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Residual Toxicity of some Herbicides

(i) 2, 4–D, MCPA and TCA

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Abstract : Residual toxicity studies of 3 herbicides viz. 2,4-Dichlorophenoxy acetic acid, 2-methyl 4-Chlorophenoxy acetic acid and Trichloroacetic acid in four common soil groups : Reddish Brown Earth, Reddish Brown Latasolic, Immature Brown Loam and Low-humic Gley, indicate that the herbicidal effect of the compounds examined decrease during incubation, more rapidly in LHG soils than in others. 2, 4-D and MCPA decomposed faster than TCA. The residual toxicity of herbicides examined except TCA decreased at a slower rate under flooded conditions than under unflooded conditions. Studies carried out with autoclaved soils show that microbial activity is responsible for the decrease in toxicity except in TCA. Residual toxicity decreased more rapidly in soils previously incubated with these herbicides. Leaching tests indicate that the three herbicides tend to get adsorbed mostly in the first 3 in. of the soil except in LHG where accumulations were more in the 1 to 2 in. layer.

1. Introduction

Since 1895 when the herbicidal property of $CuSO_4$ was discovered by Bennet, a large number of herbicides, with different degrees of selectivity have been developed, to be utilized in our endeavours to achieve a higher level of food production.

The ultimate recipient of most of the herbicides is the soil, which is a complex mixture of organic and inorganic particles inhabited by microscopic and macroscopic organisms. The molecules of the herbicide that enter the soil are subjected to physical and chemical changes. Physically, the phytotoxic compounds get adsorbed on soil colloidal particles and this process has been shown to be influenced by a number of factors related to the nature of the herbicide molecule[3] and the soil.[8] Desorption of the adsorbed molecules also take place as shown by Williams[23] and Talbert and Fletchell.[22]

Chemical changes of herbicide molecules are brought about by chemical and biological factors. Armstrong *et al.*[4] and Zaki *et al.*[24] have shown chemical transformations of the soil incorporated herbicides while decomposition of herbicides by soil microorganisms has been demonstrated by a number of workers.[16,17,18] Microorganisms are known to utilize these organic molecules as a source of energy.[12,15] However, some compounds such as 2, 3, 6—TBA are recalcitrant[2] and are known to remain undecomposed in soil over long periods.[9,10]

Those herbicides that get decomposed by soil microorganisms also remain in the soil for varying periods prior to their decomposition. This period called the lag period, depends on the nature of the soil and the compound.[5]

In view of these findings, a study of the residual toxicity of herbicides commonly used is of importance in obtaining the maximum benefit of herbicides applied and also in controlling environmental pollution. The studies reported in this paper were carried out to examine the residual toxicity of some of the commonly used herbicides in Sri Lanka.

2. Materials and Methods

2.1. Materials

The commercially available compounds of the following herbicides were used :

1. 2,4—Dichlorophenoxy acetic acid amine salt (2,4—D).
2. A mixture of sodium and potassium salt of 2 methyl 4—chlorophenoxy acetic acid (MCPA).
3. Trichloro acetic acid sodium salt (TCA).

Four soil groups were used in this study and their characteristics are indicated in Table 1.

TABLE 1. Some characteristics of the soils used in the study

Type of Soil	% sand	% silt	% clay	% o.matter	pH
Reddish Brown Earth	38.5	18.5	43.0	0.65	7.8
Reddish Brown Latosolic	36.5	15.3	49.2	1.14	5.9
Immature Brown Loam	40.8	24.6	34.6	1.28	5.7
Low-Humic gley	28.5	18.5	52.7	2.06	7.2

2.2. Methods

2.2.1. *Experiment* 1. *Residual toxicity of herbicides under unflooded conditions.*

250 g of soil of each group was separately mixed with herbicide solutions to give the following concentration in the soil.

*2, 4—D	1.5 ppm
*MCPA—	2.0 ppm
*TCA—	10 ppm

* Some characteristics of these compounds are given in the appendix.

The moisture content was brought to 50% field capacity and the soil-herbicide mixture was incubated at room temperature. Three replicates were included for each soil group. At fortnightly intervals, the residual toxicity of the soil-herbicide mixture was determined by bio-assay tests (5) using mustard as a test plant. Incubation was continued over a period of 13 weeks.

2.2.2. *Experiment* 2. *Residual toxicity of herbicides under flooded conditions*

Soils were mixed with herbicides as in Experiment 1 and were incubated under similar conditions except for the fact that flooded conditions were maintained by keeping water 1 in above the surface of soil. Residual toxicity of the incubated soils was determined at fortnightly intervals over a period of 13 weeks by bio-assay tests.

2.2.3. *Experiments* 3 *and* 4. *Residual toxicity of herbicides in sterile soils.*

Similar to Experiments 1 and 2 respectively except for the fact that sterile soils (soils heated to 150°C for 48 hours) were used.

2.2.4. *Experiment* 5. *Residual toxicity of herbicides in soils previously treated with the herbicides.*

Soils used in Experiment 1 were kept moist over a period of one year. These soils were re-incubated with herbicides added as in Experiment 1 and the residual toxicity was determined by bio-assay tests at fortnightly intervals.

2.2.5. *Experiment* 6. *Residual toxicity of herbicides in the field.*

This experiment was conducted on field scale at Kundasale. The herbicides were applied to weed-free plots 15 ft × 15 ft at recommended rates indicated in the appendix. The number of weeds in these plots was determined at fortnightly intervals.

2.2.6. *Experiment* 7. *Adsorption of herbicides.*

100 ml of the herbicide solution was leached through a soil column 4 in long. (It was found that 100 ml of solution was just sufficient to wet the whole soil column). The soil column was removed as 1 in blocks and the residual toxicity of these blocks was examined by bio-assay tests.

3. Results and Discussion

3.1. *Experiment* 1.

The results obtained in Experiment 1 are given in Table 2. These results indicate that there is an initial drop in the concentration of herbicides which could be attributed to adsorption on clay and organic matter in the soils used. Adsorption of herbicides in soils has been reported by a number of workers.[8]

TABLE 2. Residual concentration of the herbicides in soils incubated under unflooded condition at fortnightly intervals in ppm

	Weeks 0	1	3	5	7	9	11	13
2,4—D								
RBE	1.5	1.0	1.0	1.0	0.8	0.6	0.4	0.2
RBL	1.5	1.0	1.0	1.0	0.9	0.8	0.7	0.6
IBL	1.5	1.0	1.0	1.0	0.9	0.8	0.6	0.4
LHG	1.5	0.8	0.7	0.6	0.5	0.3	0.1	0.05
MCPA								
RBE	2.0	1.0	1.0	1.0	0.8	0.6	0.4	0.2
RBL	2.0	1.0	1.0	1.0	0.9	0.8	0.7	0.6
IBL	2.0	1.0	1.0	0.8	0.7	0.6	0.4	0.4
LHG	2.0	0.8	0.8	0.6	0.5	0.4	0.2	0.1
TCA								
RBE	10	8	8	8	6	4	4	4
RBL	10	8	8	8	6	6	6	4
IBL	10	8	8	6	6	6	6	4
LHG	10	8	8	6	6	4	4	2

All the three herbicides examined have decomposed in the four soils during the incubation period, decomposition being most rapid in LHG soil. This is likely to be due to higher microbial activity in the LHG soil brought about by the relatively high organic matter content. It is known that decomposition of herbicides in soil is brought about mainly by microorganisms.[2,5,7]

In all soils other than LHG, 2,4-D, MCPA and TCA have begun to decompose after the fifth week ; but in LHG, decomposition has started at an earlier stage. Previous studies, too, have shown rapid decomposition of these herbicides.[14,19] The decomposition of 2,4-D and MCPA is slower in RBL and IBL soils ; this is possibily due to the relatively low pH of these soils. It has been reported that microbial activity is less in acidic soils.[1] However, the rate of decomposition of TCA appears to be more or less the same in all the soils. This is likely to be due to chemical factors being more dominant in the decompositions of this compound. Chemical transformations of soil incorporated herbicides have been reported.[4,24]

3.2. *Experiment* 2.

The results of this experiment (Table 3) indicate an initial reduction in the concentration of the herbicides as in Experiment 1. Subsequently, however, there is a relatively small drop in the concentration of the herbicides except TCA. The decreased microbial activity in the flooded soils due to anaerobic conditions prevailing is likely to have resulted in the little decomposition of the herbicides except TCA. TCA has decomposed faster under flooded condition than under unflooded condition indicating that anaerobic soil microorganisms favour its decomposition. Anaerobic biodegradation of chlorinated hydrocarbon insecticides has shown to be favoured by a fall in the redox potential.[20]

TABLE 3. Residual concentration of the herbicides in soils incubated under flooded condition at fortnightly intervals in ppm.

	Weeks 0	1	3	5	7	9	11	13
2, 4—D								
RBE	1.5	1.0	1.0	1.0	1.0	1.0	0.8	0.8
RBL	1.5	1.0	1.0	1.0	1.0	1.0	1.0	0.8
IBL	1.5	1.0	1.0	1.0	1.0	1.0	0.8	0.6
LHG	1.5	1.0	1.0	1.0	1.0	0.8	0.8	0.6
MCPA								
RBE	2.0	1.5	1.5	1.5	1.0	1.0	1.0	1.0
RBL	2.0	1.5	1.0	1.0	1.0	1.0	1.0	1.0
IBL	2.0	1.5	1.0	1.0	1.0	1.0	1.0	1.0
LHG	2.0	1.5	1.0	1.0	1.0	0.8	0.8	0.8
TCA								
RBE	10	10	8	6	0	0	0	0
RBL	10	10	8	4	0	0	0	0
IBL	10	10	8	6	4	2	0	0
LHG	10	10	8	4	4	10	10	10

Trichloroacetate during the course of its decomposition appears to have formed another toxic compound in LHG soils in the ninth week of incubation. This compound has a toxicity equivalent to 10 ppm of TCA and has not decomposed in the subsequent 6 weeks. Audus has reported of a similar process with 2, 4 dichlorophenoxyethyl sulphate.[6]

3.3. *Experiment* 3.

Residual concentrations of the three herbicides incubated in sterile soils under unflooded condition (Table 4) show that almost no decomposition has taken place during the incubation period suggesting that the soil microorganisms are responsible for the decomposition of these compounds. Audus[5] also has shown that decomposition of agro-chemicals in soil is mostly brought about by organisms.

3.4. *Experiment* 4.

Results of Experiment 4 (Table 5) are similar to that in Experiment 3 but TCA incorporated soils show lower toxicity than in Experiment 3 during the latter part of incubation period. This suggests that TCA has undergone chemical changes under flooded condition probably due to non-biological factors resulting in a decrease in the toxicity level. Zaki *et al.*[24] also have reported of such non-biological chemical changes of herbicides in soils.

3.5. *Experiment* 5.

Investigations by Audus[7] have shown that decomposition of herbicides is rapid in soils previously treated with them. This could be attributed to adaptation of soil microorganisms as suggested by Cohn and Monod[11] and Hirsch and Alexander[13] or due to the evolution of strains capable of decomposing the compounds as shown by Kearney *et al.*[17]

TABLE 4. Residual concentration of the herbicides incubated in sterile soils under unflooded condition at fortnightly intervals in ppm.

	Weeks 0	1	3	5	7	9	11	13
2, 4—D								
RBE	1.5	1.0	1.0	1.0	1.0	1.0	1.0	0.8
RBL	1.5	1.0	1.0	1.0	1.0	1.0	1.0	0.8
IBL	1.5	1.0	1.0	1.0	1.0	1.0	1.0	0.8
LHG	1.5	1.0	1.0	1.0	1.0	1.0	1.0	0.8
MCPA								
RBE	2.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
RBL	2.0	1.0	1.0	1.0	1.0	1.0	1.0	0.8
IBL	2.0	1.0	1.0	1.0	1.0	1.0	1.0	0.8
LHG	2.0	1.0	1.0	1.0	1.0	1.0	1.0	0.8
TCA								
RBE	10	8	8	8	8	8	8	6
RBL	10	8	8	8	8	8	6	6
IBL	10	8	8	8	8	8	6	6
LHG	10	8	8	8	8	8	8	6

TABLE 5. Residual concentration of the herbicides incubated in sterile soils under flooded condition at fortnightly intervals in ppm.

	Weeks 0	1	3	5	7	9	11	13
2, 4—D								
RBE	1.5	1.0	1.0	1.0	1.0	1.0	1.0	0.8
RBL	1.5	1.0	1.0	1.0	1.0	1.0	1.0	0.8
IBL	1.5	1.0	1.0	1.0	1.0	1.0	1.0	0.8
LHG	1.5	1.0	1.0	1.0	1.0	1.0	1.0	0.8
MCPA								
RBE	2.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
RBL	2.0	1.0	1.0	1.0	1.0	1.0	1.0	0.8
IBL	2.0	1.0	1.0	1.0	1.0	1.0	1.0	0.8
LHG	2.0	1.0	1.0	1.0	1.0	1.0	1.0	0.8
TCA								
RBE	10	8	8	6	4	4	2	2
RBL	10	8	8	6	6	4	2	2
IBL	10	8	8	6	6	4	2	2
LHG	10	8	8	4	4	4	2	2

The results of the Experiment 5 (Table 6) show that the findings of Audus[5] could be applied to the three herbicides examined. However TCA in LHG soils appear to have formed a toxic compound during the latter part of incubation like in the case of Experiment 2.

TABLE 6. Residual concentration of the herbicides incubated in soils previously treated with the herbicides in ppm.

	Weeks							
	0	1	3	5	7	9	11	13
2, 4—D								
RBE	1.5	1.0	0.5	0.2	0	0	0	0
RBL	1.5	1.0	0.5	0.2	0	0	0	0
IBL	1.5	1.0	0.5	0.2	0	0	0	0
LHG	1.5	1.0	0.5	0.2	0	0	0	0
MCPA								
RBE	2.0	1.0	0.1	0	0	0	—	—
RBL	2.0	1.0	0.2	0	0	0	—	—
IBL	2.0	1.0	0.2	0	0	0	—	—
LHG	2.0	1.0	0.2	0	0	0	—	—
TCA								
RBE	10	8	6	2	0	0	0	—
RBL	10	8	4	0	0	0	0	—
IBL	10	8	4	0	0	0	0	—
LHG	10	8	4	0	10	10	10	—

3.6. *Experiment* 6.

Results of Experiment 6 (Table 7) which was carried out at Kundasale indicate that the three herbicides tested have degraded within the 12 week period confirming the findings of Experiment 1.

TABLE 7. Number of weeds per 5 square yards at fortnightly intervals in plots treated with herbicides

Herbicide	Average number of weeds per 5 square yards (av. of 3) Weeks after application of the herbicide					
	2 Weeks	4 Weeks	6 Weeks	8 Weeks	10 Weeks	12 Weeks
2, 4—D	10	15	22	26	32	44
MCPA	9	17	24	30	38	49
TCA	12	18	30	40	48	51

3.7. *Experiment* 7.

The leaching experiments carried out (Table 8) indicate that all the compounds studied tend to remain mosuly in the 1 to 3 in. of the soil. Relatively higher adsorption of the three herbicides in the 1st inch of LHG is likely to be due to the high organic matter content of the soil. Sheets[21] has shown that organic matter is mostly responsible for adsorption of the organic pesticides. In addition to organic matter a number of other factors such as clay content, cation exchange capacity and pH are known to cause adsorption of agrochemicals in soils.[8]

TABLE 8. Concentration of the herbicides in ppm in soil columns leached with 100 ml of herbicide solution.

Herbicide		RRE	RBL	IBL	LHG
2, 4—D	0—1"	0.5	0.3	0.4	0.6
	1—2"	1.0	1.2	0.9	0.1
	2—3"	0.6	0.6	0.8	0.8
	3—4"	0.4	0.4	0.4	0.3
MCPA	0—1"	0.4	0.5	0.4	0.1
	1—2"	0.9	0.8	0.9	0.9
	2—3"	1.2	1.4	0.9	0.9
	3—4"	0.8	0.6	1.1	0.7
TCA	0—1"	2.0	2.0	4.0	5.0
	1—2"	5.0	4.0	5.0	6.0
	2—3"	8.0	9.0	6.0	5.0
	3—4"	2.0	2.0	2.0	2.0

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APPENDIX

2,4—D :— 2, 4—Dichlorophenoxy acetic acid amine salt selectively destroys all species of sedges and broad-leaved weeds growing in paddy, pastures, etc. at 1 fl oz in 2 gallons of water.

MCPA :— A mixture of Na and K salt of 2, methyl —4—chlorophenoxy acetic acid. Selectively destroys most species of broad-leaved weeds and sedges growing in paddy, sugarcane, pastures and lawns, at 1 fl oz.

TCA :— Sodium salt of trichloroacetic acid. Used as a selective weed killer at 5–25 lbs per acre. At 50 lbs/acre TCA acts as a total weed killer and controls Illuk, Bermuda grass and Cooch grass.

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