Combination Effects of Three Different Pesticides, Three Soil Orders and Two Moisture Contents on some Soil Chemical Characteristics

Nashmeel Saeed Khudhur* and Abdul-ghany Omer Ismaeel Sarmamy**
***Department of Environmental Science, College of Science, University of Salahaddin, Kurdistan Region, Iraq.**
****Department of Biology, College of Science, University of Salahaddin, Kurdistan Region, Iraq.**

Abstract

A pot experiment was designed to study the combination effects of three different pesticides, three different soil orders and two soil moisture contents on some soil chemical characteristics. The main obtained results at the end of this study were: the lowest pH value (6.43±0.006) was shown by the combined treatment CS2W1. The combination P1S2W2 showed the highest increasing effect on soil EC (4.64±0.012 $dS.m^{-1}$) and the lowest EC values (1.56±0.003 $dS.m^{-1}$) was observed in P1S1W2. Mancozeb in Agholan soil with 50% soil moisture content (P2S1W1) showed the highest soil CEC. The combinations P1S2W1, P2S2W2, P3S3W1, P3S3W2 and CS1W1 showed the highest organic matter level by value of 20.698±0.001 $g.kg^{-1}$. The combined treatment P1S2W1 showed the highest total nitrogen content (5.062±0.002 $g.kg^{-1}$). The combinations P2S2W1, P2S3W1, P2S3W2, P3S1W2 and CS1W1 showed the highest soil total sulfur level (0.0007±0.000 $g.kg^{-1}$). The combined treatment P3S3W2 showed the highest total zinc value of 254.08±0.003 $mg.kg^{-1}$. The combination P1S1W1 showed the highest total manganese by value of 574.47±0.006 $mg.kg^{-1}$.

Keywords: Soil Chemical Characteristics, Pesticides, Soil order, Moisture content.

Introduction

Soil is a complex mixture of inorganic and organic solids, microorganisms, plant roots associated with organic matter, water, air, gas and possibly contaminants, which all interact in a dynamic equilibrium. Soil offers shelter and habitat for a countless number of organisms which not only use it as a habitat and a source of energy, but also contribute to its formation, strongly influencing the soil's physical and chemical properties as playing its role in the cycle of material flow between atmosphere, lithosphere, hydrosphere and biosphere and the nature of the vegetation that grows on it (Bohn et al., 2001; Bardgett, 2005 and Mirsal, 2008). Soil pollution is undesirable alteration in its physical, chemical or biological characteristics that harmfully affect the organism's life (Pandey et al., 2005). The environmental contamination by toxic xenobiotic chemicals, arising mainly from agricultural and industrial sources increase the amount of effluents thrown into the air, water and soil and affect on the quality of food and human health which are important sources of pollution and may result in ecotoxicological effects on terrestrial, groundwater and aquatic ecosystems (Bordjiba et al., 2001). Because of the relative lack of new areas suitable for agriculture, the performance of the existing agricultural areas has to be substantially enhanced. Pesticides such as insecticides, herbicides, fungicides, etc., have been extensively used in agrochemical practice to protect plant against different pests. Although these pesticides are intended to be used at low concentrations, their application may cause contamination of soil, resulting in chemical and biological disturbance of this environment (Cserháti *et al*., 2004). Pesticide is a general term that includes a variety of chemical and biological products used to kill or control pests such as rodents, insects, fungi, weeds and etc. The active portion of a pesticide known as the active ingredient is generally formulated by the manufacturer as emulsifiable concentrates or in solid particles like dust, granules, soluble powder, or wettable powder (Dömötörová and Matisová 2008). As pesticides are applied they usually come into contact with soil, where they undergo a variety of transformations that provide a complex pattern of metabolites (Camino-Sanchez *et al*., 2011). These processes can be grouped into those that affect persistence, including chemical and microbial degradation, and those that affect mobility, involving sorption, plant uptake, volatilization, wind erosion, runoff, leaching and upward movement in soils through capillary forces (Andreu and Pico, 2004 and Ahmad *et al*., 2011). The amount of macro- and microelements in the soils may affect plants qualities due to industrial contamination (Stevovic *et al*., 2010). Contaminated soils may become poor in nutrients or may exhaust plant nutrition faster than needed (Amin, 1985). Shittu *et al*., (2004) observed that the pH, organic carbon, nitrogen and phosphorus of both rhizosphere and subsurface soil increased from the 10^{th} to 30^{th} day of treatment by diazinon at concentration of 160 $mg.kg^{-1}$ with a highest increment of 10-fold recorded in phosphorus and 6-fold increment in organic carbon content of subsurface soil. Hamadamin (2006) concluded that the adsorption rate of glyphosate was higher than metalaxyl and this was increased with increasing SOM. Sahriff (2008) observed that adsorption of propanil was higher than atrazine and picloran and SOM was the primary source for adsorption of atrazine and propanil while clay content was more affected by picloran adsorption in addition both soil pH and CEC were affected soil affinity toward the 3 pesticides. Peignéa *et al*., (2009) observed that the biological variables exhibited spatial variability of the same order of magnitude as physicochemical parameters of soil and they were identified zones with different levels of organic matter, microbial biomass and specific respiratory activity. Abdul Al-Rahman (2010) concluded that chlorpyrifos has the greater affinity than MCPA for 12 different soils in Kurdistan Region. Khudhur (2011) observed that cyren C reduced soil iron content and glyphosate reduced sodium while increased soil total phosphorus. Bordjiba and Belaze (2013) assessed soil pollution by pesticides and they observed that the soil is rich in organic matter, with basic pH and unsalted poor in minerals with a very low conductivity probably due to the presence of pesticides. Unfortunately, there are few studies conducted on pesticides in Kurdistan Region, thus we found an importance to conduct this study to determine the effect of three different groups of pesticides in combination with three different soil orders and two levels of moisture content on some soil chemical properties.

Materials and methods

1. Soil sample collection

Soils which had no previous history of pesticide use and of different orders including Entisols, Vertisols and Inceptisols were collected in May 2011 from three different agricultural fields in Erbil province including Agholan, Debaga and Girdarasha (Figure 1). Samples were collected from the upper layer of the soils (0-30 cm depth) at a random pattern around each field according to (USAID. 2008). The soil samples were brought to the greenhouse of the College of Science. Samples from each soil order were separately screened from gravels and stones, pulverized, air-dried and sieved by 2-mm sieve.

2. Pesticide preparation and soil treatment

The most abundant and usable pesticides in Kurdistan Region including glyphosate herbicide (48%), mancozeb fungicide (80%) and diazinon insecticide (10%) were selected (Table 1) for this study according to the yearly report of plant protection in the Department of Plant Protection in Erbil/General Directorate of Agriculture during 2010-2011. These pesticides were prepared at their commercial recommended doses according to their active ingredients (a.i.) as described by (Hill, 2008). Each pesticide was placed in a sprayer (the amount of spraying water for each pesticide was as 60 liters/donum) and ready for application. Four separated portions from each soil order was sprayed separately by glyphosate, mancozeb and diazinon while the last portion from each soil order was left without pesticide treatment. The soil portions were mixed to obtain a homogenous distribution. Then the pesticide-treated soils were sealed and left for an overnight at room temperature.

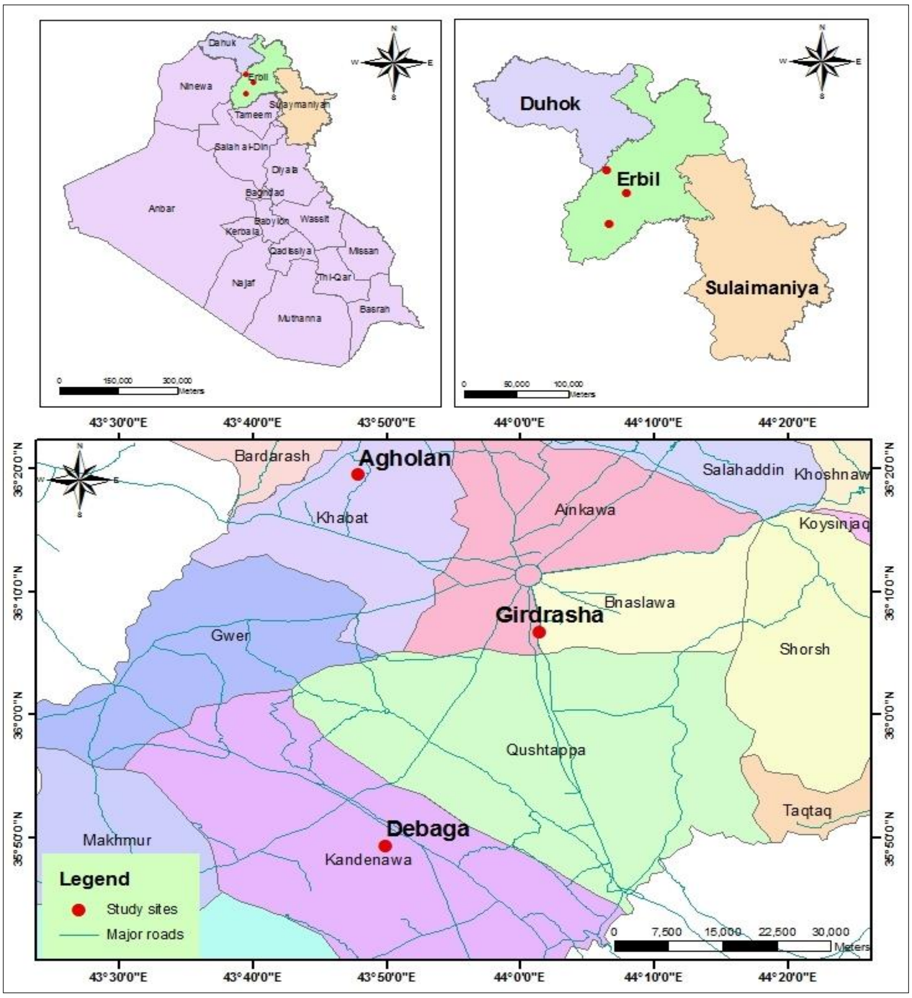

Figure 1: Map showing: Iraq, Erbil and the studied aria.

Table 1: Description of the studied pesticides.

Common name	glyphosate	mancozeb	diazinon
Chemical name	N (phosphonomethyl) glycine	[[1,2-ethanediylbis-[carbamodithioato]] (2-)] manganese, mixture with [[1,2-ethanediylbis-[carbamodithioato]]-(2-)] zinc	[O,O-diethyl O-(2-isopropyl-4-methyl 6-pyrimidinyl) phosphorothioate]
Trade name	Roundup, Glyphosate, Round up ultra, Touchdown, Kalach, Herbazad, Fomac, Fortin, Clean up	Aazimag®, Fore®, Dithane M-45®, Manzate 200®.	Knox Out, Spectracide and Basudin
Chemical family	Phosphonoglycine (not classified by families)	Carbamate	Organophosphate
Molecular	$C_3H_8NO_5P$	$(C_4H_6MnN_2S_4)_x (Zn)_y$	$C_{12}H_{21}N_2O_3PS$

e-ISSN (2522-7130) p-ISSN (2410-1036)

formula			
Molecular weight	169.08 $g.mol^{-1}$	(365.3) + (65.4) $g.mol^{-1}$	304.3 $g.mol^{-1}$
Recommended dose	1-2 L. $donum^{-1}$	10-15g.5L^{-1}.$donum^{-1}$	1-2.5kg.$donum^{-1}$
Half-life in soil	45-60 days	1-7 day	9-11 days
Analysis method	GC-MS, HPLC-flourescens, LC-MS/MS	Spectrophotometeric, HPLC, GC, headspace solid phase micro-extraction GC or reversed phase ion-pair chromatography	HPLC-UV, GC/MS
LD50	>5000 $mg.kg^{-1}$	>8000 $mg.kg^{-1}$	1000 $mg.kg^{-1}$
Toxicity class	U=Unlikely to present acute hazard	U=Unlikely to present acute hazard	II=Moderately hazardous

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

3. Pot experiment layout and statistical analysis

A factorial experiment (4×3×2) was conducted using Completely Randomized Design (CRD) with three replications under twenty-four combined treatments for two months with five sampling periods at biweekly intervals (Khudhur, 2013). For this purpose 72 pre-labelled and similar plastic pots (average diameter 15 cm and height 17 cm) were used and each filled with 4 kg pesticide-treated soil and a sample was taken from each pot. The pots were provided by a below-container to collect the irrigation water and return-back to the pots. Then the pots were covered with filter papers and they were irrigated daily by tap water at 50% and 100% moisture content. Statistical analysis was performed using SPSS version 11.5 and Microsoft Office Excel 2010 and the means were compared using Revised Least Significant Differences (R.LSD) at the level of significant of 0.05.

4. Laboratory analysis for soil chemical characteristics

In the laboratory, the collected soil samples from each pot were submitted to analysis for soil chemical properties. Soil pH and EC were measured from the saturation extract (Ryan *et al.*, 2001). Cation exchange capacity (CEC) was determined by saturating the soils with 1M NaOAc at pH 8.2 and washed with absolute ethanol (exchangeable Na was replaced with 1M NH_4OAc pH 7) then Na concentration was analyzed by flame photometer (Bashour and Sayegh, 2007). Walkley-Black procedure 1934 for soil organic matter and micro-Kjeldahl procedure for soil total nitrogen were followed according to van Reeuwijk (2002). Ascorbic acid combined with potassium antimonyl tartrate of Murphy and Riley 1962 which described by Pansu and Gautheyrou (2006) was used for determination of total phosphorus. Total sulfur was determined by turbidimetric method as described by Pansu and Gautheyrou (2006). Total zinc and manganese were determined by atomic absorption spectrophotometer (Jones, 2001) described.

Results and discussion

All treatments were effective and caused an increase in soil pH during the 2nd sampling period (table 2). During the last sampling periods (4th and 5th samplings), pH values were reduced and glyphosate showed the highest significant effect on soil pH and this come in agreement with the results obtained by Sailaja and Satyaprasad (2006) who found that glyphosate application altered the soil pH towards acidic side and this may be due to the production of glyphosate metabolite aminomethyl-phosphoric acid which decrease soil pH (Khan, 1980). Diazinon showed the lowest value of pH during the 4th sampling probably because diazinon contains sulfur in its composition which may be used as a source of nutrient in the form of sulfate (SO_4^{-2}) by microorganisms and it must undergo a biological oxidation and this process produces large amounts of acid, and occasionally elemental sulfur is used to decrease soil pH (Hodges, 2012). The lowest pH values shown by the combination CS2W1 during the 1st and 5th samplings, and the combinations P1S3W2, P1S2W2 and P3S3W2 showed the lowest pH values during the 2nd, 3rd and 4th sampling periods respectively.

Table 2: Combined treatment effects on soil pH during five sampling periods (Mean±S.E.).

Treatments	1st sampling 9/6/2011 (24h after application)	2nd sampling 24/6/2011 (2 weeks after application)	3rd sampling 9/7/2011 (4 weeks after application)	4th sampling 24/7/2011 (6 weeks after application)	5th sampling 8/8/2011 (8 weeks after application)
P1S1W1	7.87±0.012 ab	7.88±0.000 fg	7.16±0.006 abcde	6.65±0.029 m	6.91±0.012 a
P1S1W2	7.78±0.012 ab	7.73±0.006 gh	7.27±0.003 a	6.86±0.035 b	6.67±0.006 h
P1S2W1	7.79±0.017 ab	7.95±0.000 cdef	7.22±0.012 abc	6.73±0.017 h	6.80±0.058 bc
P1S2W2	7.78±0.012 ab	7.75±0.006 gh	7.01±0.000 f	6.53±0.017 v	6.65±0.000 h
P1S3W1	7.89±0.006 ab	8.19±0.006 ab	7.20±0.000 abcd	6.92±0.012 a	6.72±0.012 fg
P1S3W2	7.770±0.006 ab	7.640±0.006 h	7.12±0.220 bcdef	6.56±0.006 s	6.54±0.006 ij
P2S1W1	7.890±0.006 ab	8.150±0.338 ab	7.020±0.012 ef	6.77±0.006 f	6.66±0.006 h
P2S1W2	7.78±0.012 ab	8.13±0.000 abc	7.22±0.012 abc	6.81±0.012 d	6.76±0.006 cdef
P2S2W1	7.87±0.012 ab	8.15±0.012 ab	7.24±0.006 ab	6.72±0.012 i	6.82±0.017 b
P2S2W2	7.71±0.012 b	7.79±0.006 fgh	7.24±0.012 ab	6.55±0.006 t	6.57±0.006 ij
P2S3W1	7.87±0.015 ab	8.11±0.006 abcd	7.22±0.000 abc	6.69±0.006 k	6.95±0.012 a
P2S3W2	7.76±0.006 ab	7.89±0.006 efg	7.16±0.006 abcde	6.47±0.000 w	6.58±0.006 i
P3S1W1	7.89±0.000 ab	8.27±0.012 ab	7.01±0.006 f	6.57±0.000 r	6.64±0.000 h
P3S1W2	7.95±0.000 a	7.95±0.000 cdef	7.27±0.006 a	6.84±0.006 c	6.73±0.006 ef
P3S2W1	7.82±0.006 ab	8.13±0.000 abc	7.16±0.006 abcde	6.55±0.006 u	6.75±0.000 def
P3S2W2	7.82±0.006 ab	7.92±0.017 defg	7.07±0.006 def	6.63±0.006 o	6.48±0.006 l

P3S3W1	7.89±0.006 ab	8.22±0.006 ab	7.19±0.006 abcd	6.75±0.012 g	6.76±0.000 cdef
P3S3W2	7.88±0.006 ab	7.91±0.012 efg	7.06±0.012 def	6.46±0.006x	6.53±0.006 jk
CS1W1	7.50±0.000 c	8.29±0.017 a	7.09±0.028 cdef	6.65±0.000 n	6.57±0.000 ij
CS1W2	7.89±0.006 ab	8.26±0.006 ab	7.28±0.012 a	6.79±0.003 e	6.78±0.012 bcd
CS2W1	7.38±0.012 c	8.12±0.000 abc	7.16±0.012 abcde	6.58±0.000 p	6.43±0.006 m
CS2W2	7.82±0.338 ab	8.12±0.006 abc	7.06±0.006 def	6.71±0.006 j	6.77±0.006 cde
CS3W1	7.84±0.006 ab	8.19±0.006 ab	7.20±0.058 abcd	6.69±0.006 l	6.49±0.006 kl
CS3W2	7.82±0.000 ab	8.08±0.012 bcde	7.06±0.012 def	6.58±0.012 q	6.68±0.012 gh

Glyphosate showed the highest soil EC values during the sampling periods except for the 2nd sampling which was shown by diazinon (table 3). Soil EC of the three different soils were increased gradually after treatment and the highest increase was recorded in Debaga soil all over the study. 100% soil moisture content revealed significant increasing in soil EC during the 1st, 2nd, 3rd and 5th sampling periods and this may refer to the effect of the studied pesticides and/or ionic composition of irrigation water used during the study or the interaction effect of both pesticides with irrigation water. During the 2nd and 4th samplings, both of the combinations P3S3W2 and P2S2W2 produced significant increasing in soil EC, and the combination of P1S2W2 showed the highest increasing effect on soil EC during both the 3rd and 5th samplings. The lowest EC values were observed in the combinations, P2S1W2 during the 1st and 4th samplings, P1S1W2 during the 3rd and 5th samplings; the observations of Bordjiba and Belaze (2013) in polluted soil with mancozeb seem to confirm the truth with the combination P2S1W2.

Table 3: Combined treatment effects on soil EC values (dS.m^{-1}) during five sampling periods (Mean±S.E.).

Treatments	**1st sampling 9/6/2011 (24h after application)**	**2nd sampling 24/6/2011 (2 weeks after application)**	**3rd sampling 9/7/2011 (4 weeks after application)**	**4th sampling 24/7/2011 (6 weeks after application)**	**5th sampling 8/8/2011 (8 weeks after application)**
P1S1W1	1.66±0.000 bc	2.21±0.000 v	2.99±0.003 o	3.02±0.006 l	3.43±0.003 l
P1S1W2	1.30±0.003 ef	2.87±0.000 o	1.79±0.003 x	1.29±0.006 v	1.56±0.003 x
P1S2W1	1.56±0.000 cd	2.49±0.006 s	4.36±0.003 i	4.39±0.003 f	3.83±0.003 j
P1S2W2	1.43±0.000 de	3.91±0.006 j	4.78±0.006 a	4.34±0.006 g	4.64±0.012 a
P1S3W1	0.50±0.289 jkl	3.46±0.006 m	2.20±0.029 v	2.64±0.006 o	3.42±0.006 m
P1S3W2	1.54±0.000 cd	4.18±0.003 h	4.62±0.003 c	4.29±0.009 h	4.36±0.009 e
P2S1W1	0.88±0.000 i	2.20±0.029 w	4.47±0.003 g	1.45±0.012 u	2.55±0.014 r
P2S1W2	0.45±0.000 l	2.24±0.003 u	2.43±0.003 u	1.02±0.009 x	2.20±0.000 t
P2S2W1	0.58±0.000 jkl	2.59±0.003 q	2.75±0.003 r	2.95±0.003 m	3.49±0.003 k
P2S2W2	1.64±0.000 bc	4.46±0.003 c	4.38±0.003 h	4.94±0.003 a	4.48±0.029 c
P2S3W1	1.01±0.000 hi	2.43±0.003 t	2.79±0.006 q	2.41±0.006 q	3.14±0.017 n

P2S3W2	1.71±0.000 b	4.44±0.006 d	4.71±0.003 b	3.66±0.006 i	4.07±0.017 h
P3S1W1	0.63±0.000 j	1.90±0.029 x	4.60±0.003 d	3.51±0.012 j	3.05±0.014 p
P3S1W2	0.61±0.000 jk	4.38±0.003 e	2.67±0.003 t	1.80±0.009 t	1.82±0.005 v
P3S2W1	1.46±0.000 d	3.50±0.029 l	3.17±0.003 m	4.48±0.003 d	3.11±0.003 o
P3S2W2	0.94±0.000 hi	4.50±0.029 b	4.52±0.003 f	2.22±0.003 s	4.39±0.003 d
P3S3W1	0.94±0.000 hi	2.64±0.003 p	2.69±0.003 s	2.81±0.006 n	2.28±0.006 s
P3S3W2	0.88±0.000 i	4.53±0.003 a	3.47±0.003 l	4.90±0.009 b	4.18±0.006 f
CS1W1	1.08±0.000 gh	2.56±0.006 r	3.61±0.003 k	2.31±0.009 r	4.04±0.014 i
CS1W2	0.96±0.000 hi	3.78±0.006 k	3.09±0.006 n	1.15±0.006 w	1.69±0.002 w
CS2W1	1.93±0.000 a	4.14±0.006 i	4.50±0.058 e	4.68±0.012 c	4.59±0.003 b
CS2W2	1.18±0.000 fg	4.29±0.003 f	4.26±0.006 j	2.50±0.020 p	2.88±0.006 q
CS3W1	0.46±0.052 kl	3.23±0.003 n	1.84±0.003 w	3.50±0.016 k	4.15±0.029 g
CS3W2	1.91±0.000 a	4.27±0.003 g	2.83±0.003 p	4.40±0.026 e	1.94±0.012 u

According to the table 4, the highest soil CEC values were shown by glyphosate during the 1st, 2nd, 4th and 5th samplings except for the 3rd sampling period which was shown by diazinon. The highest CEC was in Agholan soil while the lowest CEC was in Debaga soil during the study, probably, because higher organic matter in Agholan soil increased CEC through an increase in available negative charges (Turner and Clark, 1966). 100% soil moisture content showed the highest soil CEC during the 1st, 2nd and 4th samplings while showed the lowest CEC values during the 3rd and 5th samplings and this may refer to surrounding temperature increase at the end of the study. Mancozeb in Agholan soil with 50% soil moisture content (P2S1W1) at the end of the study and with 100% during the 1st and 2nd samplings showed the highest soil CEC, and the combinations P3S1W1 and P1S2W2 during the 3rd and 4th samplings respectively revealed the highest soil CEC and the reasons behind that is unknown.

Table 4: Combined treatment effects on soil CEC (c.mol.kg^{-1}) values during five sampling periods (Mean±S.E.).

Treatments	**1st sampling 9/6/2011 (24h after application)**	**2nd sampling 24/6/2011 (2 weeks after application)**	**3rd sampling 9/7/2011 (4 weeks after application)**	**4th sampling 24/7/2011 (6 weeks after application)**	**5th sampling 8/8/2011 (8 weeks after application)**
P1S1W1	36.61±0.001 b	33.15±0.001 g	33.08±0.000 h	32.16±0.000 k	34.26±0.018 d
P1S1W2	35.81±0.001 c	33.79±0.001 e	34.12±0.001 g	38.70±0.001 c	34.81±0.004 c
P1S2W1	27.07±0.001 s	31.26±0.000 i	25.53±0.001 w	40.13±0.001 b	28.79±0.003 l
P1S2W2	31.92±0.001 h	29.70±0.020 m	26.24±0.000 t	42.19±0.000 a	26.58±0.007 t
P1S3W1	29.35±0.001 n	30.68±0.001 j	26.36±0.001 s	32.08±0.000 l	29.36±0.010 i
P1S3W2	30.47±0.001 j	30.46±0.001 k	27.75±0.001 q	35.62±0.001 e	28.44±0.002 o
P2S1W1	31.17±0.001 i	33.65±0.002 f	34.80±0.001 d	34.99±0.000 f	35.41±0.003 a
P2S1W2	42.33±0.000 a	37.59±0.001 a	34.84±0.000 c	36.60±0.001 d	35.29±0.004 b
P2S2W1	27.02±0.001 t	21.98±0.001 w	27.91±0.012 o	26.24±0.000 u	27.32±0.000 r
P2S2W2	25.65±0.001 v	22.28±0.001 v	26.16±0.001 u	26.78±0.010 r	24.39±0.001 w
P2S3W1	27.38±0.001 r	23.28±0.001 t	32.45±0.000 i	28.53±0.007 o	26.49±0.001 u

P2S3W2	27.70±0.011 ^{p}	28.01±0.000 ^{q}	29.11±0.000 ^{m}	26.65±0.013 ^{s}	28.23±0.002 ^{p}
P3S1W1	31.97±0.001 ^{g}	36.25±0.001 ^{b}	42.01±0.001 ^{a}	34.60±0.029 ^{g}	34.08±0.019 ^{e}
P3S1W2	32.47±0.000 ^{e}	33.92±0.000 ^{d}	36.47±0.003 ^{b}	34.53±0.001 ^{h}	32.82±0.004 ^{g}
P3S2W1	24.85±0.009 ^{x}	21.55±0.000 ^{x}	31.79±0.000 ^{j}	24.70±0.000 ^{w}	24.35±0.001 ^{x}
P3S2W2	25.21±0.001 ^{w}	34.63±0.000 ^{c}	30.82±0.000 ^{k}	23.19±0.001 ^{x}	27.07±0.002 ^{s}
P3S3W1	28.97±0.001 ^{o}	22.87±0.002 ^{u}	27.24±0.001 ^{r}	26.57±0.011 ^{t}	28.67±0.003 ^{m}
P3S3W2	30.05±0.001 ^{l}	28.18±0.003 ^{p}	27.88±0.000 ^{p}	28.11±0.003 ^{p}	29.22±0.001 ^{j}
CS1W1	33.95±0.001 ^{d}	29.55±0.000 ^{n}	34.77±0.001 ^{e}	34.06±0.001 ^{j}	33.80±0.001 ^{f}
CS1W2	32.38±0.001 ^{f}	23.52±0.001 ^{s}	34.30±0.001 ^{f}	34.45±0.003 ^{i}	28.97±0.004 ^{k}
CS2W1	26.46±0.001 ^{u}	28.93±0.000 ^{o}	25.89±0.001 ^{v}	26.99±0.009 ^{q}	25.16±0.006 ^{v}
CS2W2	27.46±0.001 ^{q}	24.94±0.001 ^{r}	24.85±0.001 ^{x}	25.74±0.001 ^{v}	27.55±0.001 ^{q}
CS3W1	29.47±0.001 ^{m}	31.82±0.001 ^{h}	28.23±0.001 ^{n}	30.47±0.006 ^{m}	29.44±0.000 ^{h}
CS3W2	30.32±0.000 ^{k}	30.11±0.001 ^{l}	29.64±0.000 ^{l}	29.06±0.001 ^{n}	28.55±0.001 ^{n}

Diazinon showed the highest levels of soil organic matter during the 1st, 2nd and 4th samplings (table 5) and similar observation given by Shittu *et al.*, (2004). The highest levels of soil organic matter were observed in Debaga soil during the 1st and 4th samplings, Girdarasha soil during the 2nd sampling, both Agholan and Debaga soils during the 3rd sampling and both Debaga and Girdarasha soils during the 5th sampling and there unknown reason behind that. During the 1st, 3rd and 4th samplings, 100% soil moisture content revealed the highest soil organic matter, but in the 2nd and 5th samplings 50% soil moisture content caused the greatest increasing in soil organic matter. Different significant effects on soil organic matter have been shown by the combined treatments between pesticides, soil orders and soil moisture content. At the beginning of the study the combined treatment P3S3W2 showed the highest level of soil organic matter. During the 2nd sampling the combined treatments P1S1W1, P2S2W1, P3S1W1 and P3S3W1 showed the highest level of soil organic matter. The combination of P2S2W2 during the 3rd sampling and the combinations of P2S2W2, P3S3W1, P3S3W2, CS2W1 and CS2W2 during the 4th sampling showed the highest organic matter amounts. At the end of the study the combinations of P1S2W1, P2S2W2, P3S3W1, P3S3W2 and CS1W1 showed the highest organic matter levels.

Table 5: Combined treatment effects on soil organic matter ($g.kg^{-1}$) values during five sampling periods (Mean±S.E.).

Treatments	**1st sampling 9/6/2011 (24h after application)**	**2nd sampling 24/6/2011 (2 weeks after application)**	**3rd sampling 9/7/2011 (4 weeks after application)**	**4th sampling 24/7/2011 (6 weeks after application)**	**5th sampling 8/8/2011 (8 weeks after application)**
P1S1W1	3.450±0.001 ^{f}	17.249±0.000 ^{a}	6.899±0.000 ^{e}	10.349±0.000 ^{c}	10.349±0.000 ^{d}
P1S1W2	6.899±0.003 ^{e}	6.899±0.001 ^{d}	10.349±0.000 ^{d}	10.349±0.000 ^{c}	13.799±0.000 ^{c}
P1S2W1	13.799±0.003	10.349±0.001 ^{c}	6.899±0.000 ^{e}	17.249±0.001 ^{a}	20.698±0.001

	c				a
P1S2W2	13.799±0.002 c	6.899±0.001 d	10.349±0.000 d	13.799±0.000 b	13.799±0.996 c
P1S3W1	3.450±0.003 f	10.349±0.001 c	6.899±0.001 e	10.349±0.000 c	17.249±0.000 b
P1S3W2	17.249±0.002 b	6.899±0.003 d	6.899±0.002 e	6.899±0.001 d	17.249±0.000 b
P2S1W1	3.450±0.003 f	6.899±0.003 d	6.899±0.001 e	6.899±0.001 d	10.349±0.000 d
P2S1W2	10.349±0.003 d	3.450±0.002 e	6.899±0.001 e	6.899±0.003 d	10.349±0.000 d
P2S2W1	13.799±0.003 c	17.249±0.000 a	6.899±0.001 e	10.349±0.003 c	17.249±0.000 b
P2S2W2	17.249±0.002 b	6.899±0.003 d	20.698±0.001 a	17.249±0.000 a	20.698±0.001 a
P2S3W1	10.349±0.002 d	10.349±0.003 c	17.249±0.001 b	6.899±0.003 d	17.249±0.000 b
P2S3W2	20.698±0.002 a	6.899±0.003 d	6.899±0.001 e	17.249±0.000 a	13.799±0.001 c
P3S1W1	10.349±0.001 d	17.249±0.002 a	3.450±0.001 f	6.899±0.001 d	13.799±0.001 c
P3S1W2	13.799±0.002 c	6.899±0.003 d	6.899±0.002 e	6.899±0.002 d	10.349±0.001 d
P3S2W1	13.799±0.002 c	10.349±0.001 c	3.450±0.001 f	13.799±0.002 b	17.249±0.000 b
P3S2W2	17.249±0.002 b	10.349±0.000 c	3.450±0.001 f	13.799±0.001 b	17.249±0.001 b
P3S3W1	10.349±0.000 d	17.249±0.000 a	13.799±0.001 c	17.249±0.000 a	20.698±0.001 a
P3S3W2	20.698±0.001 a	10.349±0.001 c	3.450±0.001 f	17.249±0.000 a	20.698±0.001 a
CS1W1	13.799±0.003 c	6.899±0.003 b	13.799±0.000 c	6.899±0.002 d	20.698±0.000 a
CS1W2	17.249±0.000 b	3.450±0.001 e	10.349±0.000 d	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 f	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 d	17.249±0.001 a	17.249±0.002 b
CS3W1	6.899±0.001 e	13.799±0.000 c	3.450±0.001 f	6.899±0.001 d	17.249±0.000 b
CS3W2	10.349±0.001 d	10.349±0.001 d	3.450±0.000 f	6.899±0.001 d	17.249±0.001 b

According to the table 6, mancozeb showed the highest soil total nitrogen during the 1st and 4th samplings, probably, because when mancozeb apply to soil it undergo rapid chemical

e-ISSN (2522-7130) p-ISSN (2410-1036)

hydrolysis to ethylenethiourea and ethyleneurea which in turn rapidly hydrolyses to ammonium carbonate by urease activity of microorganisms resulting in the formation of nitrate and ammonia which comprise a portion of total nitrogen in soil (Shukla and Mishra, 1996) and these changes stimulates soil microbial activity as evidenced by increased ammonification and nitrification rates as well as increases total viable bacterial counts especially after short-term exposure (Monkiedje *et al.*, 2002); but diazinon showed the highest total nitrogen during the 2nd and 3rd samplings, similar observations were given by Barakah *et al.*, (2007) and 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 was translated to nitrogen content increase before the 4 weeks of the experiment as concluded by Shittu *et al.*, (2004). Glyphosate showed the highest total nitrogen at the end of the study probably because glyphosate decomposition comprises a portion of total nitrogen (FAO, 2012). The lowest value of total nitrogen recorded in control during the 1st, 4th and 5th samplings. Agholan soil showed the highest total nitrogen content at the beginning and at the last sampling periods, and similar observations were given by Lancaster *et al.*, (2006) and Barakah *et al.*, (2007), whereas Debaga soil showed the highest total nitrogen during the 2nd and 3rd sampling periods. The greatest total nitrogen level was recorded in 100% soil moisture content at the end of the experiment and this may refer to that 100% soil moisture prepare a suitable condition for microorganisms to play their role to decompose organic matter to simple components and increase soil nitrogen content. The combined treatments CS1W2 in the 1st sampling, P3S2W2 in the 2nd sampling, P2S1W2 in the 3rd sampling, P3S1W2 in the 4th sampling and P1S2W1 in the 5th sampling showed the highest total nitrogen contents.

Table 6: Combined treatment effects on soil total nitrogen ($g.kg^{-1}$) values during five sampling periods (Mean±S.E.).

Treatments	1st sampling 9/6/2011 (24h after application)	2nd sampling 24/6/2011 (2 weeks after application)	3rd sampling 9/7/2011 (4 weeks after application)	4th sampling 24/7/2011 (6 weeks after application)	5th sampling 8/8/2011 (8 weeks after application)
P1S1W1	3.063±0.001 h	1.563±0.001 v	2.313±0.004 r	2.972±0.001 j	1.452±0.002 o
P1S1W2	3.024±0.002 i	1.595±0.001 t	3.146±0.002 j	2.258±0.096 n	3.631±0.003 d
P1S2W1	3.700±0.029 f	2.954±0.000 o	2.917±0.005 n	2.905±0.001 klm	5.062±0.002 a
P1S2W2	0.740±0.001 w	4.023±0.001 i	3.043±0.001 k	5.115±0.001 f	2.152±0.002 j
P1S3W1	1.468±0.002 q	1.505±0.001 w	2.234±0.001 t	5.094±0.001 f	1.437±0.000 p
P1S3W2	2.313±0.001 l	3.226±0.001 l	2.258±0.001 s	3.700±0.002 h	3.571±0.001 e
P2S1W1	0.756±0.001 v	2.229±0.001 q	3.024±0.002 l	3.708±0.002 h	2.917±0.001 f
P2S1W2	1.675±0.000 n	1.559±0.001 v	17.035±0.002 a	2.215±0.001 no	3.676±0.002 c
P2S2W1	4.449±0.002 b	3.638±0.001 k	5.846±0.001 d	9.267±0.002 d	4.384±0.001 b
P2S2W2	3.829±0.002 c	3.676±0.001 j	2.985±0.001 m	4.330±0.003 g	1.602±0.002 n
P2S3W1	3.723±0.001 e	2.935±0.001 p	2.211±0.003 u	6.495±0.001 e	0.000±0.003 u

e-ISSN (2522-7130) p-ISSN (2410-1036)

P2S3W2	3.017±0.001 j	1.577±0.001 u	4.636±0.001 g	10.359±0.002 c	2.298±0.002 i
P3S1W1	3.676±0.000 g	5.996±0.001 e	3.043±0.001 k	11.123±0.002 b	2.863±0.002 g
P3S1W2	2.899±0.002 k	7.778±0.000 c	2.414±0.002 o	12.579±0.002 a	1.414±0.001 r
P3S2W1	3.731±0.001 d	7.353±0.001 d	4.421±0.000 h	2.869±0.002 m	0.713±0.002 s
P3S2W2	1.545±0.001 o	18.421±0.001 a	5.518±0.001 e	3.638±0.001 i	2.113±0.002 m
P3S3W1	1.528±0.000 p	4.384±0.001 h	16.279±0.000 b	2.887±0.000 lm	0.710±0.003 st
P3S3W2	2.298±0.001 m	3.030±0.001 m	5.315±0.002 f	2.947±0.001 jk	2.811±0.003 h
CS1W1	1.455±0.001 s	4.497±0.001 g	3.024±0.002 l	2.917±0.001 kl	2.138±0.001 k
CS1W2	4.970±0.002 a	4.839±0.001 f	2.344±0.002 q	2.211±0.002 o	2.134±0.001 k
CS2W1	1.423±0.001 t	2.201±0.000 s	3.653±0.002 i	5.072±0.000 f	1.426±0.001 q
CS2W2	0.735±0.001 x	2.966±0.002 n	14.301±0.000 c	2.917±0.000 kl	2.121±0.002 l
CS3W1	1.461±0.002 r	2.220±0.006 r	3.024±0.001 l	0.000±0.001 q	1.423±0.002 q
CS3W2	0.783±0.001 u	9.251±0.001 b	2.381±0.000 p	1.471±0.001 p	0.707±0.001 t

Glyphosate showed the greatest significant effect on soil total phosphorus during the 1st, 2nd, 3rd and 5th samplings. These results agree with that observed by Khudhur (2011) and this may due to the degradation of glyphosate by soil microorganisms and returning elemental phosphorus to soil, or binding of glyphosate to soil in a manner similar to the binding of natural organophosphate compounds and competing with inorganic phosphate for adsorption sites thus increasing soil phosphorus content (Sprankle *et al.*, 1975). The lowest values of total phosphorus were recorded in control treatment during the studied periods of the experiment except for the 4th sampling (table 7). The highest soil total phosphorus content during different samplings were observed in soil of Girdarasha, while the lowest total phosphorus contents were revealed by Debaga soil during the 1st, 2nd, 3rd and 5th samplings. The greatest significant effect on total phosphorus was revealed by 50% soil moisture content and the lowest effect showed by 100% soil moisture content during the study and the reason is unknown. Glyphosate in Girdarasha soil with 50% soil moisture content (P1S3W1) showed the greatest effect on soil total phosphorus during the studied period except for the 4th sampling in which the combined treatment CS2W1 showed the highest effect.

Table 7: Combined treatment effects on soil total phosphorus ($g.kg^{-1}$) values during five sampling periods (Mean±S.E.).

Treatments	1st sampling 9/6/2011 (24h after application)	2nd sampling 24/6/2011 (2 weeks after application)	3rd sampling 9/7/2011 (4 weeks after application)	4th sampling 24/7/2011 (6 weeks after application)	5th sampling 8/8/2011 (8 weeks after application)
P1S1W1	0.574±0.001 f	0.434±0.001 e	0.486±0.001 e	0.828±0.001 g	0.369±0.003 f
P1S1W2	0.164±0.001 r	0.363±0.002 gh	0.463±0.001 f	0.648±0.002 i	0.204±0.002 i
P1S2W1	0.039±0.000 w	0.132±0.002 q	0.203±0.002 p	0.398±0.001 n	0.015±0.000 o
P1S2W2	0.310±0.003 l	0.032±0.000 v	0.224±0.001 n	0.255±0.001 t	0.017±0.000 o
P1S3W1	1.177±0.000 a	1.248±0.001 a	0.913±0.001 a	0.929±0.001 e	0.820±0.001 a

P1S3W2	0.741±0.001^{c}	0.163±0.002^{p}	0.862±0.002^{b}	1.315±0.001^{c}	0.816±0.001^{b}
P2S1W1	0.195±0.001^{q}	0.365±0.001^{g}	0.385±0.001^{g}	0.588±0.001^{j}	0.268±0.002^{g}
P2S1W2	0.865±0.000^{b}	0.249±0.002^{k}	0.377±0.001^{h}	0.421±0.002^{l}	0.149±0.002^{l}
P2S2W1	0.202±0.000^{p}	0.048±0.001^{s}	0.281±0.002^{k}	0.228±0.002^{u}	0.049±0.001^{o}
P2S2W2	0.146±0.001^{s}	0.065±0.001^{r}	0.253±0.001^{l}	0.360±0.001^{o}	0.003±0.000^{o}
P2S3W1	0.431±0.000^{i}	0.450±0.006^{d}	0.606±0.001^{c}	0.863±0.001^{f}	0.517±0.001^{d}
P2S3W2	0.298±0.000^{m}	0.271±0.000^{j}	0.494±0.001^{d}	0.527±0.001^{k}	0.602±0.002^{c}
P3S1W1	0.610±0.002^{d}	0.283±0.001^{i}	0.315±0.001^{j}	0.413±0.001^{m}	0.155±0.001^{k}
P3S1W2	0.374±0.001^{k}	0.420±0.002^{f}	0.229±0.002^{m}	0.414±0.001^{m}	0.061±0.002^{o}
P3S2W1	0.050±0.001^{t}	0.199±0.001^{o}	0.130±0.002^{t}	0.273±0.001^{s}	0.005±0.000^{o}
P3S2W2	0.009±0.000^{x}	0.606±0.001^{b}	0.185±0.001^{q}	0.284±0.001^{r}	0.045±0.001^{o}
P3S3W1	0.597±0.000^{e}	0.540±0.002^{c}	0.497±0.001^{d}	0.809±0.002^{h}	0.384±0.001^{e}
P3S3W2	0.434±0.001^{h}	0.238±0.001^{l}	0.169±0.002^{r}	0.343±0.002^{q}	0.125±0.001^{m}
CS1W1	0.047±0.000^{u}	0.230±0.003^{m}	0.146±0.001^{s}	0.343±0.002^{q}	0.027±0.000^{o}
CS1W2	0.239±0.000^{n}	0.359±0.002^{h}	0.210±0.000^{o}	0.352±0.002^{p}	0.056±0.000^{o}
CS2W1	0.020±0.002^{v}	0.038±0.001^{t}	0.098±0.001^{u}	1.636±0.001^{a}	0.043±0.000^{o}
CS2W2	0.235±0.001^{o}	0.001±0.000^{w}	0.149±0.002^{s}	1.080±0.003^{d}	0.209±0.000^{h}
CS3W1	0.489±0.001^{g}	0.206±0.000^{n}	0.320±0.002^{i}	1.314±0.001^{c}	0.089±0.000^{n}
CS3W2	0.415±0.000^{j}	0.027±0.001^{u}	0.282±0.001^{k}	1.582±0.002^{b}	0.187±0.000^{g}

Diazinon in the 1st sampling, glyphosate in the 3rd sampling and mancozeb in the 4th sampling periods showed the lowest soil total sulfur levels (table 8), and this may due to the proliferation of microorganisms responsible for thiosulphate oxidation which in turn mineralize the organic matter followed by volatilization of organic and inorganic sulfur compounds to derive energy and carbon for their cellular constituent resulting in lower buildup of total sulfur in soil. Girdarasha soil showed the highest value of total sulfur at the beginning of the study and Agholan soil showed the highest values during the 2nd, 4th and 5th samplings. Debaga soil showed the lowest total sulfur value at the beginning and at the end of the study and Girdarasha soil showed the lowest total sulfur levels during the 2nd and 4th sampling. 50% soil moisture content showed the greatest total sulfur values during the 1st, 4th and 5th sampling periods. During the 1st and 2nd sampling periods the combination P1S3W1 and during the 4th and 5th sampling periods the combination P3S1W1 showed the highest soil total sulfur levels.

Table 8: Combined treatment effects on soil total sulfur (g.kg^{-1}) values during five sampling periods (Mean±S.E.).

Treatments	**1st sampling 9/6/2011 (24h after application)**	**2nd sampling 24/6/2011 (2 weeks after application)**	**3rd sampling 9/7/2011 (4 weeks after application)**	**4th sampling 24/7/2011 (6 weeks after application)**	**5th sampling 8/8/2011 (8 weeks after application)**
P1S1W1	0.014±0.000^{b}	0.024±0.000^{h}	0.0003±0.000^{a}	0.0039±0.000^{g}	0.0003±0.000^{f}
P1S1W2	0.0015±0.000	0.022±0.000^{j}	0.0003±0.000	0.002±0.000^{k}	0.0003±0.000

	t		a		f
P1S2W1	0.013±0.000^{c}	0.0213±0.000^{k}	0.0001±0.000^{a}	0.004±0.000^{f}	0.0006±0.000^{b}
P1S2W2	0.0086±0.000^{g}	0.020±0.000^{m}	0.0003±0.000^{a}	0.0003±0.000^{o}	0.0005±0.000^{c}
P1S3W1	0.020±0.000^{a}	0.0323±0.000^{a}	0.0007±0.000^{a}	0.0003±0.000^{o}	0.0002±0.000^{h}
P1S3W2	0.010±0.000^{e}	0.0266±0.000^{e}	0.001±0.000^{a}	0.0036±0.000^{i}	0.0005±0.000^{c}
P2S1W1	0.0015±0.000^{t}	0.0316±0.000^{b}	0.002±0.000^{a}	0.003±0.000^{j}	0.0005±0.000^{c}
P2S1W2	0.004±0.000^{m}	0.017±0.000^{p}	0.003±0.000^{a}	0.002±0.000^{k}	0.0006±0.000^{b}
P2S2W1	0.0028±0.000^{p}	0.030±0.000^{c}	0.004±0.000^{a}	0.0006±0.000^{n}	0.0007±0.000^{a}
P2S2W2	0.0019±0.000^{s}	0.0163±0.000^{q}	0.005±0.000^{a}	0.004±0.000^{f}	0.0006±0.000^{b}
P2S3W1	0.0021±0.000^{r}	0.0267±0.000^{d}	0.006±0.000^{a}	0.0002±0.000^{p}	0.0007±0.000^{a}
P2S3W2	0.0088±0.000^{f}	0.014±0.000^{s}	0.006±0.000^{a}	0.0002±0.000^{p}	0.0007±0.000^{a}
P3S1W1	0.0049±0.000^{k}	0.026±0.000^{g}	0.008±0.000^{a}	0.011±0.000^{a}	0.00035±0.000^{e}
P3S1W2	0.006±0.000^{j}	0.013±0.035^{t}	0.009±0.000^{a}	0.005±0.000^{c}	0.0007±0.000^{a}
P3S2W1	0.0021±0.000^{r}	0.023±0.000^{i}	0.008±0.000^{a}	0.002±0.000^{k}	0.0006±0.000^{b}
P3S2W2	0.0009±0.000^{u}	0.0099±0.000^{v}	0.009±0.000^{a}	0.00005±0.000^{q}	0.0005±0.000^{c}
P3S3W1	0.0024±0.000^{q}	0.0211±0.000^{l}	0.010±0.000^{a}	0.0017±0.000^{l}	0.0006±0.000^{b}
P3S3W2	0.0001±0.000^{v}	0.004±0.000^{x}	0.011±0.000^{a}	0.006±0.000^{b}	0.00026±0.000^{g}
CS1W1	0.0031±0.000^{o}	0.019±0.000^{n}	0.010±0.000^{a}	0.0047±0.000^{d}	0.0007±0.000^{a}
CS1W2	0.011±0.000^{d}	0.018±0.000^{o}	0.011±0.028^{a}	0.001±0.000^{m}	0.0004±0.000^{d}
CS2W1	0.0045±0.000^{l}	0.010±0.000^{u}	0.010±0.000^{a}	0.005±0.000^{c}	0.0004±0.000^{d}
CS2W2	0.0032±0.000^{n}	0.0265±0.000^{f}	0.010±0.000^{a}	0.0045±0.000^{e}	0.0006±0.000^{b}
CS3W1	0.008±0.000^{h}	0.016±0.000^{r}	0.011±0.000^{a}	0.0045±0.000^{e}	0.0004±0.000^{d}
CS3W2	0.007±0.000^{i}	0.008±0.000^{w}	0.010±0.000^{a}	0.0037±0.000^{h}	0.0002±0.000^{h}

At the 1st sampling period mancozeb showed the lowest value of total zinc, in the 2nd sampling period the highest value was observed in glyphosate treatment and the lowest value was recorded in control probably because glyphosate is a chemical chelator and binds with mineral elements and can immobilize them (Strautman, 2007; Songa *et al.*, 2009 and Huber, 2010). Generally, the second sampling exhibited the lowest values of total zinc for all of the studied pesticides in comparing with the other periods. In the 3rd and 4th sampling periods respectively both mancozeb and glyphosate showed the highest total zinc values, while during the 5th sampling diazinon showed the highest total zinc value (table 9). Agholan soil showed the highest soil total zinc during the 1st, 3rd and 4th samplings, but Girdarasha soil revealed the greatest total zinc content during the 2nd and 5th samplings, while Debaga soil showed the lowest content of total zinc during the 1st, 2nd and 3rd samplings, probably, because total zinc content is positively correlated with organic matter, clay content and cation exchange capacity so both Agholan and Girdarasha soils contain higher organic matter and clay content and have higher cation exchange capacity in comparing with Debaga soil (Hodges, 2012); at the end of the study total zinc was significantly reduced in Agholan soil and this may refer to the reduced pH values by the use of pesticides because soil total zinc is reversely correlated with soil pH. 50% soil moisture content revealed the highest total zinc during the 1st and 2nd samplings and 100% soil moisture content revealed the highest total zinc during the 3rd, 4th and 5th samplings, and the reason is unknown. The combined treatment P3S1W1 during the 1st and 4th sampling periods and the combined treatments P1S1W2, P2S1W2 and P3S3W2 showed the highest total zinc values during the 2nd, 3rd and 5th sampling periods.

Table 9: Combined treatment effects on soil total zinc ($mg.kg^{-1}$) values during five sampling periods (Mean±S.E.).

Treatments	**1st sampling 9/6/2011 (24h after application)**	**2nd sampling 24/6/2011 (2 weeks after application)**	**3rd sampling 9/7/2011 (4 weeks after application)**	**4th sampling 24/7/2011 (6 weeks after application)**	**5th sampling 8/8/2011 (8 weeks after application)**
P1S1W1	92.66±0.046 f	61.62±0.000 k	62.50±0.000 u	246.10±0.029 l	73.15±0.000 e
P1S1W2	80.24±0.001 j	98.87±0.001 a	251.42±0.006 f	259.40±0.028 h	54.96±0.001 n
P1S2W1	72.26±0.006 n	60.29±0.000 m	173.81±0.002 p	219.49±0.003 q	50.09±0.001 r
P1S2W2	80.24±0.001 k	62.50±0.000 i	261.62±0.006 d	265.61±0.003 g	190.22±0.002 c
P1S3W1	60.29±0.001 u	65.16±0.000 g	75.36±0.000 t	358.74±0.003 b	62.06±0.006 i
P1S3W2	58.07±0.000 v	67.38±0.000 e	241.22±0.003 j	288.23±0.001 d	64.28±0.000 f
P2S1W1	62.06±0.003 r	60.29±0.000 m	222.60±0.004 l	320.60±0.029 c	63.39±0.000 g
P2S1W2	65.16±0.000 p	55.85±0.001 q	322.82±0.003 a	250.53±0.002 j	58.51±0.000 k
P2S2W1	60.73±0.003 t	55.41±0.000 r	54.08±0.000	152.97±0.003	55.85±0.001

			^{w}	^{u}	^{m}
P2S2W2	105.08±0.000 ^{d}	61.17±0.000 ^{l}	321.93±0.005 ^{b}	279.36±0.003 ^{e}	53.63±0.000 ^{o}
P2S3W1	64.28±0.000 ^{q}	87.34±0.001 ^{b}	282.02±0.006 ^{c}	267.83±0.002 ^{f}	62.50±0.000 ^{h}
P2S3W2	72.70±0.000 ^{m}	62.50±0.001 ^{i}	247.43±0.006 ^{h}	169.82±0.004 ^{t}	57.18±0.001 ^{l}
P3S1W1	144.54±0.001 ^{a}	61.17±0.000 ^{l}	172.04±0.003 ^{q}	360.51±0.005 ^{a}	60.73±0.012 ^{j}
P3S1W2	61.62±0.001 ^{s}	64.72±0.000 ^{h}	235.46±0.002 ^{k}	199.98±0.005 ^{s}	55.85±0.001 ^{m}
P3S2W1	54.96±0.002 ^{w}	70.49±0.001 ^{d}	243.44±0.003 ^{i}	203.08±0.002 ^{r}	53.19±0.001 ^{p}
P3S2W2	52.30±0.000 ^{x}	62.06±0.003 ^{j}	211.06±0.001 ^{m}	248.32±0.004 ^{k}	53.19±0.000 ^{p}
P3S3W1	106.85±0.003 ^{b}	66.49±0.001 ^{f}	96.21±0.001 ^{s}	21.26±0.000 ^{x}	150.31±0.003 ^{d}
P3S3W2	92.22±0.000 ^{g}	56.30±0.001 ^{p}	170.27±0.004 ^{r}	110.84±0.005 ^{v}	254.08±0.003 ^{a}
CS1W1	86.01±0.000 ^{i}	61.17±0.000 ^{l}	185.34±0.002 ^{o}	54.52±0.000 ^{w}	62.06±0.009 ^{i}
CS1W2	69.16±0.000 ^{o}	58.96±0.000 ^{o}	247.87±0.002 ^{g}	243.88±0.002 ^{m}	34.57±0.000 ^{t}
CS2W1	106.41±0.004 ^{c}	51.42±0.000 ^{t}	58.96±0.000 ^{v}	256.74±0.005 ^{i}	51.42±0.000 ^{q}
CS2W2	74.92±0.000 ^{l}	54.08±0.000 ^{s}	53.63±0.000 ^{x}	234.13±0.007 ^{n}	42.99±0.000 ^{s}
CS3W1	92.22±0.000 ^{h}	74.03±0.000 ^{c}	203.97±0.003 ^{n}	220.38±0.004 ^{p}	53.19±0.001 ^{p}
CS3W2	93.55±0.000 ^{e}	59.40±0.001 ^{n}	251.86±0.002 ^{o}	221.26±0.004 ^{o}	197.76±0.003 ^{b}

Glyphosate showed the highest value of total manganese during the studied periods except for the 4th sampling and similar observation was given by Khudhur (2011), probably, because glyphosate is a strong chelator which causes immobilization of manganese inside the soil and increasing its concentration (Huber, 2007 and Songa *et al.*, 2009). During the 4th sampling diazinon showed the highest total manganese and the lowest values of total manganese were recorded in control during the 1st, 2nd, 3rd and 5th sampling periods (table 10). Agholan soil revealed the highest value of soil total manganese during the studied periods, but Girdarasha soil during the 1st, 2nd, 4th and 5th samplings showed the lowest value of total manganese. 50% soil moisture content during the 1st, 2nd and 5th samplings and 100% soil moisture content showed the highest total manganese contents during the 3rd and 4th samplings and this may refer to the environmental conditions of temperature, moisture or wind during this investigation. The combinations P1S1W1, P1S1W2 and P2S1W1 showed the highest total manganese contents at the beginning of the study because Agholan soil contains higher manganese content which becomes chelated by glyphosate regardless to the moisture content. The combined treatment P2S1W1 during the 2nd sampling period showed the highest total manganese, probably, because the active ingredient of mancozeb consists of zinc 0.9% and manganese 7% (Rohm and Hass, 1980) and during degradation confer a portion of soil manganese content; and the combined treatment CS2W1 during the 4th sampling and the combination P1S1W1 during the 5th sampling showed the highest total manganese.

Table 10: Combined treatment effects on soil total manganese ($mg.kg^{-1}$) values during five sampling periods (Mean±S.E.).

Treatments	1st sampling 9/6/2011 (24h after application)	2nd sampling 24/6/2011 (2 weeks after application)	3rd sampling 9/7/2011 (4 weeks after application)	4th sampling 24/7/2011 (6 weeks after application)	5th sampling 8/8/2011 (8 weeks after application)
P1S1W1	574.47±0.003 a	540.62±0.012 l	574.47±0.006 c	547.39±0.009 l	574.47±0.006 a
P1S1W2	574.47±0.006 a	533.85±0.009 m	574.47±0.003 c	581.24±0.006 g	554.16±0.006 cd
P1S2W1	533.85±0.009 e	567.70±0.008 d	520.31±0.003 f	513.54±0.003 r	500.00±0.003 hi
P1S2W2	533.85±0.006 e	594.78±0.003 b	506.77±0.006 h	527.08±0.006 n	527.08±0.003 f
P1S3W1	479.69±5.187 j	567.70±0.008 e	486.46±0.003 k	486.46±0.008 v	472.92±0.005 k
P1S3W2	493.23±0.003 i	547.39±0.009 k	716.64±0.002 a	472.92±0.006 x	500.00±0.008 hi
P2S1W1	574.47±0.006 a	608.32±0.003 a	588.01±0.009 b	567.70±0.006 j	567.70±0.009 ab
P2S1W2	567.70±0.029 b	567.70±0.006 f	554.16±0.006 d	642.17±0.008 b	540.62±0.006 e
P2S2W1	527.08±0.003 f	527.08±0.003 n	493.23±0.006 j	594.78±0.008 e	506.77±0.006 gh
P2S2W2	479.69±0.006 j	560.93±0.009 i	506.77±0.006 h	527.08±0.006 o	513.54±0.003 g
P2S3W1	479.69±0.003 j	527.08±0.006 o	479.69±0.006 l	486.46±0.008 w	486.46±0.008 jk
P2S3W2	472.92±0.003 k	527.08±0.009 p	466.15±0.002 n	493.23±0.006 u	472.92±0.008 k
P3S1W1	554.16±0.003 c	588.01±0.009 c	540.62±0.006 e	574.47±0.003 i	540.62±0.009 e
P3S1W2	540.62±0.006 d	554.16±0.003 j	520.31±0.006 f	635.40±0.015 c	560.93±0.006 bc
P3S2W1	493.23±0.006 i	527.08±0.006 q	500.00±0.058 i	567.70±0.003 k	493.23±0.006 ij
P3S2W2	479.69±0.006 j	500.00±0.008 r	479.69±0.009 l	621.86±0.005 d	493.23±0.008 ij
P3S3W1	479.69±0.006	493.23±0.006	459.38±0.006	506.77±0.006	439.07±15.59

	j	w	o	s	m
P3S3W2	411.99±0.009 m	500.00±0.014 s	445.84±0.006 p	594.78±0.008 f	459.38±0.002 l
CS1W1	493.23±0.006 i	567.70±0.006 g	513.54±0.003 g	581.24±0.006 h	547.39±0.009 de
CS1W2	466.15±0.005 l	567.70±0.012 h	513.54±0.009 g	533.85±0.006 m	256.29±0.011 n
CS2W1	472.92±0.005 k	486.46±0.008 x	493.23±0.006 j	676.02±0.010 a	479.69±0.009 k
CS2W2	513.54±0.003 g	500.00±0.034 t	439.07±0.005 q	520.31±0.006 p	432.30±0.008 m
CS3W1	506.77±0.006 h	500.00±0.011 u	432.30±0.006 r	520.31±0.009 q	439.07±0.006 m
CS3W2	493.23±0.008 i	500.00±0.008 v	472.92±0.006 m	506.77±0.006 t	472.92±0.008 k

Conclusion and recommendations

Glyphosate and diazinon showed more positive effects on soil chemical parameters than mancozeb which increased only total nitrogen. Soil orders showed different significant effects on soil properties. 100% soil moisture content showed more significant effects on soil chemical properties. Different significant effects on soil characteristics were shown by the interactions among pesticides, 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.

References

Abdul Al-Rahman, C.H. 2010. Physico-chemical behavior of chlorpyrifos and MCPA pesticides in some calcareous soils. Ph.D. Thesis, University of Salahaddin-Erbil.

Ahmad, I.; F. Ahmad and J. Pichtel. 2011. Microbes and Microbial Technology. Springer Science+Business Media, LLC. 516pp.

Amin, M.F. 1985. Pollution of soil with certain heavy metals and their impact on leaf litter decomposition and bacterial and fungal populations of soil. M.Sc. Thesis, University of Salahaddin, Erbil, Iraq.

Andreu, V. and Y. Pico. 2004. Determination of pesticides and their degradation products in soil: critical review and comparison of methods. Trends in Anal. Chem. 23(10-11): 772-789.

Barakah, F.N.; M.I. Ababutain and A.M. Heggo. 2007. Effect of lannate and diazinon pesticides on some soil microorganisms. Alexaneria Sci. Exch. J. 28(1): 38-53.

Bardgett, R.D. 2005. The Biology of Soil: A Community and Ecosystem Approach. Oxford University Press. 242pp.

Bashour, I.I. and A.H. Sayegh. 2007. Methods of Analysis for Soils of Arid and Semi-Arid Regions. Food and Agriculture Organization of the United Nations, Rome. 119pp.

Bohn, H.L.; B.L. McNeal and G.A. O'connor. 2001. Soil Chemistry. Second Edition. John Wiley and Sons, Inc.

Bordjiba, O. and A. Belaze. 2013. Study of the effect of pesticides on some physico-chemicals and microbiological parameters of soil and water in north-eastern Algeria. TOJSAT: The Online J. Sci. Technol. 3(1): 153-159.

Bordjiba, O.; R. Steiman; M. Kadri; A. Semadi and P. Guiraud. 2001. Removal of herbicide from liquid media by fungi isolated from a contaminated soil. J. Environ. Qual. 30(2): 418-426.

Camino-Sanchez, F.J.; A. Zafra-Gomez; J. Ruiz-Garcıa; R. Bermudez-Peinado; O. Ballesteros; A. Navalon and J.L. Vilchez. 2011. UNE-EN ISO/IEC 17025:2005 accredited method for the determination of 121 pesticide residues in fruits and vegetables by gas chromatography-tandem mass spectrometry. J. Food Compos. Anal. 24: 427-440.

Cserháti, T.; E. Forgács; Z. Deyl; I. Miksik and A. Eckhardt. 2004. Chromatographic determination of herbicide residues in various matrices. Biomed. Chro. 18: 350-359.

Dömötörová, M. and E. Matisová. 2008. Fast gas chromatography for pesticide residues analysis. J. Chro. A. 1207: 1-16.

FAO: Food and Agriculture Organization, (2012). Soil fertility and organic components of soils: farmer-to-farmer participatory training course. Introduction to Ecological Farming: Adapted from Materials Published by EFAO, OATI, and the Institute of Bioregional Studies.

Hamadamin, S.I. 2006. Adsorption of metalaxyl and glyphosate on six Erbilian agricultural soils. M.Sc. Thesis, University of Salahaddin-Erbil.

Hill, D.S. 2008. Pests of Crop in Warmer Climates and their Control. Springer Netherlands. XII Edition.

Hodges, S.C. 2012. Soil Fertility Basics: NC Certified Crop Advisor Training. Soil Science Extension North Carolina State University.

Huber, D.M. 2010. What's new in Ag chemical and crop nutrient interactions. Fluid J. Online. 18(3): Issue 69.

Jones, J.B. 2001. Laboratory Guide for Conducting Soil Tests and Plant Analysis. CRC Press LLC. USA. 363pp.

Khan, S.U. 1980. Fundamental Aspects of Pollution Control and Environmental Science 5: Pesticides in the Soil Environment. Elsevier Scientific Publishing Company. New York. 240pp.

Khudhur, S.M. 2011. Impact of some pesticides on soil pollution. M.Sc. Thesis, University of Salahaddin-Erbil.

Khudhur, N.S. 2013. Effect of Some Pesticides on Soil Microorganisms in Hawler Governorate. PhD dissertation, Salahaddin University-Erbil.

Lancaster, S.H.; R.L. Haney; S.A. Senseman; F.M. Hons and J.M. Chandler. 2006. Soil microbial activity is affected by roundup weathermax and pesticides applied to cotton (*Gossypium hirsutum*). J. Agric. Food Chem. 54: 7221-7226.

Meister, R.T.; G.T. Fitzgerald; W.J. Miller; K.E. Nowels; C. Gorman and M. DeLuca. 2008. Crop Protection Handbook. Volume 94. Meister Media Worldwide. USA.

Mirsal, I.A. 2008. Soil Pollution: Origin, Monitoring & Remediation. Second Edition. Springer-Verlag Berlin Heidelberg. Germany. 312pp.

Monkiedje, A.; M.O. Ilori and M. Spiteller. 2002. Soil quality changes resulting from the application of the fungicides mefenoxam and metalaxyl to a sandy loam soil. Soil Biol. & Biochem. 34 (12): 1939-1948.

Moros, J.; S. Armenta; S. Garrigues and M. de la Guardia. 2007. Comparison of two vibrational procedures for the direct determination of mancozeb in agrochemicals. Talanta. 72: 72-79.

Pandey, K; J.P. Shukla and S.P. Trivedi. 2005. Fundamentals of Toxicology. New Central Book Agency (P) Ltd. India. 356pp.

Pansu, M. and J. Gautheyrou. 2006. Handbook of Soil Analysis: Mineralogical, Organic and Inorganic Methods. Springer-Verlag Berlin Heidelberg. 993pp.

Peignéa, J.; J. Viana; M. Cannavacciuolob; B. Bottolliera and R. Chaussod. 2009. Soil sampling based on field spatial variability of soil microbial indicators. European J. Soil Biol. 45(5-6): 488-495.

Plimmer, J.R.; D.W. Gammon and N.R. Ragsdale. 2003. Encyclopedia of Agrochemicals. Vol. 1. John Wiley & Sons, Inc., Publication. 1638pp.

Pretty, J. 2005. The Pesticide Detox: Towards a More Sustainable Agriculture. Earthscan Publisher. London. 294pp.

Rohm and Hass. 1980. Acute inhalation toxicity of mancozeb flowable US (TD-79-47) aerosol in rates. Report #79R-132. Acc. No, 244505.

Ryan, J.; G. Estefan and A. Rashid. 2001. Soil and Plant Analysis Laboratory Manual. Second Edition. International Center for Agricultural Research in the Dry Areas (ICARDA), Aleppo, Syria. 172 pp.

Sailaja, K.K. and K. Satyaprasad. 2006. Degradation of glyphosate in soil and its effect on fungal population. J. Environ. Sci. Eng. 48(3): 189-190.

Shariff, R.M. 2008. Thermodynamic and kinetic study for adsorption of herbicides on Kurdistan agricultural soils. Ph.D. Thesis, University of Salahaddin-Erbil.

Shittu, O.B.; A.K. Akintokun; P.O. Akintokun and M.O. Gbadebo. 2004. Effect of diazinon application on soil properties and soil microflora. Proceedings of the International Conference on Science & National Development, 25th-28th.

Shukla, A.K. and R.R. Mishra. 1996. Response of microbial population and enzymatic activities to fungicides in potato field soil. Proc. Indian Nat. Sci. Acad. 62(5): 435-438.

Songa, E.A.; O.A. Arotiba; J.H. Owino; N. Jahed; P.G. Baker and E.I. Iwuoha. 2009. Electrochemical detection of glyphosate herbicide using horseradish peroxidase immobilized on sulfonated polymer matrix. Bioelectrochem. 75: 117-123.

Sprankle, P.; W.F. Meggitt and D. Penner. 1975. Adsorption, mobility, and microbial degradation of glyphosate in the soil. Weed Sci. 23(3): 229-234.

Stevovic, S.; V.S. Mikovilovic and D. Calic-Dragosavac. 2010. Environmental impact of site location on macro- and microelements in Tansy. African J. Biotech. 9(16): 2408-2412.

Strautman, B. 2007. Concern over mineral and biologic interactions with glyphosate. LawrieCo Biologic Information Sheet.

Tomlin, C.D. 2009. The Pesticide Manual. Fifteenth Edition. Latimer Trend & Co., Plymouth. UK.

Turner, R.C. and J.S. Clark. 1966. Lime potential in acid clay and soil suspensions. Trans. Comm. II & IV Int. Soc. Soil Science. 208-215.

USAID. 2008. Soil testing. Perennial Crop Support Series. Jalalabad, Afghanistan. Publication No. 2008-001-AFG. February 8.

van Reeuwijk, L.P. 2002. Procedures for Soil Analysis, Technical Paper 9. Sixth Edition. International Soil Reference and Information Centre. The Netherlands. 101pp.

WHO. 2010. The WHO Recommended Classification of Pesticides by Hazard and Guidelines to Classification 2009. WHO Library Cataloguing-in-Publication Data. Wissenchaftliche Verlagsgesellschaft mbH, Stuttgart, Germany.

Xu, S. 2000. Environmental fate of mancozeb. Environmental Monitoring & Pest Management Department of Pesticide Regulation, Sacramento, CA 95814-3510.

e-ISSN (2522-7130) p-ISSN (2410-1036)