

# Adsorption of Bipyridylum Herbicides in Soil

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An experimental procedure has been developed that defines two degrees of 1,1'-dimethyl-4,4'-bipyridylum ion (paraquat) and 6,7-dihydrodipyrido(1,2-*a*:2',1'-*c*)pyrazidiinium ion (diquat) bonding in soil. At low concentrations, paraquat or diquat desorption requires refluxing with 18*N* sulfuric acid. As the concentration in soil increases, a portion of the paraquat or diquat can be desorbed by leaching with saturated ammonium chloride. At

high levels, some of the paraquat or diquat is unbound and can be leached with water. A particular soil has a definite capacity for each of the two types of adsorbed paraquat or diquat, and the capacities vary greatly with soil type. The data for paraquat adsorption on loam, sandy loam, sand, silt loam, and muck soils and diquat adsorption on sandy loam are given to illustrate the different degrees of bonding in the soil.

**P**araquat (1,1'-dimethyl-4,4'-bipyridylum ion) and diquat [6,7-dihydrodipyrido(1,2-*a*:2',1'-*c*)pyrazidiinium ion] are new herbicides and desiccants. These two herbicides have been studied extensively for weed control, for sod destruction prior to reseeding in lieu of mechanical cultivation, and for desiccation prior to harvest. Two characteristics of paraquat and diquat are their deactivation by adsorption on soil and their stability in soil.

Since paraquat and diquat are stable in soil, the ease with which they can be removed from soil is an important factor in their use for chemical seedbed preparation and weed control. If they are readily removed from soil aggregates, they could be available to the existing crop as well as to future crops. Coates *et al.* (1964, 1966) report that ammonium ion can replace paraquat and diquat to a certain degree in soil. In working with trace levels of paraquat and diquat in soil, the authors found that the complete recovery of paraquat and diquat from soil requires refluxing with 18*N* sulfuric acid for 5 hours.

An investigation was initiated to clarify the ease of removing paraquat and diquat from soil. In the process of this work, an experimental procedure has been developed that chemically defines two degrees of paraquat and diquat bonding in soil. The two types of bonding have been arbitrarily defined and do not necessarily indicate the only forms possible in soil. The technique described enables comparisons of paraquat or diquat adsorption characteristics in different soils. The acceptance and use of a standard procedure to characterize paraquat and diquat adsorption on soil would enable standardization of terminology and data concerning paraquat or diquat phytotoxicity in different soil types.

The two types of bonding in soil have been arbitrarily defined as "loosely" bound and "tightly" bound. Paraquat or diquat that can be leached from soil with water is defined as "unbound." The soil is fortified with an aqueous paraquat or diquat solution and then analyzed to determine the capacities for the different types of bound paraquat or diquat. Unbound paraquat or diquat is leached from soil with water, loosely bound paraquat or

diquat is desorbed by leaching with saturated ammonium chloride, and tightly bound paraquat or diquat is removed only by refluxing with sulfuric acid.

## EXPERIMENTAL

**Apparatus and Reagents.** A Beckman DB spectrophotometer was used to obtain all absorbance readings. Both 1- and 4-cm. cells were used. The filter funnels were the Büchner type with a 30-ml. capacity and a fritted disk of medium porosity.

All chemicals were of reagent grade quality. Paraquat dichloride and diquat dibromide were obtained from Imperial Chemical Industries, Agricultural Division, Jealott's Hill Research Station, Bracknell, Berkshire, England. Dowex AG 50W X-8, 100- to 200-mesh, cation exchange resin in the hydrogen form was supplied by Bio-Rad Laboratories, Richmond, Calif.

The sodium dithionite solution, 0.2% in 0.3*N* NaOH, is unstable and was not kept longer than 1.5 hours. Since paraquat and diquat solutions are somewhat light sensitive, the solutions were stored in dark bottles.

**Procedure.** Soil samples were fortified by passing 100 ml. of several concentrations of aqueous paraquat or diquat solution through 10 grams of soil in a fritted glass, Büchner type filter funnel. The mixture was stirred well and the flow rate did not exceed 4 drops per minute. After the aqueous paraquat or diquat solution had passed through the soil, the treated soil was further washed with water until a drop of the filtrate gave a negative test for paraquat or diquat with sodium dithionite.

Saturated ammonium chloride solution was filtered through the treated soil until a drop of the filtrate gave a negative test for paraquat or diquat with sodium dithionite. The mixture was stirred to obtain good contact between soil and solution.

The soil samples were quantitatively transferred from the filter funnel to a 500-ml. boiling flask, mixed with 100 ml. of 18*N* sulfuric acid, and refluxed for 5 hours. (The solution could be left overnight at this point.) The sulfuric acid extraction procedure is a modification of the method described by Calderbank and Yuen (1965) for determining paraquat in crops.

The sulfuric acid extract was filtered through glass fiber filter paper, diluted to 1800 ml. with water, and percolated

through a cation exchange resin at a flow rate of 8 ml. per minute. The cation exchange column consisted of 10 ml. of settled resin in a 50-ml. buret, which had been rinsed with 50 ml. of saturated sodium chloride followed by 50 ml. of water. After the extract had passed through the column, the column was rinsed successively with 50 ml. of water, 50 ml. of 2*N* hydrochloric acid, 50 ml. of water, and 50 ml. of 0.1-saturated ammonium chloride. (The process could be left overnight after the second 50-ml. water rinse.) Paraquat or diquat was eluted with saturated ammonium chloride at a flow rate of approximately 10 drops per minute until the eluate gave a negative test for paraquat or diquat with sodium dithionite.

The aqueous filtrate, the saturated ammonium chloride filtrate, and the column eluate were adjusted to known volumes. A 10-ml. aliquot of the test solution was mixed with 2 ml. of sodium dithionite, 0.2% in 0.3*N* sodium hydroxide, and the absorbance was immediately read at the maximum and 4 *mμ* on each side of the maximum. The aqueous solutions were read at 388, 392, and 396 *mμ* for paraquat and at 373, 377, and 381 *mμ* for diquat. The saturated ammonium chloride solutions were read at 390, 394, and 398 *mμ* for paraquat and 374, 378, and 382 *mμ* for diquat. The absorbances of standard solutions were read at three wavelengths with each set of determinations. Standard solutions of 2.0 or 0.5 *μg.* per ml. of paraquat and 4.0 or 1.0 *μg.* per ml. of diquat were used depending upon the cell path length.

The absorbance of the sample was corrected at the maximum ( $A_m$ ) for background adsorption with the equation:

$$A_{\text{corr}} = \frac{A_m^s}{2A_m^s - (A_h^s + A_l^s)} [2A_m - (A_h + A_l)]$$

where:  $A_m$  = observed absorbance of sample at wavelength of maximum absorbance ( $\lambda_m$ );  $A_l$  = observed absorbance of sample at 4 *mμ* lower than  $\lambda_m$  ( $\lambda_l$ );  $A_h$  = observed absorbance of sample at 4 *mμ* higher than  $\lambda_m$  ( $\lambda_h$ );  $A_m^s$  = absorbance of standard at  $\lambda_m$ ;  $A_l^s$  = absorbance of standard at  $\lambda_l$ ;  $A_h^s$  = absorbance of standard at  $\lambda_h$ . This method for background absorbance correction is based on a method described by Morton and Stubbs (1946).

After obtaining the corrected absorbance of the sample, a simple ratio utilizing Beer's law was used to calculate the paraquat or diquat concentration in the sample. All calculations are based on a dry soil weight basis.

The soil types were classified according to the definitions of the United States Department of Agriculture (Shaw, 1952). Particle distribution was mechanically determined using the pipet method. The organic content and pH of the soils were determined using methods described by Bear (1955). Total cation exchange capacities were determined as the ammonium ion capacity of the soils (Piper, 1944).

## RESULTS AND DISCUSSION

Soils are complex systems containing components of varying chemical and physical properties. Bailey and White (1964) point out in their review article that while the adsorption phenomena observed in soils may be a gross

**Table I. Paraquat Adsorption on Soil**  
Mg. Paraquat/G. Dry Soil<sup>a</sup>

Soil	Mg. Paraquat/G. Dry Soil <sup>a</sup>			
	Initial treatment	"Unbound," eluted with water	"Loosely" bound, eluted with saturated ammonium chloride	"Tightly" bound, extracted by refluxing with 18 <i>N</i> sulfuric acid
Loam	1.18	0.014	0.000	1.14
	5.84	0.063	0.899	4.33
	11.8	0.388	7.16	4.96
	23.4	0.276	10.9	4.98
	58.4	18.2	18.4	4.96
	118	64.8	19.8	4.94
Muck	0.057	0.000	0.040	0.013
	0.573	0.000	0.495	0.028
	1.15	0.000	1.04	0.040
	5.73	0.184	5.29	0.064
	11.5	2.27	8.22	0.077
Sand	0.052	0.000	0.048	0.005
	0.104	0.000	0.104	0.005
	1.04	0.645	0.407	0.010
	5.19	4.70	0.502	0.017
	10.4	9.90	0.572	0.021
Silt loam	0.105	0.000	0.036	0.007
	0.526	0.000	0.449	0.009
	1.05	0.000	0.855	0.039
	5.26	0.263	4.45	0.095
	10.5	5.92	5.96	0.139

<sup>a</sup> One milligram of paraquat/g. of soil is equivalent to approximately 2000 pounds of paraquat/6-inch (depth) acre for the loam, sand, and silt loam or 500 pounds of paraquat/6-inch acre for the muck.

**Table II. Paraquat and Diquat Adsorption on Sandy Loam**  
Mg. Paraquat and Diquat/G. Dry Soil

Sample	Mg. Paraquat and Diquat/G. Dry Soil			
	Initial treatment	"Unbound," eluted with water	"Loosely" bound, eluted with saturated ammonium chloride	"Tightly" bound, extracted by refluxing with 18 <i>N</i> sulfuric acid
Paraquat	0.054	0.000	0.015	0.039
	0.108	0.000	0.074	0.039
	0.539	0.000	0.505	0.054
	1.08	0.028	1.03	0.056
	10.8	10.6	1.19	0.059
Diquat	0.052	0.000	0.033	0.018
	0.105	0.000	0.080	0.023
	0.523	0.000	0.490	0.027
	1.05	0.032	0.963	0.036
	10.5	8.54	1.22	0.034

effect, the factors responsible for adsorption may be collective in nature. A herbicide would be exposed to attractive influences of varying magnitudes in soil and would be bound to the soil aggregates in varying strengths. Therefore, the quantity of adsorbed herbicide removed from soil would be dependent upon the desorbing strength of

**Table III. Chemical and Mechanical Analysis of Soils**

Soil Origin	Clay, %	Silt, %	Sand, %	Soil Type	Organic Matter, %	pH	Total Cation Exchange Capacity, Meq./100 G. Soil
California	16	37	47	Loam	1.3	6.4	33.1
Florida	...	...	...	Muck	Approx. 100	3.3	112.7
Florida	1	2	97	Sand	0.5	7.0	1.4
Alabama	9	26	65	Sandy loam	1.8	4.7	3.0
Hawaii	26	71	4	Silt loam	3.8	7.7	16.2

the leaching agent used. The use of water, saturated ammonium chloride, and refluxing sulfuric acid as desorbing agents in this work was an arbitrary choice. The defined loosely and tightly bound categories probably contain a broad spectrum of differing adsorption strengths that could be differentiated by using desorbing agents of varying strengths. However, the purpose of this work was to develop a procedure that could be used to compare soils and their affinity for paraquat or diquat and not to determine the total number of possible types of paraquat or diquat adsorption in soil.

Paraquat adsorption data obtained for loam, muck, sand, and silt loam are given in Table I. Table II compares paraquat and diquat adsorption on a sandy loam. Tables I and II give the quantity of paraquat or diquat per gram of dry soil in the initial aqueous solution used to fortify the soil; the quantity unadsorbed and removed with water (unbound); the quantity eluted with saturated ammonium chloride (loosely bound); and that remaining for extraction by refluxing with sulfuric acid (tightly bound). Table III shows the composition, pH, and the total cation exchange capacity of the different soils.

The similar adsorption characteristics of diquat and paraquat in soil are illustrated in Table II. The quantities of unbound, loosely bound, and tightly bound diquat and paraquat at any given level of treatment were almost identical. Therefore, a description of the soil bonding characteristics of one chemical applies equally well to the other. The following discussion is concerned specifically with paraquat; however, the remarks would also be pertinent to diquat.

A marked difference in the quantity of paraquat adsorbed among different soil types was observed. The tightly bound paraquat capacity was less than the loosely bound capacity in all of the soils studied. However, the ratio of loosely to tightly bound paraquat adsorption capacities varies greatly among soil types, being approximately 4, 27, and 107 for loam, sand, and muck, respectively. The value of the ratio for muck is a low estimate since the loosely bound capacity had not been reached at the highest fortification level studied.

Since the loosely bound paraquat can be leached from soil with a concentrated salt solution, while the tightly bound paraquat can be removed from soil only after the soil structure is destroyed by refluxing with sulfuric acid, the two types of adsorption differ greatly. The loosely bound paraquat is desorbed or displaced by ammonium ions and could be considered analogous to an ion ex-

change process. However, the tightly bound paraquat is removed only by destroying the soil structure indicating a dependence on the rigidity and spatial dimensions of the pore structure of the soil—that is, the tightly bound paraquat becomes trapped in the lattice structure of the soil particles. Weber *et al.* (1965) have shown by x-ray analysis that diquat and paraquat are held in the lattice of montmorillonite with the plane of the ring parallel to the silicate sheet. Knight (1966) has also done x-ray crystallography of clay fractions containing adsorbed paraquat.

The sum of the loosely and tightly bound paraquat capacities for the loam, sandy loam, and sandy soils is only a fraction of the total cation exchange capacity. The paraquat adsorption capacity was approximately 10 to 30% of the total cation exchange capacity. (This value was determined using 186/2 as the equivalent weight of the doubly charged paraquat.) However, the total cation exchange capacity of a soil is determined as the quantity of ammonium ions that a soil will exchange, and the small size of the ammonium ion would allow it to fill positions that paraquat could not. Other factors could also be contributing to the lower paraquat adsorption capacities. Nevertheless, the total cation exchange capacity of soils is useful in approximating paraquat adsorption capacities. A soil with a high cation exchange capacity will, in general, have a higher paraquat adsorption capacity than a soil with a low cation exchange capacity.

The per cent of clay in a soil can often be used as an indication of its affinity for paraquat. However, clays differ greatly in structure, and false conclusions can be obtained by making comparisons based entirely on clay content. An example of this is the silt loam that has the highest clay content of the soils studied but certainly does not have the highest paraquat adsorption capacity. The silt loam from Hawaii, a volcanic soil, no doubt has a unique crystalline structure not found in common agricultural soils. In general, sandy soils will have a low affinity for paraquat, while soils with a high clay content will have a high affinity for paraquat. This generalization should be used cautiously, but it is useful for an initial estimation.

The muck being composed of practically all organic matter is a unique soil to be considered separately. Its tightly bound capacity is not exceptionally high, but its loosely bound capacity is still steadily increasing at 8000 p.p.m. of paraquat. The high total cation exchange capacity of the muck soil parallels its high loosely bound paraquat capacity. High cation exchange capacities are

characteristic of organic soils, indicating they would also have high loosely bound paraquat capacities. The paraquat adsorption processes in the muck soil would probably differ somewhat from those in an inorganic soil, the latter being comprised of rigid crystalline lattice structures that the muck soil does not possess.

The experimental procedure described involves a limitation of fortifying soils with trace amounts of paraquat or diquat. The fritted glass disk adsorbs paraquat or diquat from aqueous solution but not from saturated ammonium chloride solution. This property does not affect the value for the sulfuric acid reflux, but the saturated ammonium chloride leachate value includes traces of paraquat or diquat adsorbed on the fritted glass plus paraquat or diquat adsorbed on the soil. The water leachate value will be low by the amount of paraquat or diquat adsorbed by the glass frit. Filters chosen randomly adsorbed between 40 to 90  $\mu\text{g}$ . of paraquat. Using 10 grams of soil, this would be equivalent to 4 to 9 p.p.m. of paraquat.

Procuring data at high levels of paraquat or diquat can be time consuming. In practice, several points at low or intermediate levels of paraquat or diquat would be sufficient to characterize and compare soils. However, in order to determine adsorption capacities, the higher levels would have to be studied.

A test has been completed to correlate bioactivity with the different types of paraquat bonding in soil. The results of this test will be published elsewhere in the near future.

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