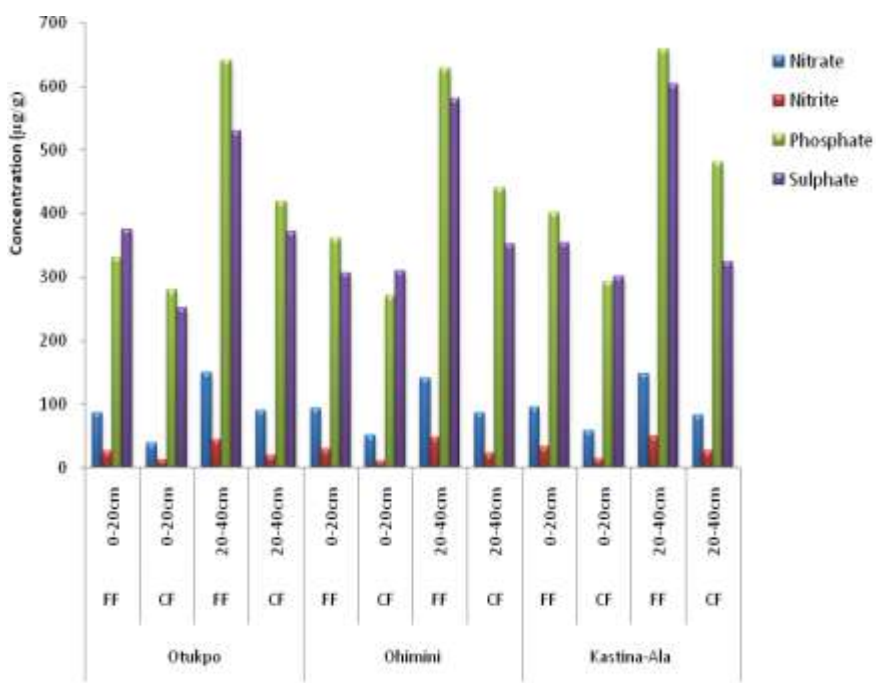

Figure 6. Concentrations (µg/g) of Some Anions in the Farms Soils

Key: FF = Farmer's Field, CF = Control Farm

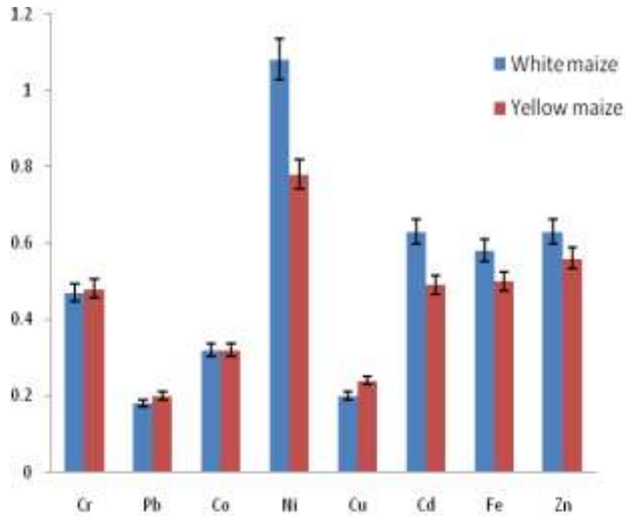

Figure 7. Soil Mean Transfer Factors of the Heavy Metals to the Maize Corn

Transfer Factor = Maize corns' Heavy Metal Content/Soil's Heavy Metal Content

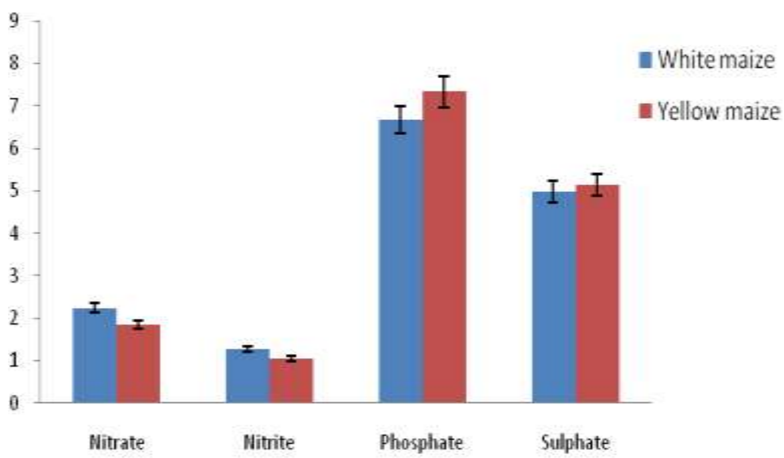

Figure 8. Soil Mean Transfer Factors of the Anions to the Maize Corn

Transfer Factor = Maize corns' Anion Content/Soil's Anion Content