Paraquat Behavior in Costa Rican Soils and Residues in Coffee

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The paraquat deactivation capacities of soils, from 20 coffee plantations, generally ranged from 100 to 500 mg of paraquat/kg of soil. Even when paraquat had been applied up to twice per year (1.2 kg ha^{-1} year) for 20 years, residues were less than 10% of the soils' deactivation capacities and in the majority of cases were less than 1%. Residues in coffee berries and beans were at or below the limit of determination of 0.02 mg/kg. This confirmed that strongly adsorbed residues in soil are not absorbed by the crop and there is no translocation of residues into the crop following accidental contamination of bushes during spraying.

INTRODUCTION

The adsorption, deactivation, and degradation of paraquat in soil have been intensively studied over the past 30 years, particularly in temperate regions. However, no data were available for soils in Central America. Therefore, considering its importance to agriculture in the region and its widespread use, the adsorption, deactivation, and persistence of paraquat in soil and residue levels in coffee, grown on soils where paraquat has been frequently used, have been investigated. This paper describes a series of studies carried out on soil and crops from Costa Rica.

Paraquat is rapidly and strongly adsorbed by soil; consequently, it has no residual biological activity and does not leach (Calderbank, 1968; Riley et al., 1976). The strong binding is primarily due to the formation of a charge-transfer complex between paraquat, a divalent cation, and negatively charged clay and organoclay surfaces (Haque and Lilley, 1972; Khan, 1973). The amount and strength of binding depend on the amount and type of clay present. Soil organic matter can also adsorb large amounts of paraquat, but not as strongly as clay minerals. Adsorbed paraquat has been arbitrarily classified into two types: loosely bound, which can be desorbed with saturated ammonium chloride, and tightly bound, which cannot be desorbed with saturated ammonium chloride (Tucker et al., 1967). The latter can only be released by destroying the clay by refluxing with 9 M sulfuric acid. Tightly bound residues do not have any activity on plants or other soil organisms and are not absorbed by plants or earthworms (Riley et al., 1976). A bioassay technique has also been developed to measure the strong adsorption capacity of soils. Paraquat is equilibrated with soil in a dilute slurry and the equilibrium solution bioassayed with wheat. The strong adsorption capacity (SAC-WB) is defined as the concentration of soil-adsorbed paraquat when the concentration of paraquat in the equilibrium solution is sufficient to inhibit the elongation of 14-day-old wheat roots by 50% relative to an untreated control. Under field conditions soil residues up to the SAC-WB value, and sometimes higher, have no biological activity (Riley et al., 1976).

Paraquat residues on plants, and possibly soil surfaces, are photochemically degraded (Slade, 1965; Calderbank, 1968); thus, not all the paraquat applied reaches the soil.

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Soil contains microorganisms that can rapidly degrade unadsorbed paraquat in culture solutions (Funderburk and Bozarth, 1967; Calderbank, 1968; Riley et al., 1976; Carr et al., 1985). However, the availability of strongly adsorbed residues to microorganisms is greatly reduced, and like many other bound residues in soil their rate of degradation is slow. Long-term field studies in the United States and the United Kingdom have shown strongly adsorbed residues have a half-life of the order of 10 years. For example, in one trial paraquat was applied at 4.5 kg ha^{-1} year^{-1} for 16 years, and soil residues were monitored. The half-life was approximately 7 years, and soil residue levels tended toward a plateau level where the rate of degradation equaled the rate of application (Hance et al., 1985). The rate of degradation is sufficient to ensure that the deactivation capacity of almost all soils will not be exceeded as a result of indefinite use of paraquat.

EXPERIMENTAL METHODS

Soil Samples. Soil samples were collected as described in the adsorption and degradation sections below.

All samples were passed through a 2-mm sieve prior to being analyzed or used in the laboratory studies. The following physicochemical properties were measured: percent sand, percent silt, percent clay, percent OM (organic matter), pH (in water), and CEC (cation-exchange capacity).

Soil Tightly Bound and Strong Adsorption Capacities. Ten soils from coffee-growing regions were collected at 0–5-cm depth during the period August 1982–April 1983 (Table I). Samples (20 g) were shaken for 24 h with 200 mL of a solution containing 30 mg/L paraquat. The supernatant liquid was then analyzed for paraquat and the amount adsorbed calculated by difference from the amount applied. Adsorption coefficients, K_d, were calculated by using the equation

$$K = $$

[adsorbed paraquat] (mg/kg)/[paraquat in solution] (mg/L)

Samples of the supernatant solution were also analyzed after 2, 4, 8, and 16 h of equilibration. The samples were then treated as follows to remove unadsorbed and loosely bound paraquat: filtered, washed with water, shaken for 24 h with 200 mL of water, filtered, shaken for 24 h with 200 mL saturated ammonium chloride, filtered, and washed with water. The remaining tightly bound paraquat was extracted by refluxing the soil with 9 M H_2SO_4 for 5 h.

A further 20 soil samples were collected (about 12 cores approximately 15 cm deep bulked together) from coffee-growing areas in July and August 1985 (Table II). The strong adsorption capacities (SAC-WB) of the soils were determined by using a wheat bioassay (Riley et al., 1976). Briefly, samples (10 g)

Table I. Paraquat Adsorption Characteristics of Costa Rican Soils

location	texture	% sand	% silt	% clay	% OM	CEC, mequiv/ 100 g	pH	paraquat adsorption equilibrium[a] solution, mg/L	adsorbed, mg/kg	K_d	tightly bound paraquat, mg/kg
Sta. María de Dota	clay loam	34	33	33	7.6	20	5.0	2.0	280	140	168
Dulce Nobre Tres Ríos	sandy loam	68	29	3	14.1	36	7.0	0.7	293	419	81
Frailes Tarrazú	sandy clay loam	53	24	23	14.3	36	4.9	1.1	289	263	100
Brazil Santa Ana	sandy clay loam	49	25	26	7.7	37	6.4	1.3	287	221	17
San Roque Grecia	sandy loam	54	29	17	8.6	36	6.1	0.9	291	323	147
La Isabel Turrialba	clay loam	41	27	32	5.4	29	5.3	1.3	287	221	273
Atirro Turrialba	clay	39	17	44	2.1	21	5.0	0.1	299	2990	188
San Marcos Tarrazú	clay loam	44	24	32	1.7	22	5.6	1.1	289	263	80
Sarchí Valverde Vega	sandy loam	57	29	14	9.1	33	5.6	0.7	293	419	100
Barba Heredia	sandy clay loam	46	26	28	3.7	24	5.8	1.3	287	221	142

[a] 20 g of soil equilibrated with 200 mL of solution containing 30 mg/L paraquat.

Table II. Paraquat Strong Adsorption Capacity (SAC-WB) and Residues of Soil from Costa Rican Coffee Growing Areas

location	texture	% coarse sand	% fine sand	% silt	% clay	% OM	CEC, mequiv/ 100 g	pH	SAC-WB, mg/kg	paraquat residues, mg/kg	paraquat residues, % of SAC-WB
San Pedro	silty clay loam	2	27	31	40	8.1	29	5.1	95	3.3	3.5
Centro de Palmares	silty clay loam	1	27	34	38	7.9	29	5.7	370	1.1	<1
San Juan de San Ramón	silty clay loam	1	25	39	35	9.5	31	6.1	250	0.52	<1
San Juan Calle Los Angeles	silty clay	1	10	35	54	6.3	22	4.9	190	0.64	<1
Dulce Nombre	silty clay loam	1	27	33	39	8.8	27	4.7	190	3.1	1.6
Sarchí Sur	silty clay loam	1	24	30	45	6.5	27	5.6	200	0.87	<1
Estero	silty clay loam	5	26	28	41	5.5	27	5.7	3000	0.37	<1
Sorco	silt loam	3	40	26	31	5.8	43	6.7	>5000	2.8	<1
Rosario	silty clay loam	1	19	35	45	9.4	33	5.4	2220	1.1	<1
Tranquerillas	silty clay loam	1	16	34	49	6.0	25	5.0	500	0.90	<1
Paraiso	clay	<1	7	15	78	6.6	23	4.9	280	2.0	<1
Santa Lusia	clay	4	14	18	64	7.3	26	4.8	170	3.9	2.3
La Isabel	silt loam	8	38	32	22	5.1	29	5.8	130	8.0	6.2
Turrialba	silty clay loam	4	20	37	39	6.4	29	5.9	470	11.0	2.3
Distrito Primero	clay	1	5	13	81	4.8	18	4.5	280	0.84	<1
San Rafael de Tres Ríos	clay loam	6	34	25	35	5.1	27	6.4	680	1.6	<1
Alajuela	silty clay loam	2	34	32	32	11.2	31	5.7	180	0.89	<1
Corvillos	silt loam	2	34	35	29	9.4	27	5.5	160	4.3	2.7
Porvenir	silty clay	1	11	26	62	3.2	15	5.6	150	3.6	2.4
El Colao	silt loam	2	41	34	23	9.6	27	5.1	100	4.8	4.8

of each soil were shaken for 16 h with 200 mL of solution, containing a range of paraquat concentrations, in polypropylene bottles. The bottles were then centrifuged and 100-mL aliquots of the supernatant decanted into the plastic pots. No adsorption of paraquat onto the plastic pots was detected when a 0.05 μg/mL solution of the herbicide was allowed to stand in the pots under the conditions of the bioassay. To prevent inhibition of root growth by aluminum toxicity, the pH of solutions from soils with a pH of less than 5.8 was adjusted by the addition of 0.1 g of calcium carbonate. The pots were enclosed in a black polythene sleeve to allow normal root development, in virtual darkness. A 1-mm mesh nylon gauze was held in place at the neck of the pot by using a Melinex strip in such a way that it just touched the surface of the solution. Six pregerminated wheat seeds were placed on the gauze, radical downward, and the pot was covered with a black plastic sheet. After 1-2 days, the sheet was removed and the pots were transferred to a glasshouse (maintained at approximately 15-30 °C) with 16 h of "daylight" supplemented by mercury vapor lights. The level of the solutions in the pots was maintained by the daily addition of distilled water. After a total of 14 days of growth in the soil supernatant solution, the plants were removed and the overall root length of each plant was measured. The mean length of the roots in each pot was expressed as a percentage of mean root length in the control soil sample. Two replicate bioassays were carried out on each soil sample. For most soils, the two replicate assays were started on different days. The root length data from the two replicate assays were plotted against the paraquat fortification levels. The fortification level equivalent to 50% inhibition of root elongation (i.e., the SAC-WB) was then deduced from the dose-response curve.

Paraquat Degradation in Soil. The persistence of paraquat was monitored in three coffee plantations and in an outdoor pot study using the same soils.

The three coffee plantations were at the following locations: Atirro (Turrialba), El Barreal (Heredia), and El Rosario (Naranjo). The soils are of volcanic origin, and halloysite is the predominant clay mineral in Atirro and El Rosario and kaolinite in El Barreal. The pH 5.7 Atirro soil contained 37% clay, 28% silt, 35% sand, and 8.5% organic matter. The pH 6.0 El Barreal soil contained 30% clay, 28% silt, 42% sand, and 9.8% organic matter. The pH 6.1 El Rosario soil contained 36% clay, 38% silt, 26% sand, and 8.2% organic matter. Paraquat had been applied once or twice a year (0.6-1.2 kg/ha) for about 20 years. In each plantation an area of 1 ha was selected for sampling. Soil samples were collected weekly for 7 months, at a depth of 0-5 cm, the surface organic matter being removed. Each sample, consisting of four subsamples, was stored at -15 °C prior to analysis. The sampling periods at each site were February 19-August 30, 1982, at Atirro, June 4-December 10, 1982, at El Barreal, and June 11-December 17, 1982, at El Rosario.

Additional soil samples were collected from these three sites in May 1984, by taking 20 cores at random. The soil was sampled to a depth of 10 cm, and each core was then divided into 0-5- and 5-10-cm horizons. The 20 samples from each horizon were then bulked together for paraquat residue and SAC-WB determinations.

The pot degradation study was started in November 1982 and finished in July 1983. Soil (10 kg) was collected from the above three sites and spread out, and 10 L of 100 mg/L paraquat solution was applied by using an atomizer to give a concentration of 100 mg/kg dry soil. The solution was applied over a period of a week, several times a day, to prevent the solution running off the soil. After mixing, subsamples (1 kg) were placed in 10 pots of 2-L capacity. Pots were kept at Rodrigo Facio University City under natural conditions. There was 629 mm of rainfall during the 9-month study. Soil samples were col-

lected on the day of application and on 11 more occasions during the next 9 months. Each sample of 100 g was stored at -15 °C before being analyzed.

The 20 sites used for SAC-WB determinations (Table II) were also analyzed for paraquat residues. The soils were collected from sites where paraquat had been regularly used for long periods. The data of first paraquat use ranged from 1969 to 1980, and the amounts applied annually were typically in the range 0.6–1.2 kg/ha.

Coffee Samples. Several sets of coffee beans were analyzed for paraquat residues.

Coffee berries were collected from the same locations as the soil degradation study. Five samples of ripe coffee berries were collected, each on different dates, from each of the Atirro, El Barreal, and El Rosario sites, during the period August–December 1982. Samples of immature berries were collected from the same three sites in May 1984, at the same time as the soil sampling. A sample of coffee beans harvested in 1983 was provided by the grower at the Atirro site.

Further samples were collected at the El Barreal and El Rosario sites in November 1984; the Atirro site could not be sampled because the crop had already been harvested. Two samples were collected from each site, one from the lower third and one from the upper third of the bushes.

Samples of coffee beans were also collected during July and August 1985 from the 20 sites selected for the soil SAC-WB survey (Table II).

Paraquat Analysis. The methods of analysis were based on that described by Calderbank and Yuen (1965). Paraquat solutions in water were analyzed without further preparation.

Residues in soil were extracted by refluxing the soil (10 or 20 g) with 9 M sulfuric acid for 5 h. The filtered digest was then percolated through a column of cation-exchange resin which retained the paraquat and some of the soil constituents. The column was then washed with water, 2 M hydrochloric acid, 2.5% ammonium chloride solution, and then water to remove as much as possible of the natural soil constituents. The paraquat was then eluted from the resin column with saturated ammonium chloride. A proportion of the column effluent was then treated with sodium dithionite in alkali. This reduces the paraquat to a free radical whose light adsorption was measured with a spectrophotometer, as described below. Crop samples (100–250 g) were refluxed with 0.5 M sulfuric acid; otherwise, the analysis followed the same procedure as for soil.

The concentration of paraquat, after reduction with alkaline dithionite, was determined by using two photometric techniques. In the first method absorbance at 392, 396, and 400 nm was determined by using a Varian Super Scan 3 spectrophotometer.

The extinction of the sample was corrected at the maximum (A_m) for background adsorption by using the equation

$$A_{corr} = [A^P_m/[2A^P_m - (A^P_h + A^P_l)]][2A_m - (A_h + A_l)]$$

where A_m is the extinction at the absorption maximum of the sample (λ_m), A_l is the extinction of the sample at 4 nm lower than the maximum (λ_l), A_h is the extinction of the sample at 4 nm higher than the maximum (λ_h), A^P_m is the extinction of the standard solution at λ_m, A^P_l is the extinction of the standard solution at λ_l, and A^P_h is the extinction of the standard solution at λ_h.

In the second method a Perkin-Elmer Lambda 5 spectrophotometer, with a 3600 data station and Quest software, was used in the second-derivative mode. This gives a higher sensitivity and reduces the risk of background absorbance affecting the results. The peak height is compared with those for standard samples.

Recovery checks were included with each batch of samples. Limits of determination, which depended on sample size and level of background absorbance, were generally 0.1 and 0.02 mg of paraquat/kg for soil and crop samples, respectively. In a few analyses of crop samples which gave relatively low backgrounds, it was possible to decrease the limit of determination to 0.002 mg/kg by using a large sample size (250 g) and the second-derivative spectrophotometer.

Table III. Concentration of Paraquat Residues (Milligrams per Kilogram of Dry Soil) in Pot Degradation Study

days after application	origin of the soil		
	Atirro	El Barreal	El Rosario
0	105	120	134
8	110	117	127
15	99	151	112
23	85	131	106
41	114	113	118
55	158	150	103
69	128	99	121
99	96	116	129
127	113	92	115
151	117	92	90
180	108	130	145
245	124	105	128

RESULTS

Paraquat Adsorption by Soils. There was no change in adsorption between 2 and 24 h, showing adsorption rapidly reached equilibrium. All the soils adsorbed large amounts of paraquat and had large adsorption coefficients, K_d values, which ranged from 140 to 2990 (Table I); thus, paraquat will not leach. The soils also tightly bound large amounts of paraquat; i.e., it was not desorbed by saturated ammonium chloride. Although the soils had a wide range of physicochemical properties (clay 3–44%; organic matter 1.7–14.3%; pH 4.9–7.0), there was no clear relationship between these properties and the paraquat adsorption coefficient, K_d, or the amounts of tightly bound paraquat. The paraquat strong adsorption capacities (SAC-WB) of soils, measured by using a wheat bioassay, are shown in Table II. The values were generally in the range 100–500 mg/kg; however, three soils had SAC-WB values greater than 1000 mg/kg. To determine if this difference was due to differences in clay mineralogy, two soils were analyzed by X-ray diffraction, by the Department of Soil Science at Reading University, U.K. The sample from Porvenir was studied because it had only a moderate SAC-WB, compared to its high clay content, and the sample from Sorco because of its very high SAC-WB. The major clay minerals in the Porvenir soil were kaolinite, a 1:1 aluminosilicate, and gibbsite. The major clay mineral in the Sorco soil was mica, 2:1 aluminum silicate with a higher cation-exchange capacity than kaolinite. Thus, the differences in SAC-WB values were due to differences in types of clay.

Paraquat Degradation. Paraquat residue concentrations in soils from the Atirro, El Barreal, and El Rosario sites, over the 7-month sampling period, varied 2–3-fold, but there was no clear trend with time. The high variability was probably due to the herbicide having been applied as "spot" treatments rather than as a uniform overall spray. Average residue levels in the 0–5-cm depth were 23.9, 20.9, and 29.7 mg/kg at Atirro, El Barreal, and El Rosario, respectively.

Results for the pot degradation study are given in Table III. There was no clear trend in residue levels with time, and the study was not long enough to be able to calculate a half-life; however, it is clearly greater than 1 year.

Samples (0–5 cm) taken in May 1984 contained 11, 10, and 6.8 mg/kg, respectively (Table IV). As expected, residues were much lower in the 5–10-cm horizon. Due to its strong adsorption paraquat cannot leach (see above). The residues in the 5–10-cm depth were presumably due to physical mixing of soil, e.g., by soil fauna and soil particles moving down cracks and pores.

Paraquat residues in the 20 soils used for the SAC-WB determinations are given in Table II.

Table IV. Paraquat Residues and Strong Adsorption (SAC-WB) Capacities of Soils Collected in May 1984

location	depth, cm	paraquat residues, mg/kg	SAC-WB, mg/kg	paraquat residues, % of SAC-WB
Atirro	0–5	11	280	3.9
	5–10	2.4	400	0.6
El Barreal	0–5	10	250	4.0
	5–10	6.1	260	2.3
El Rosario	0–5	6.8	160	4.2
	5–10	2.0	180	1.1

Table V. Paraquat Residues in Coffee Berries Collected in November 1984

location	position on bush	paraquat residues, mg/kg	
		scanning photometer[a]	second derivative photometer
El Barreal	upper third	0.017	<0.002
El Barreal	lower third	0.017	<0.002
El Rosario	upper third	0.024	<0.002
El Rosario	lower third	0.016	<0.002

[a] Corrected for background by using the adsorption values at three separate wavelengths.

Paraquat Residues in Coffee Beans. The first set of 15 samples from Atirro, El Barreal, and El Rosario, collected in 1982, were analyzed by using the adsorption values at three separate wavelengths to correct for background. Ten samples contained <0.05 mg of paraquat/kg of dry beans. Five samples contained traces of residues in the range 0.05–0.15 mg/kg. The possibility of surface contamination, e.g., with soil containing paraquat residues, could not be ruled out. Therefore, all subsequent samples were either washed with water or saturated ammonium chloride before analysis.

Samples collected in May 1984, which were analyzed by using the second-derivative spectrophotometer, contained no detectable residues (<0.002 mg/kg).

The third set of samples, collected in November 1984, were analyzed by both spectrophotometric methods. Both methods (Table V) showed there were negligible residues in the beans (<0.02 mg/kg). By use of a large sample size of 250 g and careful cleanup prior to analysis using the second-derivative photometer, the limit of determination was 0.002 mg/kg. No residues were detected.

The 20 coffee bean samples collected in July and August 1985 all contained no detectable residues, i.e., <0.02 mg/ kg.

DISCUSSION

All the Costa Rican soils were capable of strongly adsorbing large amounts of paraquat with adsorption coefficients in the range 140–2990. The strong adsorption capacities, measured by using a wheat bioassay (SAC-WB), were generally in the range 100–500 mg of paraquat/ kg and a few soils had SAC-WB values of >1000 mg/kg. The SAC-WB values were correlated to the amount and type of clay in the soils. A normal application of 0.6 kg of paraquat/ha would give a residue of only about 0.3 mg/ kg in the top 15 cm of soil, even if it is assumed, incorrectly, that there is no degradation of the paraquat. Residues up to, and sometimes in excess of, the SAC-WB value have no effects on plants or other organisms (Riley et al., 1976). Thus, Costa Rican soils can completely deactivate hundreds of times the normal application rate.

The field and outdoor pot studies showed that the strongly adsorbed residues had a relatively long persistence. These results are similar to those from studies in temperate regions (Hance et al., 1985; Riley et al., 1976).

The amounts of paraquat applied were not accurately known. However, paraquat residues in the soils (Tables II and IV) were generally less than that expected from the amounts applied (0.6–1.2 kg of paraquat ha^{-1} year^{-1} up to 20 years); this was presumably due to photodegradation of paraquat on weeds plus a slow degradation of the strongly adsorbed soil residues. Consequently, soil residues were less than 10% of the SAC-WB values and in the majority of cases were less than 1% of the SAC-WB. Even if residues remain predominantly in the top 5 cm, paraquat use can be continued for hundreds of years without fear of building up harmful residues in Costa Rican soils.

Coffee berries and beans contained negligible residues; in most cases they were nondetectable, i.e., <0.02 mg/ kg, even in plantations where paraquat has been used for 20 years. This confirmed that strongly adsorbed residues in the soil are not absorbed by the crop and there is no translocation of residues into the crop following accidental contamination of bushes during spraying. The results also show the residues are well below the negligible tolerance level of 0.05 mg/kg set by the U.S. Environmental Protection Agency for coffee beans (FAO/WHO, 1976; CFR, 1986).

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