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A Field Study of the Chemical Degradation of Paraquat Dichloride Following Simulated Spillage on Soil

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Because of the irreversible effects that can result from the ingestion of the herbicide paraquat dichloride (1,1'-dimethyl 4,4'-bipyridinium dichloride), it is essential that any spills of this material should be immediately treated to decrease or eliminate the resulting potential toxic hazard. Spillages of concentrated pesticide may occur in many ways, but the most common result during the loading of spray equipment and during transportation and storage. These spillages often occur in driveways or at filling and storage sites, which can be near the homes of families in agricultural areas. Such spills are, therefore, a potential hazard to the health of small children, pets, and domesticated animals who come into contact with the highly contaminated soil. A study recently completed at this laboratory investigated the gastric availability of paraquat dichloride in soil by incubation of the soil with simulated human gastric juice (STAIFF et al. 1980). This study showed that for periods of up to one year there is a danger of exposure to relatively high levels of paraquat dichloride through the contaminated soil. Thus, it is imperative that this soil should be either dug up and removed or the toxic residue should be degraded by chemical treatment.

The purpose of this study was to evaluate degradative procedures that might prove useful for treatment of paraquat spills. The two chemical treatments tested were reduction and hydrolysis. Both reactions should result in the elimination of the possibility of cyclic reduction-oxidation with resultant generation of superoxide radicals, which has been proposed as the primary event responsible for the pulmonary fibrosis caused by paraquat (BUS et al. 1974). This pulmonary fibrosis can occur with oral or intravenous administration or local instillation of paraquat (KIMBROUGH and GAINES 1970).

The first reaction studied was degradation by chemical reduction. Reduction involves the formation of "dihydroparaquat" or more reduced forms, which has been reported to be an irreversible reaction (CALDERBANK 1968). Another author has indicated that paraquat must be reduced to at least the tetrahydroproduct before this process becomes irreversible (LEDWITH 1977). Complete reduction of paraquat to N,N'-dimethyl 1,1'2,2'3,3'6,6'-octahydro 4,4'-bipyridyl (DMOBP) by treatment with sodium borohydride is the basis for the gas chromatographic procedure for analysis of paraquat (UKAI et al. 1973). Reduction under experimental field conditions, of DDT (STAIFF et al. 1977) methyl

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parathion, and endrin and dieldrin, using acidified powdered zinc, has shown promise as an effective procedure for the chemically assisted degradation of unwanted pesticides.

The second reaction studied was degradation by alkaline hydrolysis. Paraquat is known to be unstable in solution above pH 12 (CALDERBANK 1968) and, therefore, should be degraded in soil by bases.

This present study explores several practical ways of rapidly degrading paraquat residues from simulated spills on soil using commercially available chemicals.

MATERIALS AND METHODS

Preparation of Simulated Spills and Chemical Treatment. Simulated spills were produced in an outside soil plot using a liquid paraquat concentrate containing 29.1% by weight of paraquat dichloride (240 g of cation per liter). A soil that is typical for our area of the Pacific Northwest was used. This soil was a sandy loam, approximately 6.0 to 10.2% clay, 26 to 29% silt, 60 to 67% sand, and 1.0 to 3.4% organic matter. The pH of the soil ranged from 6.6 to 7.8 with a mean of 7.2. The soil was filtered through a 0.5 cm^2 mesh screen to remove large stones, sticks, and other foreign material. The simulated spills were contained in unglazed clay pots, 13.5 cm in diameter and 12 cm deep. The hole in the center of the bottom of each pot was left open to provide drainage. These pots were buried nearly to their upper edge in the native soil of the plot. A soil volume of one liter, when tamped lightly and smoothed, filled each pot to within 1.5 to 2.0 cm of the top. Five soil-filled pots were prepared for each treatment as well as for a set of untreated paraquat controls.

Uniform, reproducible simulated "spills" were produced by adding 100 ml of paraquat dichloride concentrate to each soil-filled pot. This resulted in the formation of a pool of liquid over the entire soil surface of each pot. The pools of liquid were allowed to settle into the soil before any further experimental work was attempted. In all cases, the liquid was completely absorbed into the soil within one hour.

Two sets of simulated "spills" were treated with sodium borohydride. One of these sets was prepared by the addition of paraquat dichloride to sandy loam soil and the other set was prepared in the same manner, but using washed sand instead of soil. After the concentrated herbicide had soaked into the soil or sand, a solution containing approximately a 50% stoichiometric excess of sodium borohydride in water was added to the top of each clay pot. Due to vigorous foaming, it took approximately three hours to incorporate all of the sodium borohydride solution into a set of five pots containing the soil and paraquat dichloride. It took considerably less time with the clean washed sand and paraquat dichloride. The aqueous borohydride solution was added to the pots very slowly, with mixing, in five to ten ml increments. Foaming was allowed to subside between each addition of reactant.

A second reductive reaction was carried out using powdered zinc/acetic acid. Approximately a 75% stoichiometric excess of powdered zinc (57 g) was thoroughly mixed into the paraquat and soil mixture in each pot of the set, then 150 ml of 10% acetic acid was incorporated into the total mixture. Some bubbling occurred, but it was slow and not nearly as pronounced as with the sodium borohydride reduction.

Decontamination by alkaline hydrolysis involved the slow addition, with stirring, of 200 ml of 10% sodium hydroxide solution to a simulated paraquat spill contained in a clay pot. No bubbling was observed during this experiment.

Sampling and Analysis of Residues. Initial soil samples were obtained 24 hours after treatment. This period of time was necessary for the soil to become sufficiently dry for satisfactory sampling. A second sample was obtained four months later at the end of the summer. At each sampling time two soil samples were obtained from each pot. A clean cork borer was pressed 2.5 cm into the soil to obtain each sample. Both samples were air dried to a constant weight. One was extracted with slightly acidified water for spectrophotometric analysis of intact paraquat, and the other was extracted with ethyl acetate for gas chromatographic analysis of the volatile conversion products. The dried samples (each approximately 20 g) were shaken on a Burrell wrist action shaker for 20 minutes with 100 ml of appropriate solvent. The extracts were filtered and stored in amber bottles pending analysis. Ethyl acetate extracts were dried with anhydrous sodium sulfate by filtration through a layer of Na_2SO_4 and by addition of Na_2SO_4 to the filtrate prior to storage. Acidified water extracts were analyzed by appropriate dilution of a one ml portion with water, addition of alkaline dithionite solution, and determination of the optical density at 395 nm according to the Chevron Chemical Company (1973) procedure. A yellow color was obtained in the 4 month samples from the alkaline hydrolysis, which interfered with the spectrophotometric trace analysis for paraquat. A portion of these aqueous extracts was therefore treated with sodium borohydride so that any intact paraquat in the original extracts could be estimated gas chromatographically by the amount of DMOBP formed (UKAI et al. 1973).

Ethyl acetate extracts were analyzed for the paraquat reduction product DMOBP using a Tracor MT-220 gas chromatograph equipped with a flame ionization detector. A 1.83 m x 6.3 mm glass column packed with 5% KOH + 5% polyethylene glycol 6000 on 80/100 mesh Gas Chrom Z was employed and a 1.83 m x 6.3 mm glass column packed with 3% carbowax + 1% KOH on 80/800 mesh Chromosorb WHP was used for confirmation.

All of the appropriate controls and reagent blanks were analyzed to compensate for any background interferences.

RESULTS AND DISCUSSION

Results of treatments to chemically degrade simulated spillage of paraquat dichloride on soil are shown in Table 1. These data indicate the amount of paraquat residues remaining one day after treatment and after the "spills" had been exposed to weathering for four months. All treatments were effective in decreasing the paraquat content of the simulated spills on soil.

TABLE 1
Paraquat Dichloride Remaining in Soil After Treatment with Commercially Available Chemicals

Chemical Treatment	Paraquat Dichloride in Soil (ppm)[a]	
	Initial (1 day)	4 months
None	9,590 ± 1,140	6,300 ± 232
$NaBH_4$-Soil	nd[b]	nd
$NaBH_4$-Washed Sand	nd	nd
Powdered Zinc/Acetic Acid	58.5 ± 2.4	69.0 ± 7.8
Alkali (10% NaOH)	487 ± 28	nd[c]

[a] Mean ± standard error for 5 replicates.

[b] Below lower limit of sensitivity of methods.

[c] Yellow impurity interfered with spectrophotometric analysis. Lack of paraquat dichloride confirmed by gas chromatography of extracts reduced with sodium borohydride. Below lower limit of sensitivity of method.

Sodium borohydride treatment was especially effective in that all paraquat residues were degraded by the time the initial samples were taken. Vigorous foaming occurred when the borohydride solution was added to simulated spills in sandy loam soil. This prompted a test of the effect of borohydride solution on soil without any herbicide added. The resultant foaming was nearly as vigorous as with the simulated spills, indicating that much of the visible activity was due to reaction with soil constituents rather than with paraquat. A similar test of the effect of borohydride solution added to washed sand did not result in visible reaction, so spill treatment was repeated in a set of pots that contained paraquat dichloride on washed sand rather than on soil. Foaming was also noted during this treatment, but was due to reaction of borohydride with paraquat.

In order to verify that the major product formed by borohydride reduction of paraquat under the conditions employed was DMOBP and to follow the persistence of this product, extracts were analyzed by gas chromatography. The soil plots were found to initially contain a mean of 674 ppm of the completely reduced paraquat conversion product DMOBP. After four months these plots contained a mean of 354 ppm of DMOBP. The initial mean DMOBP content of the washed sand plots was 27.1 ppm. After four months no DMOBP could be detected in the washed sand. The rather low initial levels of DMOBP found in both soil and sand as compared to the amount of paraquat in untreated controls (mean of 9,590 ppm) was due to a combination of probable causes: The vigorous foaming carried quite a lot of the contaminated surface soil outside of the sampling area, and a considerable amount of the reduced product in the upper soil (or sand) must have been leached to below the 2.5 cm sampling depth as the reducing solution percolated down through the soil and sand.

As indicated in Table 1, treatment with powdered zinc/acetic acid was nearly as effective as borohydride treatment in reducing paraquat residues. At the initial sampling approximately 99% of the original paraquat had been degraded. No further degradation was apparent after four months.

Table 1 also indicates that essentially all the paraquat was degraded by alkaline hydrolysis within the first 24 hours after treatment and that no residue was detectable after four months.

All of the treatments described in this report could provide some hazard to the person performing the chemical degradation. Safe use of these and other chemicals requires a knowledge of their hazards and toxicity as well as handling procedures.

Although both reductive and alkaline hydrolytic treatments were effective in degrading paraquat spills on soil, we have limited information on the toxicity of the conversion products. The observed degradation of the bipyridinium cation may eliminate or greatly reduce the toxic potential of this herbicide to cause the irreversible pulmonary fibrosis that is associated with paraquat dichloride exposure. Confirmation that any of these treatments will completely eliminate the toxic hazard of paraquat dichloride spills will require further testing of the persistence and toxic nature of the reaction products.

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