The Impact of Four Herbicides on Soil Minerals

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Abstract: The aim of this study was to investigate the interaction of atrazine, primextra, paraquat and glyphosate with soil minerals. The treatments were carried out for a period of 6 weeks; at company recommended rates of 4l/h (at 350 mL in 15 L sprayer) for paraquat, glyphosate and primeextra while recommended rate of 3 kg/h (atrazine powder) was used for atrazine treatment (soil treatments were carried out in triplicates). Soil moisture content was determined using Satorious Moisture content Analyser. Soil mineral concentration were then determined by injecting sample solutions (extract) and standard solution for each mineral into the atomic absorption spectrophotometer into sample fray and the mean signal response was recorded for each of the element at their respective wavelength. The concentrations of the minerals were then calculated. Herbicide treated soils showed reduction in the moisture content from the second to the sixth weeks of treatment. There was significant ($p<0.001$) reduction in Sodium ion (Na) and Calcium ion (Ca) concentration compared to the control. The potassium, Magnesium, Iron and Zinc (K, Mg, Fe and Zn) increased significantly ($p<0.001$) compared to the control. Ths study has elucidated the ability of herbicides to chelate with soil minerals thereby reducing their availability for uptake by plants. It has also been shown that soil minerals are utilised by plants and microbes during microbial degradation.

Keywords: Calcium, concentration, herbicide, iron, magnesium, potassium, zinc

INTRODUCTION

The overall use of pesticides poses varying degrees of threat to the environmental media quality, it is therefore envisaged that their use will continue to grow, especially in poor countries if the food security of an ever expanding population is to be assured (Mbuk et al., 2009). On the field, co-application of fertilizers and pesticides is common practice as it is necessary. In addition to inputs from fertilizers and other anthropogenic activities, metals occur naturally in soils in various stages of oxidation. Often, the mobility or fixation of these in soil is influenced by the organic matter, clay minerals and hydroxyl-oxides constituent in the soil, mostly in conjunction with pH effects (Mbuk et al., 2009).

Atrazine is a triazine herbicide used to control many broad leaf and some grassy weeds (Dossantes et al., 2004). Atrazine is moderately persistent in the environment with the half life of one to twelve months. However, the herbicide has been reported to persist in soils for up to a decade (Dossantes et al., 2004). Metolachlor is a pre emergent herbicide that is also used to control broad leaf and grassy weeds. Metolachlor is primarily used on corn, soybean,

peanuts, sorghum, potatoes, cotton, safflower, woody ornamentals (Rivard, 2003). When absorbed through roots and shoots just above the target weeds, it acts as a growth inhibitor by suppressing synthesis of chlorophyll, proteins, fatty acids and lipids, isoprenoids (including gibberellins) and flavonoids (including anthocyanins). Metolachlor is considered to be moderately persistent in different soil types and has an average field dissipation half-life of 114 days (Kollman and Segawa, 2000). Metolachlor is considered to moderately adsorb to soil. The adsorption of the pesticide increases with increased soil organic matter and clay content and can slow its movement in soil. Metolachlor is often used in combination with other broadleaved herbicides (e.g., atrazine, metobromuron and propazine) to extend the spectrum of activity (Ayansina and Oso, 2006).

Glyphosate is a nonselective, systemic herbicide that controls most annual and perennial weeds (and other plants) by inhibiting the synthesis of aromatic amino acids needed for protein formation. Glyphosate binds strongly to cations that are adsorbed to soils (Carlisle and Trevors, 1988). This binding is unlike other organic compounds that primarily adsorb to

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organic matter in soils. Glyphosate binding is similar to phosphate binding and it is possible that phosphate accumulation in soils could reduce the capacity for glyphosate binding (Gimsing *et al*., 2004).

Paraquat is a broad spectrum herbicide that destroys plant tissue by contact action. It is highly soluble in water and because of its ionic properties is strongly adsorbed by soil particles and is essentially immobile in soil (Costenla *et al*., 1990). The strong binding of paraquat to clay minerals is the factor most likely associated with its long half-life in soils (Clive, 2006).

The fate of herbicides such as that of any organic molecule released into the environment is determined by their physico-chemical characteristics. The solubility of herbicide is important in predicting its behavior in water and its mobility in soil. Agrochemical water solubility is a function of temperature, pH and ionic strength and is affected by the presence of other organic substances such as dissolved organic matter (Pierzynski *et al*., 2005). The ability of herbicides to adsorb on soils and sediments and their tendency to desorb are the most important factors affecting soil and water contamination. Adsorption depends on both molecule and soil physico-chemical properties. In soil surfaces responsible for adsorption are colloidal particles and among these are organic matter and clays. Organic matter due to its chemical affinity with agrochemical molecules, has the greatest adsorption strength. High surface area and the interlayer charge of clays, such as expandable phyllosilicates, make these sorbents good for organic molecules.

The aim of this study is to determine the effect of some herbicides (atrazine, primextra, glyphosate and paraquat) on soil minerals.

MATERIALS AND METHODS

Area description: This study was conducted in a cassava farm located in Ijebu-Ode local government area, Ijebu-Ode, Ogun State, Nigeria. Soil treatments were carried out between January and February 2009, while soil samples were collected every 2 weeks to the sixth week of treatment in February 2009.

Soil sampling: Top soil up to 5 cm depth samples was collected from cassava farm in Ijebu-Ode (Ogun State, Nigeria) with no prior pesticide treatment. The soil samples were sieved through a 2.0 mm width mesh to remove stones and plant debris.

Herbicides: The herbicides used in this study were obtained from a local agricultural dealership store in Ibadan. The herbicides that were used are; Atrylone 80 WP, trademark of Insis Limited, (atrazine), primextra, a product of Syngenta, (a combination of atrazine and

metolachlor), Glysate, Nantong Ji Angshan Agrochemicals, (glyphosate) and Gramoxone, a product of Syngenta, (paraquat).

Soil treatments: The treatments were carried out for a period of 6 weeks, at company recommended rates of 4l/h (at 350 mL in 15 L sprayer) for paraquat, glyphosate and primeextra while recommended rate of 3 kg/h (atrazine powder) was used for atrazine treatment (soil treatments were carried out in triplicates).

Soil moisture content. Five grams of soil sample (sieved soil) was weighed into a tarred dish and placed on a Satorious Moisture content Analyser. The analyser temperature was set at 105°C, the analyser was covered and the moisture content was determined (the values were displayed on the analyser screen).

Mineral analysis: To 2.0 g of soil sample, 30 mL of IN NH_4OAC (ammonium acetate solution) was added and the flasks were shaken on a mechanical shaker for 2 h. The mixture was centrifuged at 2000 rpm for 10 mins and the clear supernatant was decanted into 100 mL volumetric flasks. About 30 mL of ammonium acetate solution (NH_4OAC) was added twice into the flasks and shaken on a mechanical shaker for 30 min each and centrifuged at 2000 rpm and the clear supernatant was then transferred into the same volumetric flasks respectively. Sample extract was made up to 100 mL volume with the NH_4OAC solution.

The mineral contents (calcium, sodium, potassium, magnesium, zinc and iron) in the samples were determined using the atomic absorption spectrophotometer fitted with a hollow cathode lamp and a fuel rich flame (air acetylene). Sample solutions (extract) and standard solution for each mineral were injected into the atomic absorption spectrophotometer into sample fray and the mean signal response was recorded for each of the element at their respective wavelength. The concentrations of the minerals were calculated as follows:

$$\text{Concentration} = \frac{\text{Std. conc} \times \text{Sample Abs} \times 100 \times \partial f}{\text{Std. Abs.} \times \text{weight of sample}}$$

where,
∂f = Dilution factor
Std. conc = Standard concentration
Std. Abs. = Standard absorbance

RESULTS

Herbicide treated soils showed reduction in the moisture content from the second to the sixth weeks of treatment. Soils treated with glyphosate had the lowest percentage moisture content of 0.74 after six weeks of
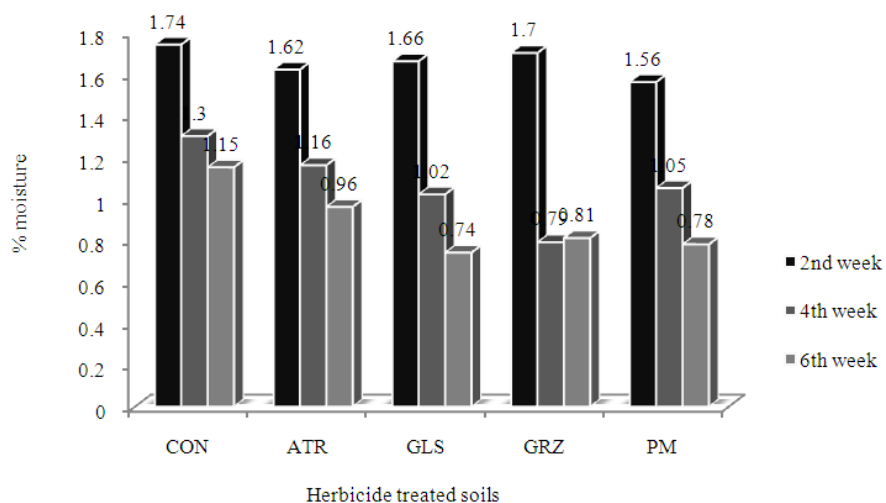
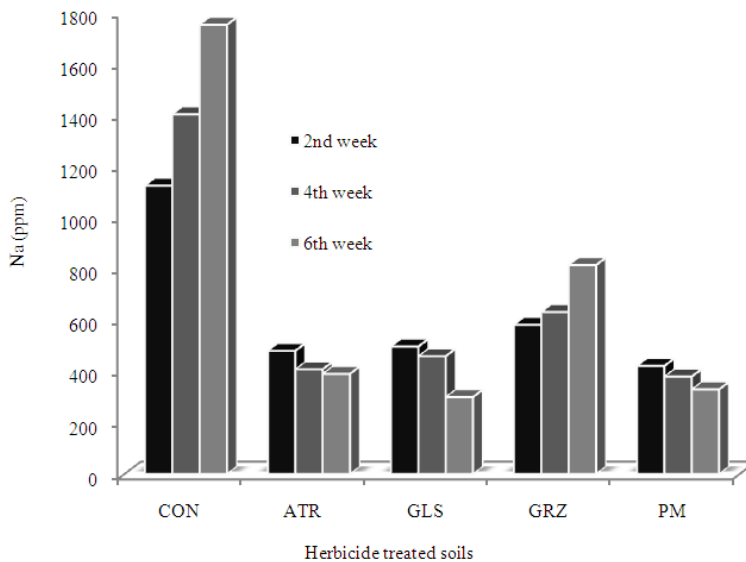Fig. 1: Moisture content of soil samples

Fig. 2: Sodium (Na) content of soil samples

treatment, while the control samples showed the highest percentage moisture content after two weeks of treatment (Fig. 1).

Upon treatment with herbicides there was significant ($p<0.001$) reduction in sodium ion (Na) concentration compared to the control but as the weeks of treatment increased from the 2nd to the 6th week the Na concentration increased insignificantly ($p>0.946$) (Fig. 2). Soils treated with atrazine, glyphosate and primeextra had their sodium concentration reduced from the second to the sixth week of treatment, while for soils treated with paraquat, the sodium ion

concentration increased from the second to the sixth weeks of treatment. In the control samples the sodium concentration increased from the second to the sixth week of treatment (Fig. 2). Of all the herbicide treated soils those treated with paraquat had the highest sodium concentration of 814.4 ppm after six weeks of treatment. In the second and fourth weeks it also had the highest sodium concentration of 581.4 and 631.5 ppm, respectively (Fig. 2). Soils treated with glyphosate had the lowest sodium concentration of 299.9 ppm after the sixth week of treatmnent. Meanwhile primeextra treated soils had the lowest sodium
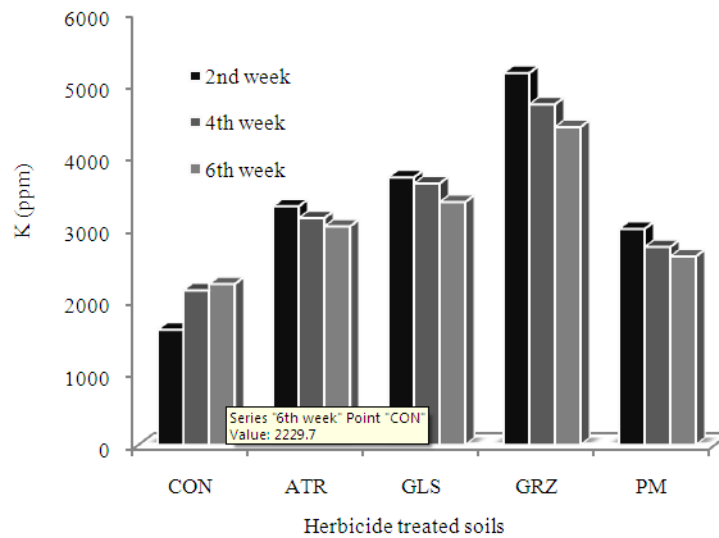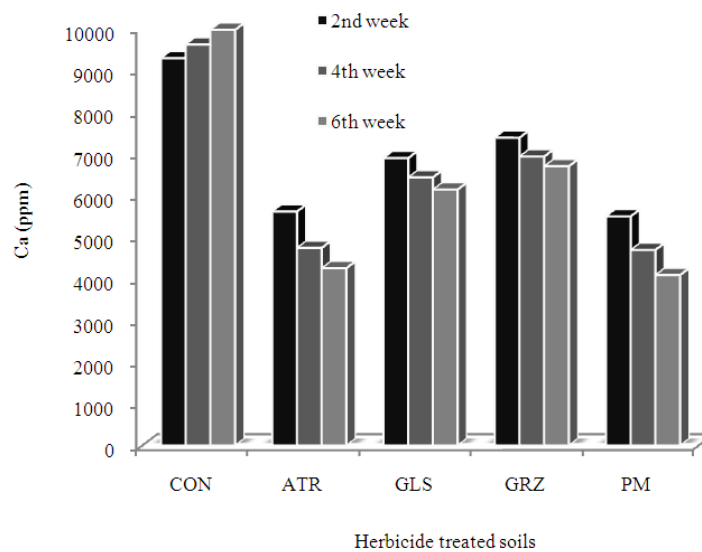
Fig. 3: Potassium content of soil samples

Fig. 4: Calcium content of soil samples

concentration of 421.3 and 379.9 ppm after the second and fourth weeks of treatment, respectively. The control sample recorded the highest sodium concentration of 1751.1 ppm after the sixth week of treatment (Fig. 2).

The potassium ion (K) concentration increased significantly ($p < 0.001$) when treated with the herbicides compared to the control. But the reduction in K concentration from the second to the sixth week of treatment was insignificant ($p > 0.943$) for the herbicide treated soils (Fig. 3). The control samples had the lowest K concentration of 1595.8, 2143.3 and 2229.7 ppm after the second, fourth and sixth weeks of treatment (Fig. 3). Soils treated with paraquat had the highest K concentrations of 5158.8, 4723.7 and 4409.3 ppm after the second, fourth and sixth weeks of treatment, of all the herbicide treated soil, primeextra treated soils had the lowest K concentrations of 2994.8, 2744.4 and 2613.3 ppm after the second, fourth and sixth weeks of treatments respectively (Fig. 3). Apart from the control samples all herbicide treated soils had minimal reductions in K concentration from the second to the sixth weeks respectively.

Calcium ions (Ca) reduced significantly ($p < 0.001$) upon treatment with the herbicides compared to the control. The control samples showed insignificant
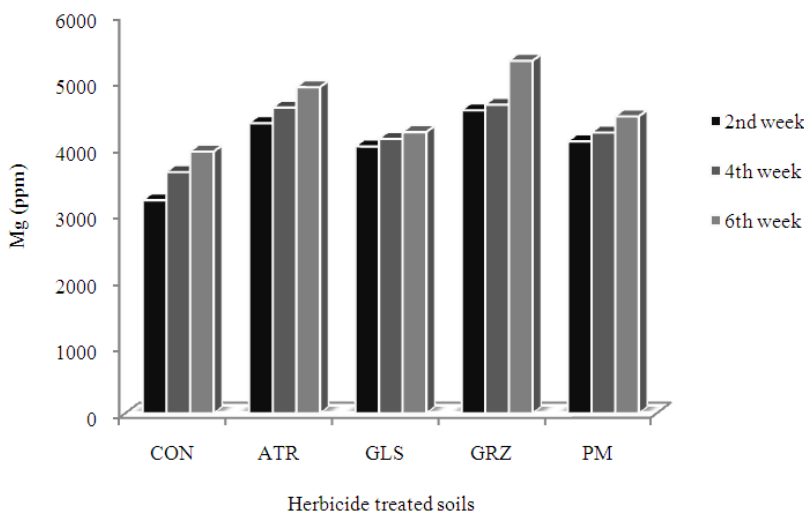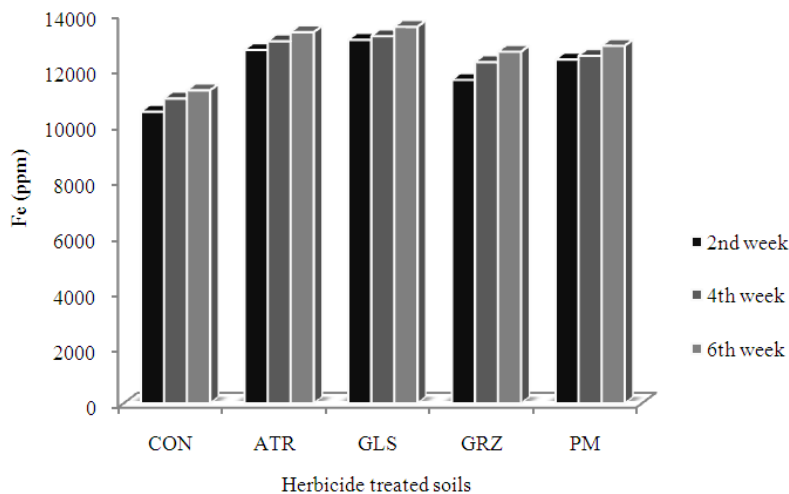
Fig. 5: Magnesium (Mg) content of soil samples

Fig. 6: Iron content of soil samples

reduction (p>0.856) from the second to the sixth week of treatment compared to the herbicide treated soils (Fig. 4). Primeextra treated soil had the lowest Ca concentration of 5492.6, 4687.3 and 4086.7 ppm after the second, fourth and sixth week of treatment respectively. In all treated soil samples paraquat treated soil samples recorded the heighest Ca concentration of 7378.3, 6927.3 and 6694.3 ppm after the second, fourth and sixth weeks of treatment respectively (Fig. 4). The Ca concentration of control samples increased from the second to the sixth weeks of treatment recording the highest Ca contents of 9284.3, 9614.7 and 9964.7 ppm at the second, fourth and sixth weeks, respectively (Fig. 4).

The magnesium ion (Mg) concentration increased significantly (p<0.003) when treated with herbicides used in this study compared to the control (Fig. 5). Soils treated with paraquat had the highest Mg concentration of 4568, 4652.3 and 5314.7 ppm after the second, fourth and sixth weeks of treatment respectively. Soils treated with glyphosate had the lowest Mg concentration of all the herbicide treated soils (4022.7, 4137.7 and 4240 ppm after the second, fourth and sixth weeks of treatment) (Fig. 5). However the control samples showed the lowest Mg concentration of 3211.7, 3637.7 and 3946.3 ppm after the second, fourth and sixth weeks of treatment.
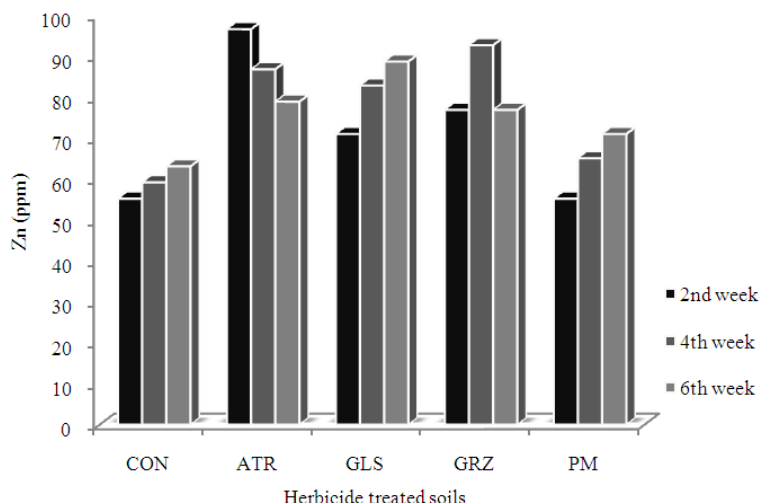
Fig. 7: Zinc (Zn) content of soil samples

Similar to the results obtained for the Mg concentration the Iron ion (Fe) concentration increased significantly ($p<0.001$) when treated with the herbicides compared to the control (Fig. 6). The control samples showed the lowest concentration of Fe (10489.3, 10964 and 11262.3 ppm after the second, fourth and sixth weeks) (Fig. 6). Glyphosate treated soils had the highest concentration of Fe (13078, 13212.7 and 13546 ppm after the second, fourth and sixth weeks, respectively). Paraquat treated soils recorded the lowest concentration of Fe after the second, fourth and sixth weeks of treatment (11638, 12276.3 and 12652.3 ppm respectively). Fe concentrations were found to increase from the second to the sixth week of treatments.

Zn concentrations increased significantly ($p<0.001$) upon treatment with herbicides compared to the control samples. The zinc ion (Zn) concentration of the atrazine treated soils reduced significantly ($p<0.005$) from second to sixth week of treatment. This contrasted the results obtained for the primextra treated soils which showed significant increase ($p<0.005$) on treatment with primextra compared to the control. Meanwhile for glyphosate treated soils there was significant ($p<0.002$) increase in the Zn concentration compared to the control (Fig. 7). Meanwhile atrazine treated soils recorded the highest Zn concentration of 96.6 ppm after the second week of treatment although it later decreased from the fourth to the sixth weeks of treatment with values of 86.8 and 78.9 ppm, respectively. Solis treated with paraquat had the highest concentration of 92.7ppm after the fourth week of treatment. For soils treated with paraquat Zn concentration increased from 76.9 to 92.7 ppm from the second to the fourth week of treatment and latter dropped back to 76.9 ppm after the sixth week of treatment (Fig. 7). Of all treatments primeextra treated soils recorded the lowest Zn concentration values of 55.2, 65.09 and 71 ppm after the second, fourth and sixth weeks of treatment.

CON = Control
ATR = Atrazine treated soil
GLS = Glyphosate treated soils
GRZ = Paraquat treated soils
PM = Primeextra treated soils

DISCUSSION

In this study there was significant increrase in the K, Mg, Fe and Zn concentrations of all the herbicide treated soil samples compared to the control. This might be due to the chelation ability of these herbicides (allowing them to accumulate in this form in soils) where they form complexes with these metal co-factors essential for enzyme activities thus immobilizing them in soil reducing their availability to plants. While some compounds chelate with a single or few metal species, glyphosate is a broad spectrum chelator with macro and micronutrients (Ca, Mg, Cu, Fe, Mn, Ni, Zn). It is this strong, broad spectrum chelating ability that also makes glyphosate a broad spectrum herbicide and a potent antimicrobial agent since the function of numerous essential enzymes is affected (Ganson and Jensen, 1988). Iron deficiency chlorosis is also becoming increasingly prevalent in cropping systems receiving frequent or prolonged applications of glyphosate (Ozturk *et al.*, 2008). Some studies describe the retention of *s*-triazines herbicides by soil constituents. Recently, simazine adsorption behaviour was studied in agricultural soils of central chile (Flores *et al.*, 2008). Soil organic matter and clay minerals are main sorbents for *s*-triazines (Garcia-Valcarcel and Tadeo, 1999;

Flores *et al*., 2008). Cations in the soil solution are bonded to the surface of clay minerals by electrostatic interactions and can return in solution by the substitution of other cations or by dilution. The most representative exchange cations are K^+, Ca^{2+}, Mg^{2+} and Na^+ (Blasioli *et al*., 2011).

There was significant reduction in the concentrations of Na and Ca after herbicide treatment compared to the control. The reduction in concentration of Na and Ca might have occurred as a result of leaching of the minerals in solution and the degradation of the herbicides consequent upon the utilisation of these soil minnerals by soil microbes and also their resultant uptake by plants. Polyvalent (Al^{3+}, Fe^{3+}, Ca^{2+} and Mg^{2+}) or monovalent (Na^+, K^+) cation affect the solubility of organic matter (Baham and Sposito, 1994). Chemical reactions between anionic functional groups of organic molecules and solution cations can reduce the surface charge density, alter structural conformation of the adsorbed species and cosequently reduce solubility. At high concentrations of ions in solution, these process increase and the solubility of organic matter is reduced by flocculation (Tipping and Woof, 1990). The nature of dissolved organic matter influences the adsorption and desorption of dimefuron, atrazine and carbetmine (Barriuso *et al*., 1992). Increased adsorption of less soluble atrazine and dimefuron, after soil pretreatment with dissolved organic matter, can be explained by an increase of soil C content via adsorption of some organic compounds from dissolved organic matter solution (Blasioli *et al*., 2011). Cosiderable work has been done to explain the mechanism of microbial degradation of xenobiotics and other contaminants (Alexander, 1999). Clay minerals appear to exert their primary influence by modifying the pysicochemical characteristics of microbial habitats, this either enhances or attenuates the growth and metabolism of individual microbial populations (Bollag *et al*., 2002). Minerals exhibit mixed fractions and they transform naturally occuring and xenobiotic substrates abiotically; at the same time, they act as sorbents, thus altering the impact of microorganisms, enzymes and chemicals. Adsorption and other binding interactions that occur on both mineral and humic surfaces are believed to reduce the bioavailability of xenobiotics (Bollag *et al*., 2002).

CONCLUSION

This study has elucidated the ability of herbicides to chelate or bind with soil minerals thereby reducing the availability for uptake of essential minerals such as K, Mg and Fe thus eliciting various malformations in the plants and making the plants suceptible to various diseases and malformations such as leaf necrosis. It has also been shown that soil minerals are utilised by plants and microbes during microbial degradation.

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