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Gastric Availability of a Liquid Concentrate Formulation of Paraquat Dichloride Following Simulated Spillage on Soil

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Paraquat dichloride (1,1'-dimethyl 4,4'-bipyridinium dichloride) has been used extensively in the United States as a herbicide for several years. It is available primarily as a 29.1% liquid concentrate containing 240 g paraquat cation per liter (2 lb /gal).

Paraquat is a strong irritant which causes burning and ulceration of the mouth, esophagus and gastrointestinal tract as well as renal and hepatic damage. Also, if enough of this herbicide is ingested, delayed death can occur several weeks later due to progressive and irreversible pulmonary fibrosis resulting in respiratory failure (WIDDOP et al. 1977). Ingestion of relatively small amounts of this herbicide by humans has proved fatal with deaths reported for adults who ingested from 10 to 15 ml of the concentrate (WIDDOP et al. 1977, KIMBROUGH 1974, Nakamura et al. 1973). In reports concerning fatal poisonings of small children the specific amounts of paraquat ingestion were generally unknown, but have been estimated to have been as low as 4 mg/kg body weight (ALMOG and TAL 1967).

Whenever herbicides are added to spray machines there is a potential danger of spillage of the concentrate formulation onto the ground. Spillages could also occur during transport or storage as a result of leakage from ruptured containers. Farm fill sites, as well as storage and handling areas, are often located in the vicinity of dwellings. Thus, spillages may present a special hazard for small children, pets, and farm animals that come into contact with soil heavily contaminated with the concentrate formulation. While there have been no reports of small children becoming ill from eating paraquat-contaminated soil, there has been a report of a child becoming seriously ill by ingesting soil contaminated with the insecticide parathion (QUINBY and CLAPPISON 1961). A case has been reported of a paraquat dichloride poisoning in a dog (fatal) and cat (nonfatal) after they ate contaminated grass (JOHNSON and HUXTABLE 1976). These cases point out the potential hazard of spillage of toxic chemicals.

The present study was undertaken to determine the gastric availability of paraquat dichloride in soil by incubation of the soil with simulated human gastric juice. Four different soil

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types were contaminated by simulated spills of a liquid concentrate formulation of paraquat dichloride and the gastric availability studied as a function of time after the spills. The resulting data was to be used to determine the toxic potential of spills of concentrated paraquat dichloride to humans; with special consideration given to small children who may ingest contaminated soil.

MATERIALS AND METHODS

Simulated spillage treatments were made in field soil plots using 29.1% paraquat dichloride liquid concentrate. In order to include the most likely soils that might be encountered, four types were chosen. These soils were given code names WEN-A, WEN-B, WEN-C, and WEN-D. An assay of these soils is given in Table 1.

TABLE 1
Assay[a] of Four Soil Types Used in Paraquat Gastric Availability Study

Type of Assay	Soil Type by Code			
	WEN-A	WEN-B	WEN-C	WEN-D
pH	7.5	6.0	9.1	8.1
% Organic Matter	1.2	1.5	0.3	0.8
Exchange Cations (meq/100 g)				
Na	0.09	0.04	4.60	0.72
K	0.47	0.77	0.31	0.68
Ca	10.30	6.25	32.00	42.50
Mg	0.92	1.38	7.10	7.60
Sum of exc. cats.	11.78	8.44	44.01	51.50
Cation Exchange Capacity	7.61	11.74	13.70	4.0
% Base Saturation	100+	71.9	100+	100+
Mechanical Analysis (%)				
Sand	76.7	60.6	45.2	7.2
Coarse Silt	16.8	28.6	46.0	18.0
Fine Silt	1.0	1.6	3.0	9.6
Clay	5.5	9.2	5.8	65.2
U.S. Text. Class.	Loamy Sand	Sandy Loam	Sandy Loam	Clay

[a]Soil Assayed by Soil Testing Lab., Washington State University, Pullman, Washington 99163

Each of these soils was sifted through 6 mm^2 wire mesh screen to obtain uniform consistency. The high clay soil (WEN-D) had to be broken up before it could be sifted through the wire mesh screen. Special metal frames 30 cm x 30 cm x 15 cm deep were placed in holes dug to accommodate them and the sifted soils added. The surface was then smoothed and tamped firmly to provide a level area on which to pour the herbicide. A volume of 1 liter of paraquat dichloride concentrate was poured onto a small metal plate held on top of the soil surface to prevent splashing and to minimize disruption of the surface. A pool approximately 1 cm deep was formed before the liquid soaked into the soil.

Samples were taken at 1 day (drying time), 1 month, 4 months, 6 months, 1 yr, 1-1/2 yrs, and 2 yrs. Cork borers were used to obtain soil samples to a depth of 2.5 cm. A single sample consisted of two cork borers of soil from each frame. There were 5 replicates of each soil type. The borers were thoroughly cleaned after sampling from each frame. At the 2-yr period one frame of each soil type was sacrificed and the paraquat contaminated soil was sampled in sequential 2.5 cm levels, as each layer was removed down to 15 cm. This was done in order to assess leaching of the unbound paraquat dichloride. Because of very arid conditions, it was necessary to moisten the soil plots one day before sampling in order to obtain suitable samples. Likewise, the plots were moistened several times during the course of this experiment to facilitate sampling for other projects in nearby areas.

The experimental plots were subjected to the natural elements such as rainfall (average approximately 25 cm per year), sunlight (over 275 days per year) and relatively high maximum temperatures of over 32°C for an average of 31 days each summer. The average winter temperature was near 0°C and the soil plots were covered with snow for an average of 2 months each winter.

The collected samples of soil were air dried to a constant weight in the laboratory. These samples of paraquat dichloride contaminated soil were added to 250 ml erlenmeyer flasks containing 100 ml of simulated human gastric juice. The composition of the simulated gastric juice is shown in Table 2.

The flasks were stoppered, swirled gently, vented, and then incubated in a Dubnoff metabolic shaker at 37°C for 20 minutes. The time of 20 minutes was chosen for incubation of the paraquat dichloride contaminated soil because it has been suggested by DECKER et al. (1968) to represent a simulated elapsed time from accidental ingestion of toxicant until definitive treatment such as gastric lavage accompanied by supportive therapy could be administered at a hospital or clinc. The shaker speed was set to provide a very gentle motion. Midway during the incubation the shaker was shut off, each flask was removed and swirled gently, and was replaced on the shaker for the duration of the period. At the end of this time, the incubation solutions were analyzed according to the Chevron Chemical Company (1973) procedure. One ml of the resulting solution was diluted with distilled water, alkaline dithionite was added, and the optical density at 395 nm was determined. Appropriate controls and reagent blanks were also analyzed to compensate for background interferences.

TABLE 2

Composition of the Simulated Gastric Juice[a] Used in Gastric Availability Experiment

Ionic Component	mEq/liter
Cl^-	182
H^+	163
K^+	11.2
Na^+	4.5
NH_4^+	1.5
Ca^{++}	0.3
Gastric mucin, 0.4% by weight	
pH 1.5	

[a]According to GUDIKSEN (1943)

RESULTS AND DISCUSSION

Paraquat dichloride is strongly adsorbed on soil. In order to quantitatively liberate this herbicide from all types of soil (especially those with high clay content) samples must be refluxed for 5 hours with 18 N H_2SO_4 (RILEY et al. 1976). Paraquat dichloride residues that are strongly bound on soil, therefore, would not be available for absorption in the gastrointestinal tract if soil containing this type of bound paraquat dichloride were ingested. We were not concerned with strongly bound paraquat dichloride in this experiment. Immediate inactivation (binding) of paraquat dichloride by soil depends upon the presence of sufficient strong adsorption sites on the soil itself (WATKIN and SAGAR 1971). If these adsorption sites are saturated, as would be the case when spillages of the herbicide concentrate occur, there would be considerable available (unbound and weakly bound) paraquat dichloride which could be extremely hazardous. In this experiment we were concerned with the available paraquat dichloride because it is this form that may present a danger to anyone who comes into contact with contaminated soil. Eventually with time and weathering, much of the available paraquat dichloride will become strongly bound and will not present the extreme danger that it does initially.

As can be seen in Table 3, the amount of available paraquat dichloride was initially quite high, ranging from 16,900 ppm in the sandy soil to 23,600 ppm in the soil with the high clay content. After 2 years the amount of available paraquat dichloride ranged from 410 ppm in the sandy soil to 1,250 ppm in the high clay soil. It is also evident in this Table that the amount of paraquat dichloride available after incubation with simulated human gastric juice, and presumably after ingestion of contaminated soil, was related to the clay content of the soil through the 12-month sampling period. CALDERBANK and TOMLINSON (1968) stated that strong adsorption of paraquat dichloride on soils is also primarily a property of clay minerals rather than soil organic matter. By the 24-month sampling period the amount of available paraquat dichloride was more closely related to the sum of the exchange cations in the soil than the clay content.

TABLE 3

Paraquat Gastric Availability in Four Types of Soil

Soil[a]	% Clay	Sum of Exch. Cats	Paraquat Dichloride (ppm)[b] at Various Times (months) after Application					
			0[c]	1	4	6	12	24
WEN-A	5.5	11.78	16,900 ± 550	9,300 ± 270	3,200 ± 480	2,200 ± 420	975 ± 75	409 ± 36
WEN-B	9.2	8.44	21,000 ± 1,300	15,000 ± 810	7,800 ± 220	4,600 ± 430	1,335 ± 38	448 ± 31
WEN-C	5.8	44.01	19,700 ± 2,500	9,750 ± 860	5,100 ± 600	3,600 ± 510	1,020 ± 100	765 ± 37
WEN-D	65.2	51.50	23,600 ± 450	22,700 ± 1,100	16,400 ± 1,500	5,800 ± 800	1,990 ± 53	1,250 ± 32

[a]See description of soil types in Table 1.
[b]Mean ± standard error for 5 replicates.
[c]Initial sampling 1 day after treatment.

Even though in this experiment we were interested primarily in the available paraquat dichloride in the soil surface layer (0-2.5 cm), a frame of each type of the 4 soils used was sacrificed after two years to ascertain available paraquat dichloride residues at different depths by 2.5 cm increments down to 15 cm. As can be seen in Table 4, paraquat dichloride was found in WEN-A and WEN-B soils at all sampling depths; whereas, with the WEN-C and WEN-D soils no paraquat dichloride was available below the 12.5 cm depth. Soil at the lowest two sampling levels for all 4 of these soil frames consisted primarily of the WEN-B type, the soil naturally occurring in the experimental plot area. There was some mixing of the two respective soil types at the 10-12.5 cm level, but in all cases the 12.5-15 cm sampling level was pure WEN-B soil.

TABLE 4

Location of Leached Paraquat Dichloride After 2 Years

Soil Depth (cm)	Unbound Paraquat Remaining in Various Soil Types[a] (ppm)			
	WEN-A[b]	WEN-B	WEN-C	WEN-D
0 - 2.5	409 ± 36	448 ± 31	765 ± 37	1,250 ± 32
2.5 - 5	657 ± 83	969 ± 57	883 ± 24	775 ± 159
5 - 7.5	604 ± 76	749 ± 89	815 ± 24	894 ± 40
7.5 - 10	648 ± 52	774 ± 135	795 ± 12	840 ± 13
10 - 12.5[c]	889 ± 8	713 ± 188	280 ± 280	204 ± 204
12.5 - 15[c]	614 ± 97	512 ± 17	0 ± 0	0 ± 0

[a]Mean ± standard error. 5 replicates for the 0-2.5 layer and 2 replicates for all other depths.
[b]See description of soil types in Table 1.
[c]The soil frames did not extend below 10 cm, the soil from 10-15 cm was native sandy loam (WEN-B).

The value of determining the available paraquat dichloride residues by the "gastric availability" method lies in the ability to directly determine the toxic potential of spillage of paraquat dichloride concentrate and to relate it to the hazard if soil contaminated with this material was ingested by children (especially small children), pets, or farm animals. Ascertaining paraquat dichloride residues by the gastric availability method also demonstrated the persistence of unbound herbicide in 4 types of soil common to this North Central Washington area, as well as the leaching behavior after 2 years in these soil types.

This experiment allows estimation of the actual amount of paraquat dichloride that would be present in the gastrointestinal tract if soil contaminated with this herbicide were ingested. If a small child weighing ~20 kg (~45 lb) ingested 80 mg of paraquat dichloride, this could be fatal, assuming 4 mg/kg as the minimum lethal dose. This amount of paraquat dichloride could be obtained by ingesting from 3.4 to 4.7 g of soil shortly after spillage of the herbicide concentrate as described in this experiment. With time, increasingly larger amounts of contaminated soil would be required to obtain a fatal dose (40 g of the high clay content soil at 12 months). The danger becomes significantly decreased after 1 year.

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