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Pesticide Degradation in Model Soil Evaporation Beds

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As a result of the large scale use of agricultural chemicals in the United States a large volume of dilute pesticide waste is generated each year. The University of California field stations utilized soil evaporation beds for the containment, concentration and degradation of these dilute aqueous pesticide wastes for a number of years (Winterlin et al. 1984).

These beds and their operation have been described in detail by Winterlin et al. (1984). In brief, the dilute pesticide wastes were fed into the bottom of soil beds where capillary action would draw the water upward to the soil surface where it would evaporate creating a "wicking" effect. As the solution moved upward in the soil it was observed that it carried the pesticides along with it allowing them to come in contact with soil colloids where chemical or microbial transformations could take place. The pesticides could also escape from the beds by volatilization. Two significant factors noted in these field station beds were 1) that the chemicals concentrated in the top 1" of soil, clearly showing the upward movement and 2) that there was little build up of chemicals over time indicating that significant degradation took place (Winterlin et al. 1984).

These beds were economical, required little maintenance and were effective at containing and degrading the chemicals, but they are no longer in use due to legislation which essentially bans any below surface disposal system. Since these beds were so effective in containing and degrading pesticide wastes, we designed a study to look at the effectiveness of a similar above ground system utilizing soil amendments and semi-controlled field conditions for enhancement of pesticide degradation in soils.

MATERIALS AND METHOD

For this project we designed and operated a model soil bed system. The system was designed to investigate the effects of a number of factors on

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the degradation of pesticides in soil. The factors or treatments studied were pH, organic amendments, metal reductants, and fixed aerobic conditions versus cycling through aerobic and anaerobic conditions (semi-anaerobic conditions).

Seven chemicals that are representative of a wide variety of agro-chemical classes were studied. Carbofuran (furadan, 7-Benzofuranol, 2,3-dihydro-2,2-dimethyl-, methyl carbamate, CAS No. 1563-66-2) is a carbamate insecticide, 2,4-D dimethylamine (Acetic acid, (2,4-dichlorophenoxy)-N- methylmethan- amine, CAS No. 2008-39-1) is a phenoxy acid herbicide, diazinon (Phosphorothoic acid, O, O-diethyl O-(6-methyl-2(1-methylethyl)-4-pyrimidinyl) ester, CAS No. 333-41- 5) and ethyl parathion (Phosphorothioic acid, O,O-diethyl O-(4-nitrophenyl) ester, CAS No. 56-38-2) are phosphate ester insecticides, propazine (1,3,5-triazine-2,4-diamine, 6- chloro-N,N'-bis(1-methyl ethyl), CAS No. 139-40-2) is a s- triazine insecticide, endosulfan (thiodan, 6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9, 9a - hexahydro-,3-oxide,(3α,5aβ,6α,9α,9aβ)- and (3α,5aα,6β,9β,9aα), CAS No. 115-29-7) is an organochlorine insecticide and trifluralin (benzeamineamine,2,6-dinitro-N,N-dipropyl-4-(trifluoro-methyl), CAS No. 1582-09-8) is a dinitro fluoroaniline herbicide.

The model soil beds consisted of fiberglass lined plywood boxes two feet wide by four feet long by two feet deep. Perforated PVC pipe was placed in the bottom of the boxes to distribute water evenly to the bottom of each soil bed. A layer of sand and gravel covered the pipe and 2" of a loamy sand soil was added to each bed. Figure 1 shows a side view of a model bed. In the soil beds at the University field stations, the dilute pesticide wastes were fed into the bottom of the beds through a distribution system. In order to ensure even distribution in the model beds the pesticides in this study were applied as a spray to the 2" layer of soil. The pesticides used were commercial formulations, applied as emulsifiable concentrates, except for carbofuran and propazine which were flowable powders.

The pesticides were applied at a rate that would give a total pesticide concentration of 100 ppm (mg a.i./Kg dry soil) in the top 16 inches of the soil. Then 10" of untreated loamy sand soil was added to each bed. Finally 6" of soil treated with amendments as shown in Figure 2 was added to the top of each bed and water was allowed to flow through the distribution system into the bottom of the bed. Since previous work by Winterlin et al. (1984), had shown that the pesticides concentrated in the top 1" of the soil in the evaporation beds, only the top six inches of soil was treated in the model beds as this is the area where treatments are likely to have the most effect.

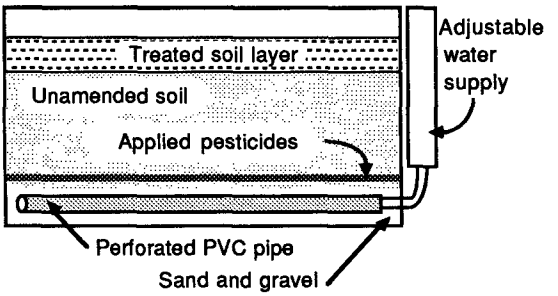

Figure 1. Diagram of a model soil bed.

As the water evaporated from the surface of the soil it created a "wicking" effect and drew more liquid up to the surface. The water moved upward through the soil, encountering the pesticides and carrying them upward where they came into contact with the layer of treated or amended soil.

The various treatments studied are diagramed in Figure 2. In one set of beds the soil used in the top six inches was amended with sulfuric acid to a pH of 4.0. The limed beds had six inches of soil treated with hydrated lime to raise the pH to 10.0. The natural beds had a top 6" of unamended loamy sand soil (pH of 7.1). The next set of beds consisted of these same treatments with added organic matter. In these beds peat moss was added to bring the organic matter content to 10% by weight and the pH was adjusted to 4 or 10 or left "natural" (pH 5.2). In the next set of beds granular zinc metal was combined with the pH treatments. Twenty mesh granular zinc was added at a ratio of 15 moles of zinc per mole of pesticide added. Finally the last set of beds combined the pH treatments with organic matter and zinc metal.

To look at differences between aerobic and anaerobic conditions, a duplicate set of beds was constructed. The water level in both sets of beds could be regulated. In the aerobic beds the water level in the bed was kept 16" below the soil surface. In the anaerobic beds the water level was held 16" below the soil surface for one month and then was raised to a level that completely covered the beds for a period of one month. Then the water level was allowed to fall back down to 16" below the surface for soil sampling before it was raised to cover the bed again. The study actually compared aerobic conditions to semi-anaerobic conditions (cycling the beds through periods of aerobic and anaerobic conditions), rather than comparing aerobic to anaerobic conditions.

Samples were taken at intervals of 2, 8, 16, and 54 weeks. They were taken from the 0-1" depth, the 1-5" depth and the 6-12" depth. These core samples were taken from four locations in each bed and combined into a

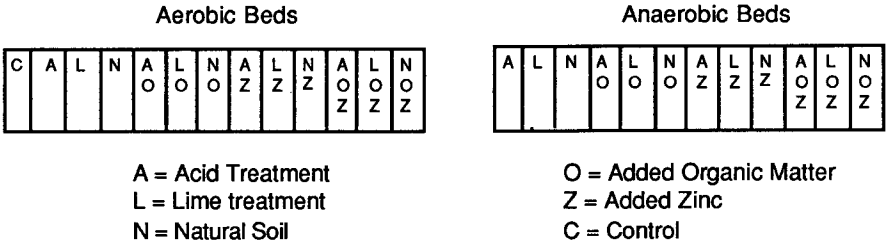

Figure 2. Diagram of model soil beds and treatments

composite sample for each representative depth. The samples were stored at -10 °C until extraction and analysis.

After removal from the freezer and thawing, samples equivalent to 20 grams of dry soil were added to 250 mL Erlenmeyer flasks. Distilled water was added to the samples to bring them up to field capacity. The samples were then extracted with 200 mL of pesticide grade ethyl acetate for 30 seconds using a Tekmar tissuemizer. To extract the 2,4-D, 10 mL of 0.1N HCl was added (10 mL of 0.2 N HCl for the samples with lime) to the samples to reduce the pH to 2, and they were extracted for an additional 30 seconds. The extract was filtered through anhydrous sodium sulfate and stored in amber bottles until analysis.

Trifluralin, diazinon, ethyl parathion, and 2,4-D (after derivitization with diazomethane) were analyzed using capillary gas chromatography on a Hewlett Packard HP 5880A GC with a Ni 63 electron capture detector. The column used was a 17.5m J&W DB-5 fused silica capillary column with a 0.251mm I.D. and film thickness of 0.25 microns, helium was used as the carrier gas. The linear velocity was 51 cm/sec with a split ratio of 1:15. The initial oven temperature was 165 °C for 3.1 minutes, then was programmed at 25 °C per minute up to 260 °C and held for 0.5 minutes.

Trifluralin, diazinon, carbofuran, propazine, and ethyl parathion were analyzed using capillary gas chromatography on a Hewlett Packard 5710A GC with a nitrogen phosphorous detector. The column used was a 15m J&W DB-225 fused silica capillary column with a 0.251mm I.D. and a film thickness of 0.25 microns. The linear velocity was 74 cm/sec using hydrogen as the carrier gas and the split ratio was 1:14. The oven temperature was isothermal at 200 °C. A Finnigan Model 700 Ion Trap Detector (using Revision 3.0 software) with a Hewlett Packard Model 5880A Gas Chromatograph was used for compound confirmation and metabolite identification.

RESULTS AND DISCUSSION

Samples from 2, 8, 16 and 54 weeks have been analyzed by capillary gas chromatography. The results show that for the most part only carbofuran and 2,4-D moved upward in the soil. The data shows the concentration of these chemicals increasing with time in the top one inch layer of soil. The remaining pesticides are found, after one year, in the same layer where they were applied, although traces of these less mobile pesticides were occasionally found in samples above 12 inches, indicating some movement. The mobility of carbofuran and 2,4-D can be explained by their water solubilities, since they are the most water soluble of the compounds used. The highest concentrations of these chemicals are generally found in the top 1" of soil. Levels in the 1-6" and 6-12" layers are much lower indicating that the chemicals are being concentrated in the top 1" of soil, as was found in the U.C. field station beds. Table 1 shows the concentrations of carbofuran and 2,4-D in the 0-6" soil layer for the 54 week sample. Carbofuran and 2,4-D concentrations in the other sampling periods exhibit similar patterns.

After 54 weeks, the lowest concentrations of 2,4-D are found in the beds that have been treated with lime. As has been noted in other studies (Alexander 1977; Ou et al. 1978) breakdown of 2,4-D is stimulated by higher pH conditions. This may be because the calcium from the lime is displacing the 2,4-D from the soil surfaces making it more available for degradation. It may also be due to the higher pH supporting a different set of microorganisms.

Table 1. Concentrations of carbofuran and 2,4-D in the 0-6" layer of soil after 54 weeks.

	CARBOFURAN (ppm)		2,4-D (ppm)	
Bed	Aerobic	Anaerobic	Aerobic	Anaerobic
A	140.39	78.84	594.00	7.65
L	36.05	66.62	214.37	<0.10
N	115.00	83.52	296.39	<0.10
AO	136.08	298.30	275.85	656.17
LO	78.08	108.80	23.79	<0.10
NO	160.84	169.63	268.37	509.98
AZ	191.95	200.78	381.11	29.71
LZ	16.85	68.74	188.04	<0.10
NZ	95.51	110.97	328.4	<0.10
AOZ	123.89	186.38	323.36	98.76
LOZ	92.36	85.66	24.93	<0.10
NOZ	134.81	213.66	299.34	592.73

The pH range between 6.5 and 8.0 is optimum for bacteria and actinomycetes (Alexander 1977). The addition of added organic matter results in a decrease in 2,4-D concentration. This is most likely due to the organic matter promoting microbial degradation and not to pH differences, as the addition of organic matter lowers the pH.

With the exception of the acid treated beds, A and AZ, zinc appears to have little effect on the aerobic degradation of 2,4-D. The difference in the A and AZ beds may be due to zinc functioning as a reducing agent in an acidic environment as was found in the studies of Butler et. al. (1981a, 1981b), although no evidence of the dehalogenated metabolites were found in this study using GC/MS.

In comparing aerobic to cycling through aerobic and anaerobic conditions, the concentration of 2,4-D is lower in the cycled beds, with the exception of the organic amended acid and natural beds (AO, NO, NOZ). Degradation of 2,4-D has been found to be slower under anaerobic conditions (Sattar and Passivirta 1980). Under anaerobic conditions a different set of microorganisms is involved in 2,4-D degradation. The cycling through aerobic and anaerobic conditions appears to promote degradation of 2,4-D, with the exception of the beds previously mentioned. The Finnigan Model 700 Ion trap Detector was used to determine 2,4-D metabolites. 2,4-dichloro phenol was the only identified metabolite of 2,4-D. It was present in amounts less than 1% of 2,4-D concentration, there was no evidence of a mono-chlorinated or fully dechlorinated compound.

As expected for a carbamate insecticide, higher pH conditions resulted in significantly lower carbofuran concentrations, due to increased hydrolysis. This pattern holds for all sets of treatments. In general, added organic matter resulted in increased carbofuran concentration. This may be due to the slightly lower pH levels in these beds resulting in lower rates of hydrolysis. Zinc appears to have little effect on carbofuran degradation.

For carbofuran, similar patterns exist in the anaerobic beds for pH, organic matter and zinc treatments as in the aerobic beds. As for differences between aerobic and anaerobic conditions, no clear pattern emerges, although in general anaerobic concentrations tend to be higher than aerobic concentrations.

For the acid, lime, and lime organic treatments, the GC/MS was used to identify metabolites of carbofuran. Carbofuran phenol was present, there was no evidence of 3-hydroxy or 3-keto carbofuran. For the four sampling periods, the concentration of carbofuran in the 0-6" layer increased with time, while the concentration of the phenol reached a maximum in Week

16 and declined after that period. The relative amount of carbofuran phenol compared to the amount of carbofuran increased from 1% at Week 2, to 7% at Week 8, reached a maximum of 18% at Week 16, and declined to 5% by Week 54. Relative amounts of the phenol compared to carbofuran were nearly the same for all the treatments, and were not significantly higher for the beds with lime. Lichtenstein and Liang (1987) found that although carbofuran is readily hydrolyzed in the soil environment, intact carbofuran is the main product present, the metabolites are not readily detected in the organic extraction phase.

There was essentially no upward movement of the other chemicals from their point of application. Based on observations of the University Field Station evaporation beds this was an unexpected result (Winterlin et al. 1984). The reason for their lack of movement in this case is not certain. The organic carbon distribution coefficients, Koc, for the chemicals would indicate a strong tendency for adsorption to soil material, with the exception of carbofuran and 2,4-D, although there is a significant dependence upon site-specific soil and environmental conditions (Jury et al. 1987). In the case of the model and field station beds we are dealing with the upward movement of water and a mixture of chemicals in a soil matrix. The aqueous pesticide wastes consisted of mixtures of active ingredients and formulation materials. It is possible that the formulation materials acted as solvent modifiers as in HPLC. The greater amounts of materials in solution in these beds could also reduce the number of adsorptive sites in the soil, thus increasing the mobility of the pesticides. The most likely explanation is the condition and use of the U.C. field stations beds which were generally higher in pH, were more often saturated from use during application periods, and the fact that the pesticides were supplied to the beds in solution rather than applied to the soil, allowing for adsorption and later desorption to take place.

Although there was essentially no upward movement of the chemicals other than carbofuran and 2,4-D, there was degradation. By the 54 week sampling period, concentrations of the chemicals were reduced by substantial amounts in the majority of beds, as shown in Table 2. Rates of degradation varied widely among the beds. In general the limed beds showed the most degradation, but degradation was less in the limed beds that also contained zinc. Reasons for the wide variation in degradation are not clear as the pesticides did not come into contact with the treated layer of soil. A possible explanation may be that the water level varied from bed to bed. The layer of pesticides may have been submerged in some beds undergoing anaerobic degradation, while in other beds aerobic degradation may have been occurring.

This study showed that lime is effective in reducing carbofuran and 2,4-D concentrations in soils, and would be an effective single treatment.

Table 2. Percent degradation after 54 weeks. Refer to Figure 2 for an explanation of treatments.

Treatment	Diazinon	Ethyl Parathion	Propazine	Thiodan	Trifluralin
AEROBIC BEDS					
A	49.58	34.74	35.99	49.09	50.64
L	77.75	69.83	75.59	78.01	75.94
N	62.54	45.45	47.97	61.03	55.10
AO	72.19	63.20	64.46	71.18	64.97
LO	53.47	43.99	41.08	53.53	52.89
NO	66.45	57.77	63.47	65.30	63.92
AZ	62.58	49.21	58.01	60.67	52.81
LZ	48.76	40.44	37.11	50.93	42.87
NZ	65.62	44.23	61.90	56.22	46.16
AOZ	59.27	24.30	50.08	49.72	32.99
LOZ	48.99	27.12	55.30	51.41	40.42
NOZ	59.01	44.92	60.35	59.77	46.54
ANAEROBIC BEDS					
A	31.63	13.37	5.66	35.89	21.74
L	71.42	44.64	37.75	60.69	48.96
N	71.55	54.33	58.41	82.58	55.16
AO	72.35	48.40	53.89	65.22	53.75
LO	79.79	67.58	59.96	72.31	62.93
NO	47.95	30.98	31.44	50.97	37.47
AZ	46.75	18.60	17.28	36.20	29.51
LZ	50.94	29.73	34.37	44.77	38.01
NZ	64.85	27.60	64.28	43.91	35.86
AOZ	41.38	11.82	54.02	28.66	19.13
LOZ	75.19	45.45	75.12	60.90	54.20
NOZ	92.80	72.68	70.79	55.13	49.65

Incorporation of lime into existing contaminated soils could be easily accomplished. for 2,4-D the most effective treatment found in this study would be semi-anaerobic conditions. This type of treatment resulted in significant decreases in 2,4-D concentrations, to levels below the limits of detection within one year. To generate semi-anaerobic conditions at a spill site might not be easy to do, but could be done easily enough in large a batch process.

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