Displacement of Diquat from Clay and Its Phytotoxicity

J. B. Weber, S. B. Weed, and J. A. Best

Montmorillonite clay was previously shown to adsorb organic cationic herbicides, making them unavailable to plants and microbes. These studies confirm the previous findings and the addition of *N*-(4-pyridyl)pyridinium chloride, a nonphytotoxic organic cation, is shown to be effective in desorbing the cationic herbicide diquat from montmorillonite for absorption by cucumber seedlings.

Adsorption-desorption studies (Weber *et al.*, 1965; Weber and Weed, 1968) indicated that two organic herbicides, diquat [6,7-dihydrodipyrido-(1,2-*a*:2′,1′-*c*)-pyrazidiinium dibromide] and paraquat (1,1′-dimethyl-4,4′-bipyridinium dichloride) were adsorbed in the interlayer spacings of montmorillonite clay minerals and that only very small amounts were displaced by inorganic cations such as Ba^{2+} and Al^{3+}. Large amounts of the herbicides could be displaced by the use of organic cations of similar size and charge density. Studies with plants (Scott and Weber, 1967; Weber and Scott, 1966) and microorganisms (Weber and Coble, 1968) indicated that when the two herbicides were adsorbed on montmorillonite clay they were not biologically available. Because of unavailability of the bound herbicides, the authors sought to determine if relatively nonphytotoxic organic cations would be effective in releasing the herbicides to actively growing plants, and to study organic cationic exchange involving plants and clay minerals.

PROCEDURE

Preliminary experiments were performed in screening an assortment of organic cations which would displace diquat from montmorillonite clay and yet not be phytotoxic to the indicator plant. The compound *N*-(4-pyridyl)-pyridinium chloride (hereafter referred to as PPCl) was effective in displacing diquat from montmorillonite and was not toxic to cucumber seedlings when 80 μmoles per pot (320 grams of quartz sand) or less were added to the growth medium.

Montmorillonite clay was Na-saturated with NaCl, washed free of chlorides, freeze-dried, and stored in sealed containers (Weber *et al.*, 1965). Samples of 100 mg. of clay were placed in 50-ml. centrifuge tubes. Diquat was added at rates of 0, 10, 20, and 30 μmoles per tube. The tubes were shaken for 1 hour, after which the clay was removed by centrifugation and the amount of diquat remaining in solution was determined spectrophotometrically. The diquat was totally adsorbed by the clay. The clay-diquat samples were resuspended, transferred to Styrofoam pots, and thoroughly mixed with 320 grams of quartz sand. Six cucumber seedlings, later thinned to four, were transplanted into the sand-clay medium. The pots were watered daily with 2X Hoagland's solution (Bonner and Galston, 1955) to a total weight of 400 grams. At 4 days, when the plants were approximately 1 inch tall, PPCl was added at rates of 0, 20, 40, and 80 μmoles per pot from a stock solution of 4 μmoles per ml. Diquat was also added to pots containing sand only (no clay) at rates of 0, 0.4, 0.8, 1.6, and 3.2 μmoles per pot to establish a standard growth-inhibition curve. Samples were also prepared containing clay or PPCl and sand only to determine the effects of these materials alone on plant growth. Three replications were employed. The pots were randomly placed in a growth chamber which was programmed as follows: diurnal temperature as described by a sine curve with a maximum of 30°C. and a minimum of 15° C., diurnal relative humidity inverse to the temperature with a maximum of 75% and a minimum of 50%, light intensity of 16,000 lumens per square meter, and day length of 12 hours. The plants were cut at soil level at 14 days. Plant height and fresh and dry weight were measured. Fresh weights were the most sensitive indicator of plant response to the herbicide and are the only data presented here.

Departments of Crop Science and Soil Science, North Carolina State University, Raleigh, N. C. 27607.

RESULTS AND DISCUSSION

The PPCl was effective in releasing diquat from the montmorillonite clay (Table I). Samples 1 through 5 show the standard growth-inhibition curve established using diquat alone. Sample 6 indicates that the 80 μmoles per pot rate of PPCl inhibited plant growth approximately 8%, but because of the cationic nature of PPCl the inhibition was reduced to zero in pots containing the clay mineral (see sample 23). Samples 7 through 10 show that PPCl, employed at the highest rate (80 μmoles per pot), significantly increased the phytotoxicity of diquat to the cucumber seedlings. Lower rates of PPCl did not have a significant effect. Samples 11 through 14 show that the 100 mg. of montmorillonite clay retained diquat in a form which was unavailable to the cucumber plants, even at herbicide rates 10 times greater than those necessary to inhibit plant growth completely. This confirms previous studies (Scott and Weber, 1967; Weber and Scott, 1966).

The relatively nonphytotoxic PPCl was very effective in displacing diquat from the montmorillonite clay, as shown in samples 15 through 26 (Table I). Each additional increment

Table I. Effect of PPCl on Releasing Diquat from Montmorillonite Clay

Sample No.	Diquat Added, μmoles	PPCl Added, μmoles	Clay Added, Mg.	Fresh Weight of Plant Shoots, Mg.	Plant Growth Inhibition,[a] %
1	0	0	0	11.8	..
2	0.4	0	0	10.8	9
3	0.8	0	0	9.8	18
4	1.6	0	0	5.1	57
5	3.2	0	0	0.9	92
6	0	80	0	10.9	8
7	0.4	80	0	9.5	13
8	0.8	80	0	6.3	43
9	1.6	80	0	2.7	75
10	3.2	80	0	0.5	95
11	0	0	100	12.0	..
12	10.0	0	100	11.2	7
13	20.0	0	100	12.0	0
14	30.0	0	100	11.4	5
15	0	20	100	12.1	..
16	10.0	20	100	12.0	0
17	20.0	20	100	11.5	5
18	30.0	20	100	7.3	40
19	0	40	100	11.8	0
20	10.0	40	100	8.6	27
21	20.0	40	100	6.1	48
22	30.0	40	100	3.8	68
23	0	80	100	11.5	0
24	10.0	80	100	5.7	50
25	20.0	80	100	3.6	69
26	30.0	80	100	1.5	87
Standard error				0.6	5

[a] Percentage inhibition with respect to comparable untreated plant.

of diquat released to the solution was readily absorbed by the plant roots, as shown by increased inhibition with increasing rates of PPCl added. No plant inhibition resulted in pots 15 through 17, because the 100 mg. of clay used had a cation-exchange capacity of 85 μeq. and all of the diquat and PPCl were adsorbed—i.e., sample 17 contained 20 μmoles (40 μeq.) of diquat and 20 μmoles (20 μeq.) of PPCl for a total of 60 μeq. The low rate of PPCl released diquat from sample 18 only, the highest rate of diquat adsorbed. Even though only a total of 80 μeq. of diquat and PPCl was added to the clay, with a cation-exchange capacity of 85 μeq., sufficient diquat was replaced to give 40% inhibition of plant growth. This suggests that addition of PPCl to the pots displaced some diquat from clay in the upper portion of the pot. Each added increment of PPCl released proportionately greater amounts of diquat from samples 20 through 22 and 24 through 26.

Table II. Diquat Released from Montmorillonite by PPCl as Measured by Cucumber Plant Inhibition

Sample No.	Plant Growth Inhibition, %	Diquat Necessary for Comparable Plant Inhibition,[a] μmoles	Diquat Adsorbed on Clay Mineral, μmoles	Diquat Released, %
18	40	1.3	30	4
20	27	1.0	10	10
21	48	1.4	20	7
22	68	2.0	30	7
24	50	1.5	10	15
25	69	2.0	20	10
26	87	2.7	30	9

[a] Taken from standard growth-inhibition curve of samples 1 through 5 (Table I).

The estimated amounts of diquat released from the clay (4 to 15%) by the various increments of PPCl are given in Table II. Because of the divalent nature of the diquat^{2+} cation and the limited number of sites on external surfaces, it is likely that most of the herbicide was adsorbed on internal surfaces of the clay particles. Assuming that 5 to 10% of the cation-exchange capacity of montmorillonite clay exists on external surfaces, however, it is possible that diquat was displaced from both external and internal surfaces.

ACKNOWLEDGMENT

The authors thank the Chevron Chemical Co., San Francisco, Calif., for providing the diquat.

LITERATURE CITED

Bonner, J., Galston, A. W., "Principles of Plant Physiology," W. H. Freeman and Co., San Francisco, Calif., 1955.
Scott, D. C., Weber, J. B., *Soil Sci.* **104,** 151 (1967).
Weber, J. B., Coble, H. D., J. AGR. FOOD CHEM. **16,** 475 (1968).
Weber, J. B., Perry, P. W., Upchurch, R. P., *Soil Sci. Am. Proc.* **29,** 678 (1965).
Weber, J. B., Scott, D. C., *Science* **152,** 1400 (1966).
Weber, J. B., Weed, S. B., *Soil Sci. Soc. Am. Proc.* **32,** 485 (1968).

Received for review December 20, 1968. Accepted March 5, 1969. Investigation supported by Public Health Service Research Grant CC 00282 from the National Communicable Disease Center, Atlanta, Ga. Paper 2781, Journal Series, North Carolina State Agricultural Experiment Station.