RESEARCH PAPER

Determination of diazinon residues in artificially polluted soils.

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A B S T R A C T:

The combination effects of diazinon insecticide (O, O-diethyl O-[6-methyl-2-(1-methylethyl)-4-pyrimidynyl]), three different soil orders (Entisols, Vertisols and Inceptisols) and two soil moisture contents (50% and 100% of field capacity) was studied in a pot experimental design. This experiment last for two months from with five sampling periods at biweekly intervals. The main obtained results of this study were the lowest pH values (6.53±0.006) shown by the combined treatment DS3W2. The combinations DS3W1, DS3W2 and CS1W1 showed the highest organic matter levels (20.698±0.001 g.kg^{-1}). The combined treatment DS3W2 showed the highest total nitrogen contents (2.811±0.003 g.kg^{-1}). Diazinon residues were above the maximum residue limit (MRL) after 24h of application. Whereas, residues have not detected in the treated soils during the other sampling periods and this may indicate complete degradation of diazinon, which may refer to diazinon properties, environmental factors, microbial activities and soil characteristics.

1.INTRODUCTION:

The continuous interaction among soil minerals, organic matter and organisms produce a dynamic system called soil. These three major components influences the physicochemical and biological properties of terrestrial system (Khudhur, 2018). The undesirable changes in soil's physical, chemical or biological characteristics known as pollution that harmfully affect the organism's life (Pandey et al., 2005). The environmental pollution by agricultural and industrial sources increase the amount of effluents in air, water and soil which affect the quality of food and human health (Bordjiba et al., 2001). Because of the relative lack of new areas suitable

for agriculture, the performance of the existing agricultural areas has substantially enhanced. Pesticides have extensively used in agrochemical practice to protect plant against different pests. Although these pesticides have intended for use at low concentrations, their application may cause pollution of soil, resulting in chemical and biological disturbance of this environment (Cserháti *et al*., 2004). As pesticides are applied, they usually meet soil and undergo a variety of transformations that provide a complex pattern of metabolites (Sanchez *et al*., 2011).

Diazinon [O, O-diethyl O-(2-isopropyl-4-methyl 6-pyrimidinyl) phosphorothioate] is a contact, non-selective and non-systemic organophosphorus insecticide with a wide range of insecticidal activity and it is first registered in the United States in 1956 (Kendall *et al*., 1993 and NPIC, 2003). This compound is available as a dust, granules, seed dressings, wettable powder and emulsifiable solution. After diazinon

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application, it is often found in the surrounding soil, surface waters and the surface of plants (Tang *et al.*, 2009). Diazinon has been widely used to control crawling insects, ticks, adult and juvenile forms of flying insects, mites and spiders at concentrations about 3-15 kg.ha^{-1} (Kendall *et al.*, 1993 and NPIC, 2003).

Pesticide residue is the part of a pesticide that remains in the environment for a period after application. The residues of persistent pesticides stay in the environment without breaking down for long periods. These pesticides are sometimes desirable, because there is no need for repeated application and they provide long-term pest control (Milne, 1998). The derivatives of pesticide residues include degradation products, metabolites, reaction products, and impurities that may have toxicological significance (Stenersen, 2004). Soil properties such as organic matter content, soil texture and soil pH play an important role in the carryover potential of residual pesticides (Johnson, 2004). The characteristics of the pesticide, including its over-all stability either as parent compound or metabolites, its volatility, solubility, formulation and the method and its site of application are among the factors that influence the persistence of pesticides. Moreover, the environmental factors like temperature in particular, precipitation, humidity and wind are among the other factors affecting pesticides' persistence (Edwards, 1975). The rate of dispersal and the persistence time of pesticides in soil depend on the physico-chemical and biological properties of the soil (Medved, 1975). Kabir *et al.*, (2008) observed that diazinon left residue up to 6 d after spray of 3 supervised fields at the field dose 1.5 ml.l^{-1} of water, however the level of residue was above the maximum residue limit (MRL) which established by FAO 1970.

Unfortunately, there are few studies conducted on pesticides in Kurdistan Region. Khider (1981) studied the effect of insecticides and fungicides on 3 strains of *Rhizobium leguminosarum*. Darwesh (2004) studied the effect of some pesticides on denitrification in different textured soils. Other studies conducted on pesticide adsorption to soil media by some authors (Hamadamin 2006, Shariff, 2008, Abdul Al-Rahman, 2010). Alshaikh (2011) studied the effect of four fungicides on the growth rate of infected soybean with mycorrhiza. Khudhur (2011) studied

the effect of some pesticides on soil and growth characteristics of faba bean.

Due to lack of studies on determination of pesticide residues in Kurdistan soils, we found an importance to conduct this study and we aim to determine the effect of diazinon pesticide in combination with three different soil orders and two levels of moisture content on some soil chemical properties.

2.MATERIALS AND METHODS

2.1. Soil sampling and analysis

Different soil orders, which had no previous history of pesticide use including Entisols, Vertisols and Inceptisols, were collected at a random pattern (0-30 cm depth) from three different agricultural fields of Erbil province in May 2011. The fields were Agholan, Debaga and Girdarasha (Figure 1).
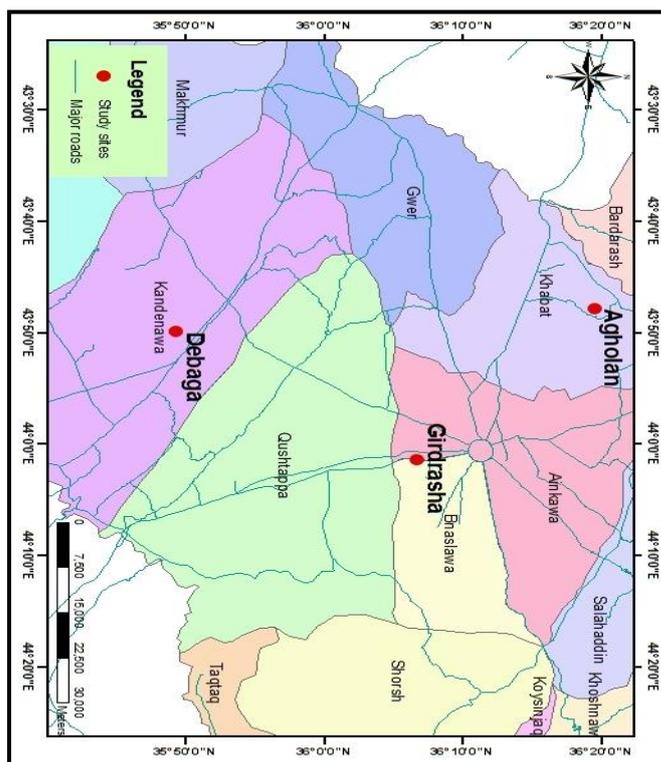

Figure 1: Map showing: Iraq, Erbil and the studied aria.

Soil samples were brought to the greenhouse of Science College. Samples from each soil order were separately screened from gravels and stones, pulverized, air-dried and sieved by 2-mm sieve. Physical, chemical and microbiological properties (Table 1) were determined according to (Ryan *et*

al., 2001, Jones, 2001, van Reeuwijk, 2002, Pansu and Gautheyrou, 2006 and Bashour and Sayegh, 2007).

Table 1: Physical, chemical and microbiological properties of the studied soils.

Soil properties			Agholan	Debaga	Girdarasha
Physical	Particle size distribution (g.kg^{-1})	Sand	23.79	20.51	19.23
		Silt	52.56	58.97	64.10
		Clay	25.64	20.51	16.67
	Texture		Silt loam	Silt loam	Silt loam
	Moisture content (%)		16.23	8	4.5
	Moisture content (ml.100g^{-1})		32.50	25.00	24.00
Chemical	pH		7.22	7.20	7.16
	Electrical conductivity (EC) (dS.m^{-1})		4.22	4.16	3.16
	Cation exchange capacity (CEC) (c.mol.kg^{-1})		33.168	26.959	28.895
	Organic Matter (OM) (g.kg^{-1})		15.524	8.624	12.074
	Total nitrogen (N) (g.kg^{-1})		2.519	1.079	2.412
	Total phosphorus (P) (g.kg^{-1})		0.143	0.127	0.452
	Total sulfur (S) (g.kg^{-1})		0.007	0.004	0.008
Microbiological	Total bacterial count (Bacterial cells.g^{-1} dry soil)		3.80×10^5	1.40×10^5	1.77×10^6
	Total fungal count (Fungal propagul.g^{-1} dry soil)		3.70×10^5	6.70×10^4	6.68×10^5

2.2. Analysis of soil physicochemical properties

In the laboratory, the collected soil samples from each pot in pre-labelled nylon bags were analysed for physical and chemical properties. Soil pH has measured from the saturation extract using pH-meter as mentioned by Ryan *et al*., (2001). The instrument was standarized before use with buffers pH (4, 7 and 9). Walkley-Black procedure 1934 for soil organic matter and micro-Kjeldahl procedure for soil total nitrogen have followed according to van Reeuwijk (2002).

2.3. Diazinon treatment

Diazinon insecticide (10%) (Table 2 and Figure 2) was prepared at its commercial recommended dose according to its active ingredients (a.i.) as described by (Hill, 2008). It is then placed in a sprayer (the amount of spraying water was as 60 liters/donum) and ready for application. Each soil order was sprayed separately by diazinon and a portion from each soil order was left without pesticide treatment (control). Soil portions were mixed to obtain homogenous distributions. Then the pesticide-treated soils were sealed and left for an overnight at room temperature.
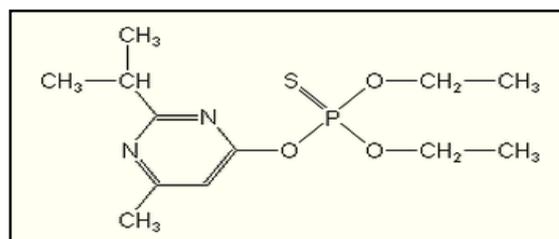

Figure 2: Diazinon structure (Xu, 2000).

Source: Xu, (2000); Plimmer *et al.*, (2003); Pretty, (2005); Moros *et al.*, 2007; Meister *et al.*, (2008); Tomlin, (2009) and WHO, (2010).

Table 2: Description of diazinon pesticide.

Common name	diazinon
Chemical name	[O,O-diethyl O-(2-isopropyl-4-methyl 6-pyrimidinyl) phosphorothioate]
Trade name	Knox Out, Spectracide and Basudin
Chemical family	Organophosphate
Molecular formula	$C_{12}H_{21}N_2O_3PS$
Molecular weight	304.3 g.mol^{-1}
Recommended dose	1-2.5kg.donum^{-1}
Half-life in soil	9-11 days
Analysis method	HPLC-UV, GC/MS
LD50	1000 mg.kg^{-1}
Toxicity class	II=Moderately hazardous

2.4. Pot experiment layout and statistical analysis

A factorial experiment (2×3×2 i.e. pesticide × soil order × moisture content) was conducted using Completely Randomized Design (CRD) with three replications under twelve combined treatments (Table 3). The experiments last for two months with conducting five samplings at biweekly intervals and the climatic condition during the study has presented in (Table 4).

Table 3: Pot experimental design.

Combined treatments	Pesticide	Soil order	Moisture content	Combined treatments	Replications
DS1W1	Diazinon	Agholan	50%	Diazinon.Agholan.50%	3
DS1W2			100%	Diazinon.Agholan.100%	3
DS2W1		Debaga	50%	Diazinon.Debaga.50%	3
DS2W2			100%	Diazinon.Debaga.100%	3
DS3W1		Girdarasha	50%	Diazinon.Girdarsha.50%	3
DS3W2			100%	Diazinon.Girdarsha.100%	3
CS1W1	Control (no pesticide)	Agholan	50%	Control.Agholan.50%	3
CS1W2			100%	Control.Agholan.100%	3
CS2W1		Debaga	50%	Control.Debaga.50%	3
CS2W2			100%	Control.Debaga.100%	3
CS3W1		Girdarasha	50%	Control.Girdarasha.50%	3
CS3W2			100%	Control.Girdarasha.100%	3

Table 4: Climatic condition during the study.

Parameters	1st sampling	2nd sampling	3rd sampling	4th sampling	5th sampling	Mean
Maximum temperature (ºC)	37.0	36.7	37.0	44.6	41.2	39.3
Minimum temperature (ºC)	24.4	26.4	28.6	33.3	30.0	28.54
Dry temperature (ºC)	31.1	31.5	33.3	38.9	35.1	33.98
Humidity (%)	29	31	23	20	29	26.4
Wind velocity (m.sec^{-1})	1.0	1.4	2.5	3.9	1.5	2.06
Wind direction	320	240	220	40	320	228
Maximum wind velocity (m.sec^{-1})	3	4	7	14	6	6.8

From: Directorate of Meteorology and Seismology in Erbil.

For this purpose, similar plastic pots (average diameter 15 cm and height 17 cm) have used and each filled with 4 kg pesticide-treated soil and control treatments remained without pesticide treatment. The pots have provided by a below-container to collect the irrigation water and return-back to the pots. Then the pots have covered with filter papers and they have irrigated daily by tap water at 50% and 100% moisture content (Khudhur and Sarmamy, 2018). Statistical analysis was performed using SPSS version 11.5 and Microsoft Office Excel 2010 and the means were compared using Duncan's Multiple Range test at the level of significant of 0.05 (Khudhur and Sarmamy, 2016).

2.5. Determination of diazinon residues

Soil samples of 20 g have extracted for 10 minutes by ultrasonic agitation with 20 ml of acetonitrile as recommended by Sáncheza *et al.* (2003). The suspensions have then centrifuged at 2000 rpm for 10 minutes and the supernatant removed. The centrifugation step has repeated twice to obtain a clear supernatant. The supernatants have then filtered through glass-fiber filters. The acetonitrile fractions were evaporated to dryness at room temperature and the residues were reconstituted in 0.4 ml mobile phase acetonitrile:water (65:35, v:v) by sonicating for 1 minute and then injected to chromatographic column. Diazinon has submitted to chromatographic analysis using high performance liquid chromatography in a reversed-phase C-18 column. The mobile phase has consisted of acetonitrile:water (65:35, v:v) at ambient temperature with injection volume of 100 µl and flow-rate of 1ml.min^{-1}. The detection wavelength of the UV-detector (Perkin Elmer) was 245 nm and the retention time was 2.77 minutes.

Stock diazinon solution (Analytical Standard 99.8% obtained from Sigma Aldrich) was prepared at 500 mg.l^{-1} with acetonitrile as described by Sáncheza *et al.* (2003). This stock solution has further diluted to prepare additional working solutions with distilled-deionized water in order to obtain final concentrations of 0.01, 0.1, 1, 10 and 100 µg.ml^{-1}. From working solutions, a calibration standard curve was prepared for soil samples pesticide peak areas. Unknown concentrations of pesticide in the soil samples have calculated by interpolation of sample's peak areas on the calibration graph (Khudhur, 2013).

3. RESULTS AND DISCUSSION

The lowest pH values shown by the combination the combination DS3W2 during the 4th sampling period (Table 5). This is probably because diazinon contains sulfur in its composition, which may use as a source of nutrient in the form of sulfate (SO_4^{-2}) by microorganisms, and it must undergo a biological oxidation. This process produces large amounts of acid, and occasionally elemental sulfur has used to decrease soil pH (Hodges, 2012).

Table 5: Effects of different treatments on soil pH values during five sampling periods (Mean±S.E.).

Treatments	1st sampling (24h after application)	2nd sampling (2 weeks after application)	3rd sampling (4 weeks after application)	4th sampling (6 weeks after application)	5th sampling (8 weeks after application)
DS1W1	7.89±0.000 [b]	8.27±0.012 [ab]	7.01±0.006 [c]	6.57±0.000 [h]	6.64±0.000 [f]
DS1W2	7.95±0.000 [a]	7.95±0.000 [g]	7.27±0.006 [a]	6.84±0.006 [a]	6.73±0.006 [d]
DS2W1	7.82±0.006 [d]	8.13±0.000 [e]	7.16±0.006 [b]	6.55±0.006 [i]	6.75±0.000 [c]
DS2W2	7.82±0.006 [d]	7.92±0.017 [h]	7.07±0.006 [c]	6.63±0.006 [g]	6.48±0.006 [i]
DS3W1	7.89±0.006 [b]	8.22±0.006 [c]	7.19±0.006 [b]	6.75±0.012 [c]	6.76±0.000 [bc]
DS3W2	7.88±0.006 [b]	7.91±0.012 [h]	7.06±0.012 [c]	6.46±0.006 [j]	6.53±0.006 [h]
CS1W1	7.50±0.000 [e]	8.29±0.017 [a]	7.09±0.028 [c]	6.65±0.000 [f]	6.57±0.000 [g]
CS1W2	7.89±0.006 [b]	8.26±0.006 [b]	7.28±0.012 [a]	6.79±0.003 [b]	6.78±0.012 [a]
CS2W1	7.38±0.012 [f]	8.12±0.000 [e]	7.16±0.012 [b]	6.58±0.000 [h]	6.43±0.006 [j]
CS2W2	7.82±0.338 [d]	8.12±0.006 [e]	7.06±0.006 [c]	6.71±0.006 [d]	6.77±0.006 [ab]
CS3W1	7.84±0.006 [c]	8.19±0.006 [d]	7.20±0.058 [b]	6.69±0.006 [e]	6.49±0.006 [i]
CS3W2	7.82±0.000 [d]	8.08±0.012 [f]	7.06±0.012 [c]	6.58±0.012 [h]	6.68±0.012 [e]

Different significant effects on soil organic matter have shown by the combined treatments between pesticides, soil orders and soil moisture content (Table 6).

Table 6: Effects of different treatments on soil organic matter (g.kg^{-1}) values during five sampling periods (Mean±S.E.).

Treatments	1st sampling (24h after application)	2nd sampling (2 weeks after application)	3rd sampling (4 weeks after application)	4th sampling (6 weeks after application)	5th sampling (8 weeks after application)
DS1W1	10.349±0.001 [d]	17.249±0.002 [a]	3.450±0.001 [d]	6.899±0.001 [c]	13.799±0.001 [c]
DS1W2	13.799±0.002 [c]	6.899±0.003 [d]	6.899±0.002 [c]	6.899±0.002 [c]	10.349±0.001 [d]
DS2W1	13.799±0.002 [c]	10.349±0.001 [c]	3.450±0.001 [d]	13.799±0.002 [b]	17.249±0.000 [b]
DS2W2	17.249±0.002 [b]	10.349±0.000 [c]	3.450±0.001 [d]	13.799±0.001 [b]	17.249±0.001 [b]
DS3W1	10.349±0.000 [d]	17.249±0.000 [a]	13.799±0.001 [a]	17.249±0.000 [a]	20.698±0.001 [a]
DS3W2	20.698±0.001 [a]	10.349±0.001 [c]	3.450±0.001 [d]	17.249±0.000 [a]	20.698±0.001 [a]
CS1W1	13.799±0.003 [c]	6.899±0.003 [d]	13.799±0.000 [a]	6.899±0.002 [c]	20.698±0.000 [a]
CS1W2	17.249±0.000 [b]	3.450±0.001 [e]	10.349±0.000 [b]	13.799±0.000 [b]	17.249±0.000 [b]
CS2W1	10.349±0.001 [d]	10.349±0.001 [c]	3.450±0.001 [d]	17.249±0.001 [a]	17.249±0.000 [b]
CS2W2	13.799±0.001 [c]	3.450±0.002 [e]	10.349±0.000 [b]	17.249±0.001 [a]	17.249±0.002 [b]
CS3W1	6.899±0.001 [e]	13.799±0.000 [b]	3.450±0.001 [d]	6.899±0.001 [c]	17.249±0.000 [b]
CS3W2	10.349±0.001 [d]	10.349±0.001 [c]	3.450±0.000 [d]	6.899±0.001 [c]	17.249±0.001 [b]

At the beginning of the study, the combined treatment DS3W2 showed the highest level of soil organic matter. During the 2nd sampling the combined treatments DS1W1 and DS3W1 showed the highest level of soil organic matter. The combination of DS3W1, DS3W2, CS2W1 and CS2W2 during the 4th sampling showed the highest organic matter amounts. At the end of the

study, the combinations of DS3W1, DS3W2 and CS1W1 showed the highest organic matter levels.

The combined treatments CS1W2 in the 1st sampling, DS2W2 in the 2nd sampling and DS1W2 in the 4th sampling showed the highest total nitrogen contents (Table 7). This increase may be due to some organisms that were able to

adapt to some re-adjustment and adaptation to the strange environment created by diazinon and later participated in degradation of the organic compound whose cumulative effect translated to nitrogen content increase before the 4 weeks of the experiment as concluded by Shittu *et al.*, (2004).

Table 7: Effects of different treatments on soil total nitrogen (g.kg^{-1}) values during five sampling periods (Mean±S.E.).

Treatments	1st sampling (24h after application)	2nd sampling (2 weeks after application)	3rd sampling (4 weeks after application)	4th sampling (6 weeks after application)	5th sampling (8 weeks after application)
DS1W1	3.676±0.000 [ab]	5.996±0.001 [bcd]	3.043±0.001 [c]	11.123±0.002 [a]	2.863±0.002 [ab]
DS1W2	2.899±0.002 [abc]	7.778±0.000 [abcd]	2.414±0.002 [c]	12.579±0.002 [a]	1.414±0.001 [bc]
DS2W1	3.731±0.001 [abcd]	7.353±0.001 [ab]	4.421±0.000 [bc]	2.869±0.002 [bc]	0.713±0.002 [bc]
DS2W2	1.545±0.001 [bcde]	18.421±0.001 [a]	5.518±0.001 [abc]	3.638±0.001 [bc]	2.113±0.002 [abc]
DS3W1	1.528±0.000 [bcde]	4.384±0.001 [cd]	16.279±0.000 [a]	2.887±0.000 [bc]	0.710±0.003 [abc]
DS3W2	2.298±0.001 [abcde]	3.030±0.001 [cd]	5.315±0.002 [bc]	2.947±0.001 [bc]	2.811±0.003 [a]
CS1W1	1.455±0.001 [abcde]	4.497±0.001 [cd]	3.024±0.002 [c]	2.917±0.001 [bc]	2.138±0.001 [ab]
CS1W2	4.970±0.002 [a]	4.839±0.001 [cd]	2.344±0.002 [c]	2.211±0.002 [bc]	2.134±0.001 [abc]
CS2W1	1.423±0.001 [de]	2.201±0.000 [c]	3.653±0.002 [abc]	5.072±0.000 [b]	1.426±0.001 [abc]
CS2W2	0.735±0.001 [e]	2.966±0.002 [cd]	14.301±0.000 [ab]	2.917±0.000 [bc]	2.121±0.002 [abc]
CS3W1	1.461±0.002 [cde]	2.220±0.006 [cd]	3.024±0.001 [c]	0.000±0.001 [c]	1.423±0.002 [bc]
CS3W2	0.783±0.001 [e]	9.251±0.001 [abc]	2.381±0.000 [c]	1.471±0.001 [bc]	0.707±0.001 [c]

Diazinon residues were 1.654, 1.645, 1.654, 1.654, 1.654 and 1.649 µg.g^{-1} air-dried soil in the combined treatments DS1W1, DS1W2, DS2W1,

DS2W2, DS3W1 and DS3W2 respectively (Table 8).

Table 8: Diazinon residues (µg.g^{-1} air-dried soil) during five sampling.

Treatments	1st sampling (24h after application)	2nd sampling (2 weeks after application)	3rd sampling (4 weeks after application)	4th sampling (6 weeks after application)	5th sampling (8 weeks after application)
DS1W1	1.654	0	0	0	0
DS1W2	1.645	0	0	0	0
DS2W1	1.654	0	0	0	0
DS2W2	1.654	0	0	0	0
DS3W1	1.654	0	0	0	0
DS3W2	1.649	0	0	0	0
CS1W1	0	0	0	0	0
CS1W2	0	0	0	0	0
CS2W1	0	0	0	0	0
CS2W2	0	0	0	0	0
CS3W1	0	0	0	0	0
CS3W2	0	0	0	0	0

The levels were above the maximum residue limit (MRL) (0.5 ppm) set by FAQ-WHO 1970 after 24h of application, similar observations given by Kabir *et al.*, (2008) who revealed that diazinon residue could detected up to 6 days after spread (DAS). Whereas, residues were not detected in the treated soils during the other sampling periods and this may indicate complete

degradation of diazinon which may refer to diazinon properties, environmental factors, microbial activities and soil characteristics. The presence of nutrient and microorganisms in the soil has been found to have greatest influence on the biodegradation of pesticides (Massiha *et al.*, 2011). Microorganisms have the ability to interact both chemically and physically with substances

leading to structural changes or complete degradation of the target pesticide molecule. *Pseudomonas* sp. utilizes diazinon as a source of carbon and energy and the enzymes responsible for organophosphorus pesticide degradation is carboxylesterase and phosphotriesterase which attack the P–O alkyl and P–O aryl bonds of organophosphates (Drufovka *et al*., 2008).

4.Conclusions and recommendations

Diazinon does not show residue even two weeks after application and this indicate that it does not adversely affect soil microbial activity if applied at its recommended application rate, thus there is no need for soil inoculation for its biodegradation, but the problem is with repeated application, which requires biodegradation. Different significant effects on soil characteristics have shown by the interactions among pesticide, soil orders and soil moisture contents. Accordingly, we can recommend the application of pesticides at recommended doses and avoiding repeated application, and recommend the application of organic matter to the soil to improve soil characteristics and increase soil microbial activity, which may have beneficial effects on the persistence and rate of movement of pesticide residues through the soil profile.

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