EFFECT OF CERTAIN HERBICIDES ON HUMIFICATION OF ORGANIC MATERIAL IN SOILS

R.A. Khalil, M. Shalaby, and Zeinab A. El-Bermawy

Dept. of Soil Sci. and Dept. of Plant Protection, Fac. of Agric., Minufiya University, Shebin El-Kom, Egypt.

تأثير اضافة مبيدات حشائش معينة على تحلل المادة العضوية فى التربة

رفعت أحمد خليل ـ محمد محمد حماده شلبى ـ زينب عبد الغنى البرماوى

قسم علوم الأراضى وقسم وقاية النبات ـ كلية الزراعة ـ جامعة المنوفية

شبين الكوم ـ مصر

ملخص البحث

أجريت هذه التجربة لدراسة تأثير اضافة مبيدات حشائش معينة (اترازين ـ كوتوران ـ وجيسابكس) على محتوى أرض طينية (pH ٧,٩) من الكربون والنتروجين والفوسفور بعد معاملتها بتبن البرسيم وتحضينها على درجة حرارة (٢٥ ± ٢°م) واضافة ٦٠٪ من قدرة الأرض على حفظ الماء وذلك لمدة ١٥٠ يوم .

أوضحت النتائج أن اضافة الاترازين أدى الى انخفاض محتوى الأرض من الكربون المتدبل والمستخلص فى حين أن اضافة كل من الكوتوران والجيسابكس أدت الى زيادتها بالمقارنة بالكونترول ـ كما أوضحت النتائج سيادة حامض الهيوميك على حامض الفلفيك فى جميع المعاملات كما وجد أن النسبة بين حامض الهيوميك : حامض الفلفيك نقصت نتيجة لاضافة المادة العضوية وزادت نتيجة لاضافة المبيدات .

أدت زيادة فترات التحضين الى زيادة كمية النتروجين المعدنى (الأمونيا والنترات) فى الأرض وقد أوضحت النتائج أن العينات التى عوملت بالكوتوران قد تفوقت على مثيلتها المعاملة بكل من الجيسابكس والاترازين .

كما أوضحت النتائج أيضا زيادة كمية الفوسفور الصالح فى الأرض باضافة كل من المادة العضوية والمبيدات المستعملة الى أن وصلت الى أعلى معدل لها بعد مرور ٧٥ يوم من التحضين ثم انخفضت بعد ذلك .

ABSTRACT

Effect of the herbicides atrazine, cotoran, and gesapax on carbon, nitrogen, and phosphorus contents of clover hay humified in an alluvial clay soil (pH 7.9) was studied at a moisture level of 60% WHC and mesophilic incubation (25 ± 2°C) along 150 days.

Application of herbicides resulted in diminising the content of humified carbon in soil. The severest effect was shown by atrazine, whereas cotoran and gesapax came respectively lower. Humic acid predominated over fulvic acid in all soil treatments. Ratio of HA/FA was ever more than one, and it was decreased with the addition of organic material, but increased with the application of herbicides.

Mineral N, as NH_4^+ and NO_3^-, produced via decomposition of the organic material was increased progressively with advancing the incubation time. Incorporation of herbicides into the soil unsupplemented with organic material declared the superior inhibitory action of cotoran over gesapax and atrazine on the microbial activities contributing to the humification process of the native organic fraction.

Available P was increased with the addition of each of organic material and herbicides. The amount of available P was promoted to reach a peak within 45-75 days of incubation, thereafter, started to decline. The effect of herbicides on P availability showed the order: gesapax > cotoran > atrazine.

INTRODUCTION

It is well known that cultivation practices affect directly and indirectly the availability of nutrients in soil. Since the application of pesticides is one of these practices, it is expected to play some role in nutrient availability, at least through the impact on the microorganisms contributing to the various biochemical processes in soils. The beneficial role of microorganisms on soil fertility and plant nutrition is undoubted. However, the effect of pesticides on soil microorganisms is contradicatory, depending on molecular structure of the compound, dose, frequency, and method of application, likewise on the soil properties, kind of microorganisms, and cultivation practices (Walker, 1967; Helling et al., 1971; Cervelli et al., 1978).

Upchruch and Manson (1962) observed that soils high in organic matter require high rates of herbicide application to maintain a given level of herbicidal action than do soil low in organic matter. Harris (1967) showed that degradation of atrazine proceeded more rapidly in soils with higher organic matter content and suggested that the degradition process may be closely associated with the organic matter. An important factor which may affect atrazine adsorption by soils, but which has received little attention, is the nature of the interaction between clay minerals and the native soil organic matter.

There is still a conspicuous lack of information on the influence of herbicides on the elemental content of organic matter in soils. Therefore, the present study was carried out to demonstrate the effect of three herbicides (atrazine, cotoran, and gesapax) used in Egyptian agriculture, where they are directly applied onto soil surface on the changes of carbon, nitrogen, and phosphorus contents during humification of organic material added to an alluvial soil of Egypt.

MATERIALS AND METHODS

Surface sample of an alluvial soil (0-30 cm) was taken from the Experimental Farm, Faculty of Agriculture, Shebin El-Kom. The sample was air-dried, ground to pass through a 2-mm sieve, and analyzed. Some physical and chemical properties of the investigated soil sample are presented in Table (1).

The herbicides cotoran, atrazine, and gesapax, usually applied onto the soil cultivated with Egyptian main field crops, are tested

Table (1): Analytical data of the investigated soil.

a) Physical properties

Organic matter %	$CaCO_3$ %	Particle size distribution %			Texural grade
		Sand	Silt	Clay	
2.15	2.80	27.02	27.02	45.96	Clay

b) Chemical properties

pH 1:2.5	EC* mmhos/cm	CEC meq/100 g	Total N %	Total P %	Soluble ions (meq/100 g)*							
					Cations				Anions			
					Ca^{++}	Mg^{++}	Na^{+}	K^{+}	Cl^{-}	HCO_3^{-}	CO_3^{--}	SO_4^{--}
7.9	0.44	28.60	0.10	0.09	0.80	0.45	1.12	0.33	0.80	0.95	-	0.95

* In the extract of soil paste.

Table (2): Herbicides used, their chemical structure and recommended rate of application

Common name of herbicide	Chemical structure	Recommended rate
Cotoran	1,1-dimethyl-3-(α-α-α-trifluro-m-tolyl)urea.	100 μg/100 g
Atrazine	6-Chloro-N-ethyl-N-isopropyl-1,3,5-triazinediyl-2,4,-diamine,2-chloro-4-ethylamino-6-isopropylamine-1,3,5-triazine.	100 μg/100 g
Gesapax	N-ethyl-N-isopropyl-6-methylthio-1,3,5-triazine-2,4-diyladiamine,2-ethylamino-4-isopropylamino-6-methylthio-1,3,5-triazine.	100 μg/100 g

herein. Structure and recommended rate of application of such herbicides are shown in Table (2).

A number of polypropylene containers (7-cm wide, 5-cm high) was assigned to this study. In each container, 100 g of soil crumbs were packed. The soil containers were splitted into two groups for the following treatments:

A. No organic material added.
B. Organic material added.

Each group was further divided into four sets to satisfy the following subtreatments:

a. No herbicide applied.
b. Atrazine.
d. Cotoran.
c. Gesapax.

Pulverized clover hay (C 49.4%, N 0.84%, and P 0.12%), was employed in this study as an organic source and was added at a rate of 3%. The herbicides were applied to soil at their recommended rates (Table 2). To each container of all sets, an activating mixture (1 mg superphosphate + 0.05 mg potassium sulphate + 0.01 mg urea) was applied. These supplements were thoroughly mixed with soil crumbs. 10-ml of fresh fertile soil-water suspension (1:5) were introduced into each container to serve as inoculum. Moisture content of the soil was brought to 60% of the water-holding capacity by deionized water. All treatments were run in duplicate. Soil containers were left uncovered and incubated at the ambient room temperature (25±2°C). Periodical sampling was conducted along 150-day experimental duration for C, N, and P determinations. Moisture losses were compensated every three days with deionized water.

At certain incubation intervals, soil samples were dried at 70°C, then again ground and sifted. The non-humified materials were electrostically removed, using rubbed plastic plate according to Turin method (Alexandrova and Naidenova, 1976).

The samples were then subjected to the following technique:

50 g of soil sample were placed in a 1000-ml polyethylene bottle, then 250-ml of freshly prepared 0.5 N NaOH were used as extractant and 2.5-ml of concentrated Sn Cl_2 were also added (Choudhri and Stevenson, 1957). The mixture was shaken by end-over-end shaker for one hour, then left to stand over night (16-18 h) at room temperature. The suspension was shaken vigorously and 5 g of Na_2SO_4 were added as coagulating agent for polyvalent cations. The mixture was centrifuged for 15 min. at 3000 rpm, and the supernatant was transferred to a 250-ml volumetric flask, whereas the soil residue was discarded (Khalifa, 1979).

Contents of total organic carbon and humic substances carbon were determined by means of Walkley and Black method (Jackson, 1958) taking in consideration the recommendation of Kononova (1966).

Available nitrogen (amonium and nitrate) was extracted by 1.0 N KCl. NH_4^+-N was determined by steam distillation using MgO and after collection in 3% boric acid, 0.01 N H_2SO_4 was used for titration. NO_3^--N was determined in the residue of distillation using the reducing agent Devarda alloy (FAO, 1980).

Available P in soil was extracted by 0.5 N $NaHCO_3$ at pH 8.5, according to Olsen's procedure and determined colourimetrically using stannous chloride (Jackson, 1958).

RESULTS AND DISCUSSION

The effect of herbicides (atrazine, cotoran, and gesapax) application on contents of carbon in soil, i.e. total humified, extracted humified, and distribution among humic substances appears in Table (3). In the treatment having no organic material, all forms of native carbon diminished with incubation time, due to mineralization that took place by microorganisms resulting in carbon loss to the atmosphere in the form of CO_2. However, in the soil treated with organic material, the content of total humified carbon, and extracted humified carbon showed gradual increase to reach a peak within 30 days of incubation, thereafter, started to decline. Such pattern is ascribed to the conversion of carbon from non-humic raw material to humic matter during the first phase, then its liberation to gaseous CO_2 in the latter phase.

The soil samples treated with atrazine revealed lower values of both total humified and extracted humified carbon when compared with the control, while the samples treated with cotoran and gesapax gave higher values of the same constituents than those of the control. This may be due to different action of the herbicides may applied on microbial activity of the soil used. For instance, some pesticides serve as sources of energy and nutrients for the chemoorganotrophic microflora in soil, thereby they are beneficial (Martin, 1972). Other pesticides may be of no effect or are detrimental to microorganisms (Chandra and Bollen, 1961, Abo El-Ghar and El-Shinnawi,1978). Nardi and Dell'Agnola (1984) found, in laboratory experiment, that atrazine, dalapan, and propanil increased mineralization of organic matter but not humification of plant residues, molinate increased both processes.

Data also show that humic acid predominated over fulvic acid in all soil treatments (Table 3). Such results confirm those of Khalifa (1979) and Khalil and Amer (1986). The ratio of humic acid to fulvic

Table (3): Content of organic carbon forms extracted from soil amended with organic material as affected by herbicides application.

Sampling time (days)	Without organic material added: Total humified carbon %	Extracted humified carbon %	Index	Carbon content of the humic substances (%): Humin	Humic acid (HA)	Fulvic acid (FA)	HA/FA	With organic material added: Total humified carbon %	Extracted humified carbon %	Index	Carbon content of the humic substances (%): Humin	Humic acid (HA)	Fulvic acid (FA)	HA/FA
Control														
15	1.200	0.380	100.00	68.33	18.33	13.34	1.37	1.490	0.605	96.03	59.36	20.45	20.19	1.01
30	1.116	0.350	92.11	68.63	18.05	13.32	1.36	1.565	0.630	100.00	59.74	22.15	18.11	1.22
45	1.095	0.330	86.84	69.86	17.90	12.24	1.46	1.520	0.582	92.38	61.71	21.29	17.00	1.25
75	1.081	0.318	83.68	70.58	17.59	11.83	1.49	1.475	0.525	83.33	64.41	20.94	14.65	1.42
105	1.049	0.300	78.94	71.40	17.10	11.50	1.49	1.422	0.490	77.78	65.54	20.20	14.26	1.42
150	1.027	0.290	76.32	71.76	16.95	11.29	1.50	1.410	0.470	74.60	66.67	19.80	13.53	1.46
Mean	1.095	0.328		70.09	17.65	12.25	1.45	1.480	0.550		62.91	20.81	16.29	1.30
Atrazine														
15	1.116	0.370	100.00	68.28	18.57	13.15	1.41	1.455	0.590	95.16	59.45	20.55	20.00	1.03
30	1.105	0.341	92.16	69.14	18.10	12.76	1.42	1.504	0.620	100.00	58.78	22.32	18.90	1.18
45	1.072	0.326	88.11	69.59	17.95	12.46	1.44	1.477	0.570	91.94	61.41	21.59	17.00	1.27
75	1.044	0.305	82.43	70.76	17.73	11.51	1.54	1.444	0.515	83.06	64.33	20.83	14.84	1.41
105	1.027	0.290	78.38	71.76	17.18	11.06	1.55	1.410	0.480	77.42	65.96	20.12	13.92	1.44
150	0.983	0.270	72.97	72.53	16.98	10.49	1.62	1.388	0.460	74.19	66.86	19.65	13.59	1.45
Mean	1.058	0.317		70.34	17.75	11.91	1.50	1.446	0.539		62.80	20.84	16.37	1.30

Table (3): (Cont.).

Sampling time (days)	Without organic material added							With organic material added						
	Total humified carbon %	Extracted humified carbon %	Index	Carbon content of the humic substances (%) Humin	Humic acid (HA)	Fulvic acid (FA)	HA/FA	Total humified carbon %	Extracted humified carbon %	Index	Carbon content of the humic substances (%) Humin	Humic acid (HA)	Fulvic acid (FA)	HA/FA
						Cotoran								
15	1.200	0.380	100.00	68.33	18.66	13.01	1.43	1.568	0.634	91.62	59.57	21.15	19.28	1.10
30	1.116	0.350	92.11	68.63	18.47	12.90	1.43	1.604	0.692	100.00	56.86	23.37	19.77	1.18
45	1.105	0.335	88.16	69.68	18.11	12.21	1.48	1.593	0.625	90.32	60.77	22.74	16.49	1.38
75	1.095	0.323	85.00	70.37	17.85	11.78	1.52	1.568	0.570	82.37	63.65	21.16	15.19	1.39
105	1.068	0.312	82.11	70.26	17.81	11.93	1.49	1.540	0.556	80.35	63.90	21.10	15.00	1.41
150	1.038	0.295	77.63	71.28	17.60	11.12	1.58	1.510	0.528	76.30	65.03	21.04	13.93	1.51
Mean	1.104	0.332		69.76	18.08	12.16	1.49	1.564	0.601		61.63	21.76	16.61	1.33
						Gesapax								
15	1.200	0.370	100.00	69.17	18.27	12.56	1.45	1.590	0.641	91.44	59.69	20.90	19.41	1.08
30	1.116	0.340	91.89	69.54	18.21	12.29	1.48	1.700	0.701	100.00	58.76	22.50	18.74	1.20
45	1.105	0.329	88.92	70.23	17.91	11.86	1.51	1.678	0.663	94.58	60.49	22.23	17.18	1.29
75	1.095	0.315	85.13	71.23	17.65	11.12	1.59	1.593	0.586	83.59	63.21	21.62	15.17	1.42
105	1.075	0.312	84.32	70.98	17.50	11.52	1.52	1.560	0.566	89.72	63.72	21.27	14.81	1.44
150	1.046	0.300	81.08	71.32	17.39	11.29	1.54	1.518	0.538	76.75	64.56	21.10	14.34	1.47
Mean	1.106	0.328		70.41	17.82	11.77	1.52	1.607	0.616		61.73	21.60	16.61	1.32

acid (HA/FA) was more than one in all cases, and it was decreased with the addition of organic material. Application of herbicides to soil treated or untreated with organic material promoted the HA/FA ratio. One or more of three possibilities might contribute to the increment of HA/FA ratio, namely, rate of humic acid formation exceeds that of fulvic acid, fulvic acid was more readily mineralized by microorganisms than humic acid, or adsorption of herbicides on humic acid molecules which might reduce the oxidation rate of humic acid.

Humin content (Table 3) revealed slight promotion by advancing time of incubation. The increase in humin content does not reflect any absolute increment, but due to diminution in both humic and fulvic acids contents. Application of each of the herbicides and organic material reduced the humin component.

Data of Table (4) denote that amounts of NH_4^+-N had been fluctuated within the experimental duration. Such values tended to be increased till 75-105 days then started to be decreased in the soil receiving no organic supplement, whereas no definite trend could be observed for the organic-material-treated soil. However, amounts of ammoniacal nitrogen detected in the enriched soil were lower during the first 75-105 days of incubation than those in the deprived soil. This does not indicate a lower rate of ammonification but rather a high extent of nitrogen immobilization by the intensively proliferating microorganisms at this stage. Since, figures of NH_4^+-N appearing, at any incubation interval, represent the net amounts resulted from the contradictory processes, namely, the providing ammonification and the consuming assimilation and nitrification, it is difficult to ascertain the effect of a particular treatment on the chemoorganotrophic ammonifying agents as such.

Table (4): Changes in mineral N (mg/100 g soil) in soil as affected by application of organic matter and herbicides.

Sampling time (days)	Without organic material			With organic material		
	NH_4^+-N	NO_3^--N	Sum	NH_4^+-N	NO_3^--N	Sum
			Control			
15	7.8	23.5	31.3	5.0	5.0	10.0
30	5.0	26.3	31.3	6.7	8.4	15.1
45	8.4	30.8	39.2	5.9	12.9	18.8
75	10.1	24.6	34.7	5.0	17.4	22.4
105	6.1	23.0	29.1	5.0	29.1	34.1
150	3.9	35.8	39.7	4.5	40.0	44.5
			Atrazine			
15	7.8	19.0	26.4	8.4	6.2	14.6
30	4.5	26.9	31.4	4.5	10.5	15.0
45	5.0	29.1	34.1	4.5	14.6	19.1
75	7.3	30.2	37.5	5.0	23.5	28.5
105	7.8	33.6	41.4	5.0	30.8	35.8
150	7.3	36.4	43.7	7.5	37.5	45.0
			Cotoran			
15	8.4	25.2	33.6	6.7	5.0	11.7
30	5.0	24.6	29.6	5.0	9.0	14.0
45	5.6	26.3	31.9	5.6	12.9	18.5
75	5.6	33.0	38.6	4.5	20.7	25.2
105	5.6	30.2	35.8	5.0	31.4	35.4
150	3.9	31.4	35.3	4.5	34.2	38.7
			Gesapax			
15	7.3	24.1	31.4	7.3	5.6	12.9
30	3.9	24.6	28.5	6.1	6.7	12.9
45	3.9	30.8	34.7	5.6	12.9	18.5
75	7.3	32.5	39.8	7.3	23.0	30.3
105	4.5	34.7	39.2	5.0	26.9	31.9
150	4.5	36.4	40.9	6.1	39.8	45.9

NO_3^--N revealed augmentation by advancing the incubation time in all variables of the experiment (Table 4). Accumulation of such form of nitrogen in the enriched soil had shown lower values than those in the deprived soil during the first 105 days of incubation, thereafter started to excell. This is correlated with the extent of nitrogen assimilation. The herbicide gesapax seemed to be of no effect on the chemolithotrophic nitrifying bacteria, whereas the other compounds tested, i.e. atrazine and cotoran had a slight depressing action on nitrification in the soil under consideration. In this connection, Marsh and Greaves (1979) and Schmidt (1982) reported that some herbicides stimulate ammonification but most of them inhibit nitrification.

Contents of mineral nitrogen (NH_4^+-N + NO_3^--N) had shown promotion with time in all soil treatments (Table 4). Figures of enriched soil had been lower during the first 75 days than those of the deprived soil, thereafter surpassed them. The herbicide cotoran was of slight inhibitory influence on N mineralization, while atrazine and gesapax were not depressive but rather somewhat stimulatory. The presence of fluoride in the structure of cotoran (Table 2) may stand behind its injurious action on the microorganisms contributing to such N transformation (Wilson, 1983). Worth while that, the herbicides used contain nitrogen in their molecular structure (Table 3), yet this could not contribute to the interpritation of results since the amounts of such structural N are two minute to be negligible.

The effect of herbicides application on available P in the soil during the humification process of organic material is illustrated in Fig. (1). Available P was increased with the addition of each of organic material and herbicides. The amount of available P was raised to reach a peak within 45-75 days of incubation, thereafter started to decrease. Increase of available P could be explained by production of CO_2 and thus formation of H_2CO_3, during organic matter

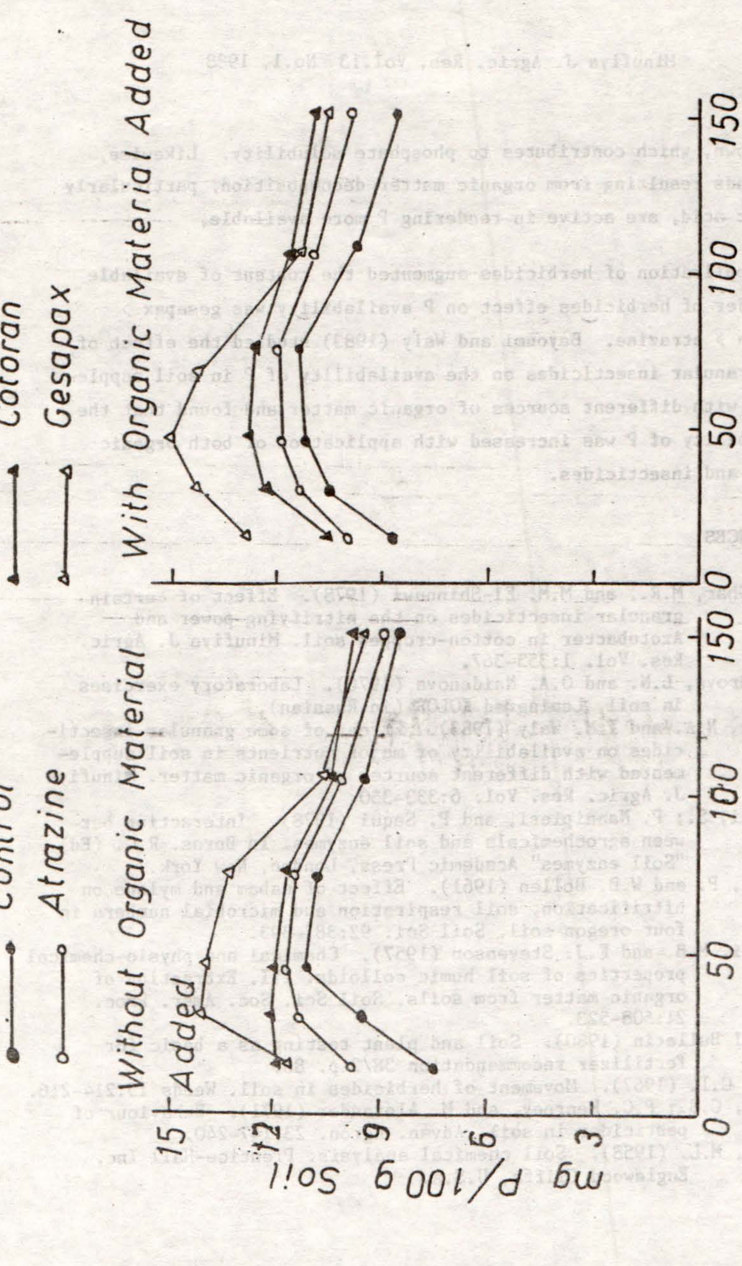

Fig (1) Changes in available P in soil as affected by application of herbicides in absence and presence of organic material.

breakdown, which contributes to phosphate solubility. Likewise, compounds resulting from organic matter decomposition, particularly organic acid, are active in rendering P more available.

Application of herbicides augmented the content of available P. Order of herbicides effect on P availability was gesapax > cotoran > atrazine. Bayoumi and Waly (1983) studied the effect of some granular insecticides on the availability of P in soil supplemented with different sources of organic matter and found that the availability of P was increased with application of both organic matter and insecticides.

REFERENCES

Aboel-Ghar, M.R., and M.M. El-Shinnawi (1978). Effect of certain granular insecticides on the nitrifying power and Azotobacter in cotton-cropped soil. Minufiya J. Agric. Res. Vol. 1:353-367.

Alexandrova, L.N. and O.A. Naidenova (1976). Laboratory exercises in soil. Leningrad KOLOS (in Russian).

Bayoumi, N.A. and T.M. Waly (1983). Effect of some granular insecticides on availability of major nutrients in soil supplemented with different sources of organic matter. Minufiya J. Agric. Res. Vol. 6:333-350.

Cervelli, S.; P. Nannipieri, and P. Sequi (1978). Interaction between agrochemicals and soil enzymes. In Burns. R.G. (Ed) "Soil enzymes" Academic Press, London, New York.

Chandra, P. and W.B. Bollen (1961). Effect of nabam and mylone on nitrification, soil respiration and microbial numbers in four oregon soil. Soil Sci. 92:387-393.

Choudhri, M.B. and F.J. Stevenson (1957). Chemical and physio-chemical properties of soil humic colloids. III. Extraction of organic matter from soils. Soil Sci. Soc. Amer. Proc. 21:508-523.

FAO soil Bulletin (1980). Soil and plant testing as a basic for fertilizer recommendation 38/2 p. 86.

Harris, C.I. (1967). Movement of herbicides in soil. Weeds 15:214-216.

Heeling, C.S.; P.C. Kearney, and M. Alexander (1971). Behaviour of pesticides in soil. Advan. Agron. 23:147-240.

Jackson, M.L. (1958). Soil chemical analysis. Prentice-Hall Inc. Englewood Cliffs. U.S.A.

Khalifa, M.L. (1979). Pedogenic studies on organic matter of some Egyptian soil. Ph.D. Thesis, Fac. of Agric., Alex. University, Egypt.

Khalil, R.A. and R.M. Amer (1986). Efficiency of various extracts in studying the distribution of humic substances in an alluvial soil of Egypt. J. Agric. Sci. Mansoura Univ. 11(2):870-875.

Kononova, M.M. (1966). Soil organic matter. Press, Oxford, U.K.

Marsh, J.A.P. and M.P. Greavs (1979). The influence of temperature and moisture on the effects of the herbicides dalapan on nitrogen transformation in soil. Soil Biol. Biochem. 11:279-285.

Martin, J.P. (1972). Side effect of organic chemicals on soil properties and plant growth. In Goring, A.I. and Hamaker, J.W. (Ed.) "Organic chemicals in soil Environment" Marcel Dekker, New York.

Nardi, S. and G. Dell'Agnola (1984). Effect of herbicides on soil organic matter. Weed Ab. 1986, 35, 6:2237.

Schmidt, E.L. (1982). "Nitrification in soil". in Nitrogen in Agriculture soils. ed. Stevenson. F.J. Madison, Wisconsin. U.S.A. p. 253.

Upchurch, R.P. and D.D. Manson (1962). The influence of soil organic matter on phystotoxicity of herbicides. Weeds 10:9-14.

Walker, N. (1967). Soil microorganisms and plant protection chemicals. In Burges, A. and Raw, F. (Eds) "Soil biology". Academic Press, London, New York.

Wilson, G. (1983). Bacterial Resistance, Disinfection, and Sterilization. P. 80-96. In: Wilson, G. and M. Dick (eds.). Topley and Wilson's principles of bacteriology, virology and immunity, Vol. 1. 7th Edition. Williams and Wilkins, Baltimore, MD.