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Sulfonylureas effect on soil chemical properties and yield crop in Semi-arid Region of Algeria

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Abstract

Pollution by pesticides and organic pollutants is mostly perceived through their presence in water and food. However, many pollutants pass through the soil where their conduct will determine the manifestation of their pollutant character. Reducing their environmental impact requires an understanding of the processes they undergo in the soil. Thus, the physico-chemical composition of the soil, temperature and the richness of the microflora are so many and various factors that contribute to the degradation of herbicide residues. The aim of this study was to investigate the interaction of Sulfonylureas herbicides with soil chemical properties in semi-arid zone of Algeria. The treatments were carried out for a stage 3-4 leaves; at company recommended rates of 150 ml/ha for Sekator while recommended rate of 120g/ha was used for Zoom treatment. Variance analysis shows no significant effect of Na content of a soil polluted with both herbicides compared to the control. Sekator herbicide treated soils showed significant decrease in conductivity, level of the organic matter, content of available phosphorus and potassium, whereas soil treated with Zoom shows a very highly significant increase in the content of available phosphorus ($p \leq 0.001$) and very highly significant decrease in the potassium content. This study has elucidated the ability of herbicides to chelate with soil chemical properties thereby reducing their availability for uptake by plants. It has also been shown that soil minerals are utilized by plants and microbes during microbial degradation.

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Introduction

Weeds are considered notorious yield reducers that are, in many situations, economically more important than insects, fungi or other pest organisms (Savary *et al.*, 2000). Presence of weeds reduces the photosynthetic efficiency; dry matter production and distribution to economical parts there by reducing sink capacity of crop resulting in poor grain yield (Patel *et al.*, 2004). Unlike some environmental problems, once invasive plants become established, they often cannot be controlled by simply removing the initial mechanisms for invasion such as human-induced disturbance or by restoring natural processes such as fire. Instead, invasive plants must be controlled directly by using, either alone or in combination, herbicide treatments, manual removal, grazing, burning, biological control agents, or other methods capable of suppressing the target species in its invaded context (Petroff and Sheley, 1999).

The use of herbicides for combating unwanted weeds in the crop fields has been increased steadily. During the application of the herbicides, a large portion of these chemicals accumulates in the top layer soil (0–15 cm) where most of the microbiological activities occur. Microorganisms degrade a variety of carbonaceous substances including the accumulated herbicides in soil to derive their energy and other nutrients for their cellular metabolism (Debnath *et al.*, 2002, Das *et al.*, 2003). The enormous variety of herbicides commercially available today makes it impossible to review all of them. Thus, this work will focus on some of the herbicides most used in the (semiarid) region of Algeria and worldwide (i.e., Sulfonylurea and Dicamba), based on our own research data.

Sulfonylurea herbicides (SUHs), introduced in 1982 by the Dupont Corporation, were developed for weed control in cereal crops all around the world. Due to their low application rates (in the range of 10–100g/ha), unprecedented herbicidal activity and low mammalian toxicity ($LD_{50} < 4000$ mg/kg). Sulfonylurea compounds, which are

composed of a sulfonyl structure linked to a urea group, represent one of the largest classes of herbicides. However, the relatively high water solubility of these herbicides may result in their leaching into deeper soils and potentially entering surface waters (Fang *et al.*, 2010). SU herbicides are weak acids (pK_a values ranging between 3 and 5) and are highly water soluble ($\log K_{ow} < 1$). Their half-lives in soil vary from 5 to 70 d depending on the herbicide, soil pH and other soil characteristics (Cessna *et al.*, 2006, Hollaway *et al.*, 2006). In soil, they are degraded either by hydrolysis or microbial activity and the degradation products of some SU may persist in soil for years (Rosenbom *et al.*, 2010).

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 objective of the present study is to determine the effect of some herbicides (Sekator and Zoom) at their recommended field rates (150 ml/ha and 120g/ha respectively) on availability of sodium, potassium and phosphorus, also level of the organic matter in the soils as well as yield of the wheat crop. These herbicides are frequently used by the farmers in their wheat fields to eradicate the unwanted weeds for better crop growth.

Materials and methods

Area description

The present study was carried out in the agricultural field of wheat located in Ras El Ayoun situated in 30 km in the North of Tebessa, and El Houidjba situated in 29, 1 km in the South of Tebessa (Fig 1). The study area is near the city of Tebessa in eastern Algeria, is among the poorest and remotest regions in the country. This area lies in the semiarid region of

Algeria and is susceptible to the various threats which surround both growing urban areas as well as developing agricultural areas. The city of Tebessa and the surrounding villages (Bekkaria, Hammamet) have seen a great deal of growth in the past decade, with the establishment of new industries and farms.



Fig. 1. Map showing the study area in semi-arid region of Algeria with blue is the study area.

Annual precipitation in the study area ranges between 200 and 350 mm, and thus the area is considered to be a semi desert area. Temperatures can rise in the summer to 45 °C. This situation of dryness accentuates the drawdown of water resource especially during the last decade because the renewal of this resource is very weak. The dry climate, the atmospheric dust, and low intensity of precipitation can also affect the groundwater quality generally causing increased salt content. The Gausson and Bagnoulsdiagram (Fig 2) reveal a dry period from mid-May to mid-October.

Sampling of soil

Soil samples were collected after 20 days of herbicides application from each replicated plot by uprooting the plants at random and keeping the root system intact as much as possible. The soil crumbs adhering to the root surface were carefully collected

and a composite soil sample for each plot was prepared. After removing the plant roots, the soil samples were then ground to pass through a 2 mm sieve width mesh to remove stones and plant debris, after which they were stored in plastic zipper bags for further analysis.

Choice of herbicides

The herbicides used in the experiment were commonly used in the agricultural fields employed by farmers to fight against weeds, which were obtained from a local agricultural store. The herbicides used were:

Sekator, it is a new selective herbicide for post-emergence control of dicotyledonous weeds in hard and common wheat and it is composed of two active substances (Fig 3): Amidosulfuron-sodium (100g/l) and 25g/l of Iodosulfuron-methyl-sodium (Viläuet *al.*, 2010).

Zoom, its fast effect is followed by leaves destruction and roots of weeds. Chemically, it has the following composition: Triasulfuron (4,1%) and Dicamba (Zouaouiet *al.*, 2013).

Soil treatments

The treatments were carried out at tillering stage for 3-4 leaves, at company recommended rates of 150 ml/ha for Sekator while recommended rate of 120g/ha (Zoom powder) was used for Zoom treatment.

Chemical analysis of soil

A total of 3 soil samples were collected from the study site at Tebessa. All samples were air-dried for two weeks then crushed manually and sieve to pass 2 mm mesh sieve.

For chemical analysis: The soil pH and electrical conductivity were measured with distilled water using a pH meter (1:5), available sodium content and available potassium content, were estimated with flame photometer method (Jackson, 1973). The stock

standard solution contains 1000 ppm/1000 ppm of sodium and potassium. From this stock standard solution 100, 80, 60, 40, 20 ppm solution of lower concentration was prepared. Aspirate Distilled Water and set the read out 00 by adjusting the zero control. Aspirate the standard solution that has higher concentration adjust the nobe to 100. For optimum performance the instrument should be allow 15 min to warm up during this warm up period a blank demonized water sample should be aspirated. Emissions were noted for all standard solution. Lastly water sample solutions were aspirated and emission was noted.

Organic carbon was determined by Anne method (BonneauandSouchier, 1994) by oxidation of carbon with excess potassium dichromate ($K_2Cr_2O_7$) in sulfuric acid medium (heat source). The amount of non-consumed dichromate was measured back by Mohr's salt.

The rate of organic matter (OM) was estimated by

multiplying the percentage of carbon by 1.72 (Mathieu and Pieltain, 2003).

Soil samples were analyzed for available P in sodium bicarbonate extract colorimetrically(Olsen and Dean, 1982).

Statistical analysis

The experimental assays used to results were repeated at least three times, under the same conditions and yielded the same results. To discriminate significant differences, all measurements were subjected to an Analysis of Variance (ANOVA) test (defined as $P < 0.05$). Data are shown as the mean \pm relative standard. The correlation studieswere made to reveal the association among the variables in the investigation (Gomez and Gomez, 1984).

Results and discussion

The analyses of variance for the different parameters are reported in Table 1, where the pH, EC, Ka, K, P and OM represent the sources of variation.

Table 1. Analysis of variance results comparing -chemical parameters obtained for herbicides applied to the soil of *Triticum* culture.

Source	statistical parameters			
	df	Mean Square	F _{obs}	P
pH	2	0,05503	13,57	0,006 **
EC	2	12245	8,08	0,02 *
Na	2	3,373	3,52	0,097 NS
K	2	1280,13	308,64	0,000***
P	2	0,644878	734,67	0,000***
OM	2	0,621	5,37	0,046 *

*: Significantdifferences ($p \leq \alpha = 0.05$).
 **: highly significant differences ($p < \alpha = 0, 01$)
 ***: very highly significant differences ($p < \alpha = 0,001$)
 NS: non-significantdifferences ($p > 0.05$)

TheHerbicide effects in soil chemical properties were significantly different between treatment variations. Soil pH decreased significantly ($p < \alpha = 0, 01$) from 8.32 up to 8.13 in the soil treated with Zoom herbicide, while soils treated withSekatorshowed no significant change in pH after treatment (Fig 4). Upon

treatment with herbicides there was augmentation in sodium ion (Na) concentration compared to the control (Fig 5) but the Na concentration increased insignificantly ($p > 0.097$). Total Na concentrations increased progressively to 2.31 ppm and 4. 15 ppm in the soils treated with Sekator, whereas it increased

from 2.31 ppm to 4.14 ppm relative to Zoom treatment.

Herbicides decreased significantly ($p < 0.001$) the total K concentration immediately after treatment (Fig 6), which decreased progressively from 52.39 ppm to 28.20 ppm in the soils treated with Sekator, and continued to decrease in the soils treated with Zoom

from 52.39 ppm to 11.29 ppm. Conductivity (Fig 7) significantly decreased immediately after herbicides treatments ($p = 0, 02$) and the decrease ranged from 254 $\mu\text{s/cm}$ to 157.67 $\mu\text{s/cm}$ and 254 $\mu\text{s/cm}$ to 133.13 $\mu\text{s/cm}$ for Sekator treatment and Zoom treatment, respectively. So exchangeable K followed a similar pattern as conductivity.

Table 2. Pearson correlation coefficient of soil properties in eastern Algeria.

Parameters	N	CE	MO	p	pH
CE	-0.69	-	-	-	-
MO	-0.115	-0.024	-	-	-
p	0.257	-0.446	0.678	-	-
pH	-0.087	0.363	-0.857	-0.892	-
K	-0.703	0.849	-0.166	-0.684	0.520

Significant 'r' at $p < 0.05$ level.

Level of the organic matter (OM) reduced significantly upon treatment with the herbicides Sekator compared to the control (Fig 8). Relative to the treatment, OM decreased by 67, 56%. However, they increased significantly when treated with herbicide Zoom used in this study compared to the control by 17, 29%. Similar to the results obtained for content of available phosphorus (P) (Fig 9). The available phosphorus significantly increased by 10.49% in the soils treated with Zoom herbicide and then significantly decreased by 2, 7% in relative to Sekator treatment. The Herbicide effects in OM and available P of soil were significantly different between treatment variations.

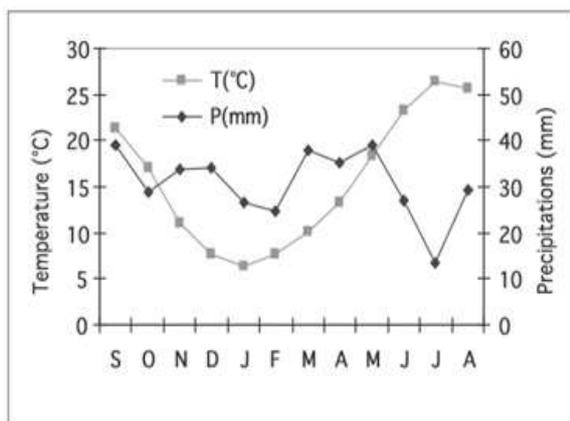


Fig. 2. Gausson and Bagnouls diagram of the study area (1972-2008).

There were significant correlation ($p < 0.05$) in 26.6% (Table 2) of the soil property pairs and that was reasonable for identification of underlying factor pattern.

This result was expected based on the characteristics of the study area indicating significant correlation among soil properties that bear relationship with one another. The established trend indicated the possibilities of grouping soil properties into similarity factors based on their correlation patterns.

Exchangeable K and available P significantly correlated with the highest number of soil properties (each correlated with 3 other soil properties), then closely followed by Na, OM, pH and EC that significantly correlated with EC and pH, available P and pH, OM and available P, Na and K respectively. The strongest negative significant ($p < 0.01$) correlations were between available P and pH ($r = -0.89$), OM and pH ($r = -0.88$), whereas the strongest positive significant correlations were between EC and K ($r = 0.85$).

After an herbicide has been applied to the soil, it has one of three fates. It can either remain dissolved in

the soil solution, be adsorbed by smaller soil colloids or be absorbed by plant roots and shoots (Fig. 10). Herbicide that is adsorbed by soil is “tied-up” or

bound to the soil and is not readily available for weed absorption (Kurt *et al.*, 2011).

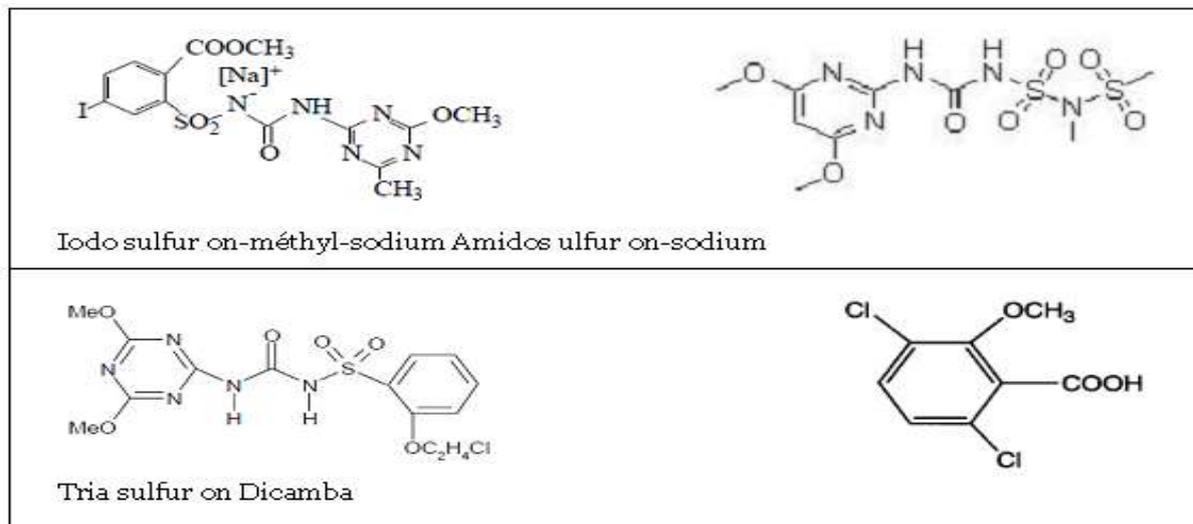


Fig. 3. Molecular structures of the pesticides considered(Vulliet *et al.*, 2002).

Based on the results, soil chemical properties did differ significantly under different treatments. Also increasing content of available phosphorus in soil results in the released of ions H⁺ by roots that dissolved the natural phosphates by making assimilable to the plant and in the case where phosphorus is not collected by the roots it is reacted with the various component of the soil and thus it is found adsorbed (Hinsinger, 2001).

irrigation causing the transfer of phosphorus to unavailable forms (Adil, 2012).It is known that the adsorption of phosphorus decreases with increasing pH to oxides or pure argillaceous minerals (Muljadi *et al.*, 1966,Hingston *et al.*, 1972). Research has shown that for soil rather different mineralogical compositions but differentiated by pH, there is an increase in adsorption with decreasing pH (Lopez-Hernandez and Burnham 1974,Parfitt, 1977, Friesen *et al.*, 1980,Eze and Loganathan, 1990).

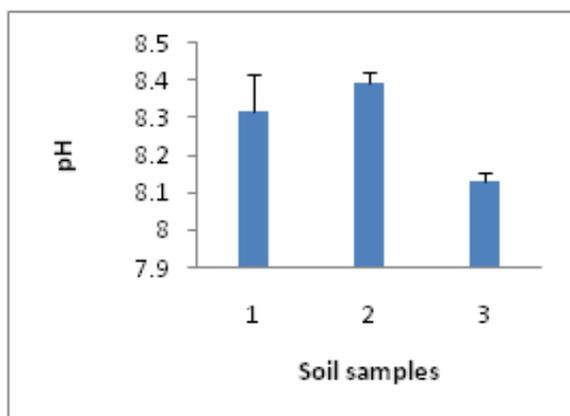


Fig. 4. Effect of herbicides in pH soil samples (1: Control, 2: Sekator treated soil, 3: Zoom treated soil).

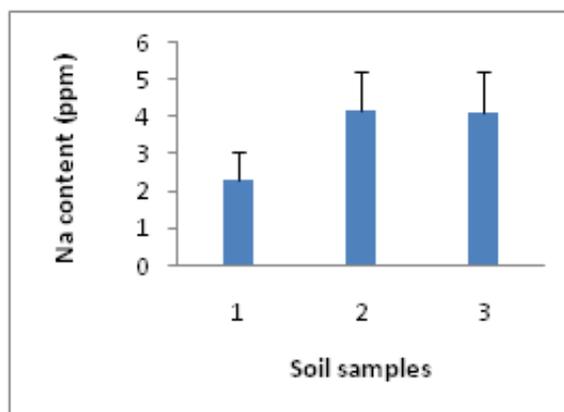


Fig. 5. Effect of herbicides in Na content soil samples (1: Control, 2: Sekator treated soil, 3: Zoom treated soil).

Decrease of the amount of assimilable phosphorus is probably due to the immobilization of reacting phosphorus with Ca²⁺ ions to a non-draining

For all treatments, the amounts of exchangeable

potassium decrease according to Cengizet *al.*,(2001). Under salt stress, potassium from the external environment is highly mobilized to the plants, explain the reduction of soil K levels under high levels of NaCl. Maalem (2011) found that the soil K decreases significantly, indicating its probable translocation to the plant, for it is in the case of salt stress.

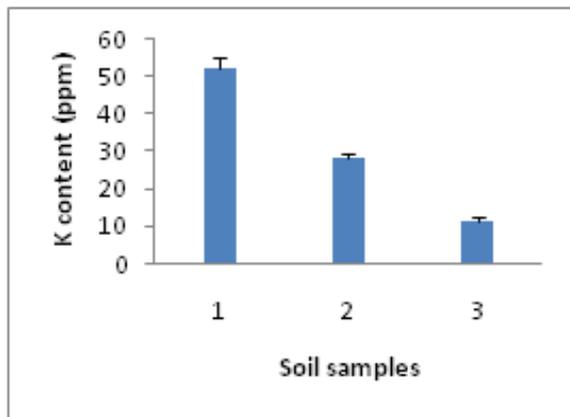


Fig. 6. Effect of herbicides in K content soil samples (1: Control, 2: Sekator treated soil, 3: Zoom treated soil).

In the similar way, the greater solubilization of insoluble phosphates by the increased phosphate solubilizing microorganisms as well as higher content of organic acids present in the root exudates of the growing plants resulted greater release of available phosphorus in the rhizosphere soil of rice. As compared to control, the increase in available phosphorus was highest under oxyfluorfen (23.2%) followed by fluchloralin (20%) and oxadiazon (14.7%), respectively (Das and Debnath, 2006).

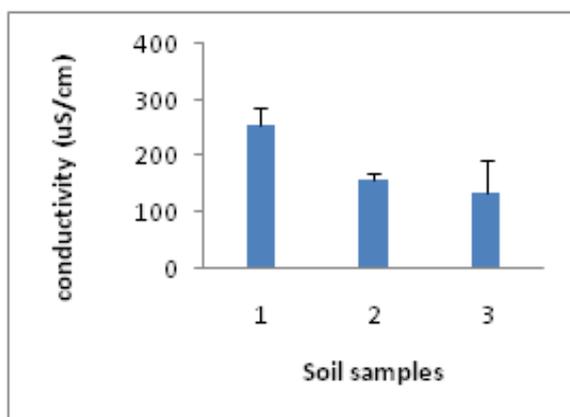


Fig. 7. Effect of herbicides in conductivity soil samples (1: Control, 2: Sekator treated soil, 3: Zoom treated soil).

Soil electrical conductivity (EC) is useful as a relative measure of the total quantity of ions in the soil solution. Soil EC has no direct effect on crop growth or yield, but it is frequently observed that there are close relationships between EC and a variety of other soil properties that are highly related to crop growth and yield (Olson, 2000).

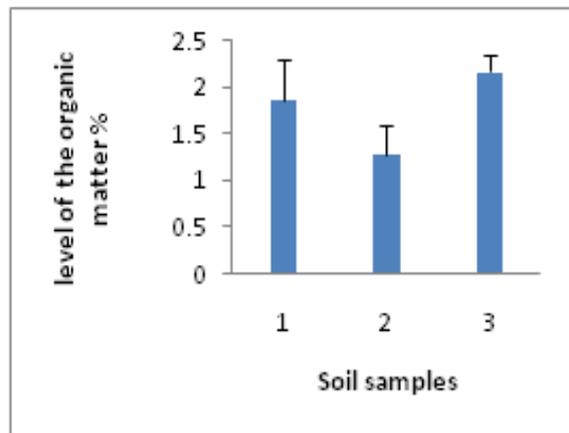


Fig. 8. Effect of herbicides in OM of soil samples (1: Control, 2: Sekator treated soil, 3: Zoom treated soil).

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).

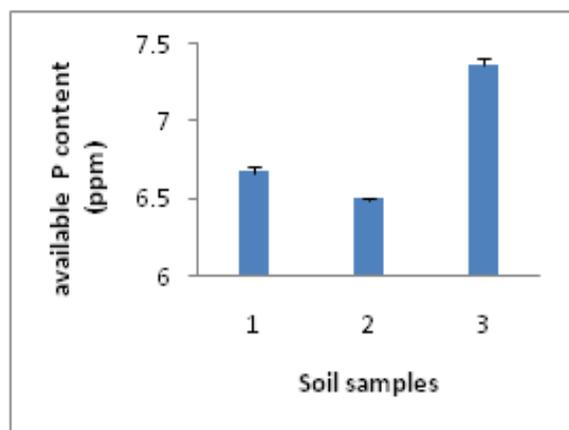


Fig. 9. Effect of herbicides in available phosphorus of soil samples (1: Control, 2: Sekator treated soil, 3: Zoom treated soil).

The nature of dissolved organic matter influences the adsorption and desorption of dimethuron, atrazine and carbetimethion (Barriuso *et al.*, 1992). Increased adsorption of less soluble atrazine and dimethuron, 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). Clay minerals appear to exert their primary influence by modifying the physicochemical 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 occurring 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).

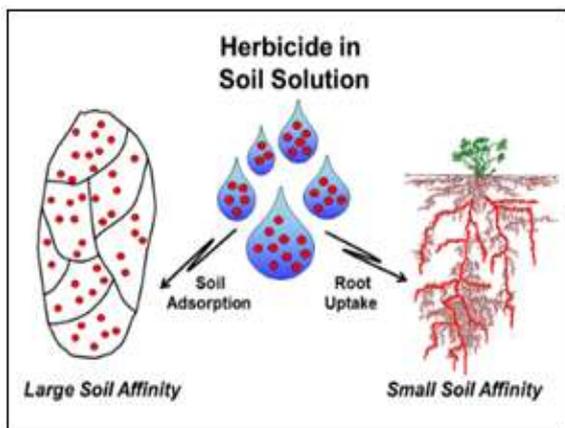


Fig. 10. Effectiveness of soil applied herbicides can depend on the physical properties of the herbicide, soil organic matter content, and soil texture. When herbicides have a strong affinity to soil. They are less effective for weed control (Kurt *et al.*, 2011).

The relationships among soil pH, organic matter, total K and other indicators are common. The change between soil pH and organic matter remained stable, which is possibly due to the reflection that the soil pH is synthesized by soil chemical properties widely affected by soil microbial activities, composition and decomposition of organic matter, morphology

transformation and release of N, P and other nutrients (Fu and Wang, 2007). In brief, the variation in exchangeable base cations and EC is controlled by the interaction of plant and soil, and the interaction of soil physical, chemical, and biological properties, which in turn controls plant nutrient availability in the sandy land ecosystem.

Conclusion

The indiscriminate use of herbicides has increasingly become a matter of environmental concern altering the soil fertility status, because of their adverse effects on soil microorganisms as well as on physicochemical properties of soil. Although the efficacy of herbicides in controlling the weeds is important, its residual impact should also be considered for environmental safety. The herbicides are used either as pre-emergence or as post-emergence; a high proportion of herbicides reaches the soil and accumulates in the microbiologically active top soil altering microbial populations and biodiversity, which are good indicators of the balance in the agroecological system. This study has elucidated the ability of herbicides (Sekator and Zoom) to chelate or bind with soil minerals there by reducing the availability for uptake of essential minerals such as K thus eliciting various malformations in the plants and making the plants susceptible 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.

The soil fertility status may also be enhanced by microbial processes including degradation of agrochemicals/herbicides, nutrient cycling and carbon sequestration. Therefore, there is a need for the advent and use of cheaper, ecofriendly alternatives that result in increased crop production along with the judicious use of the known arsenal of agrochemicals as suggested by the integrated pest and nutrient management protocols. Further, it is necessary to strengthen the scientific basis of modern agriculture, because herbicides may be advantageously used only if their persistence,

bioaccumulation, and toxicity in agroecosystem are strictly controlled.

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