JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

REVIEWS

Deactivation of the Biological Activity of Paraquat in the Soil Environment: a Review of Long-Term Environmental Fate

TERRY R. ROBERTS,† JEREMY S. DYSON,‡ AND MICHAEL C. G. LANE*,‡

JSC International, Osborne House, 20 Victoria Avenue, Harrogate, North Yorkshire HG1 5QY, United Kingdom, and Environmental Safety, Jealott's Hill International Research Center, Syngenta, Bracknell, Berkshire RG42 6E, United Kingdom

During the many years of paraquat usage, wide ranges of investigations of its environmental impact have been conducted. Much of this information has been published, but key, long-term field studies have not previously been presented and assessed. The purpose of this review is to bring together and appraise this information. Due to the nature of paraquat residues in soils, the major part (some 99.99%) of a paraquat application that reaches the soil within the typical Good Agricultural Practice (GAP) is strongly adsorbed to soils of a wide variety of textures. This is in equilibrium with an extremely low concentration in soil solution. However, the paraquat in soil solution is intrinsically biodegradable, being rapidly and completely mineralized by soil microorganisms. The deactivation of the biological activity of paraquat in soils, due to sorption, has been investigated thoroughly and systematically. It is recognized that the determination of total soil residues by severe extraction procedures provides no insight into the amount of paraquat biologically available in soil. Consequently, the key assay developed for this purpose, namely, the strong adsorption capacity−wheat bioassay (SAC-WB) method, has proved to be valuable for determination of the adsorption capacity relevant to paraquat for any particular soil. This method has been validated in the field with a series of long-term (>10 years) trials in different regions of the world. These trials have also shown that, following repeated applications of very high levels of paraquat in the field, residues not only reach a plateau but also subsequently decline. This demonstrates that the known biodegradation of paraquat in soil pore water plays an important role in field dissipation. The biological effects of paraquat in the field have been assessed under unrealistically high treatment regimes. These trials have demonstrated that the continued use of paraquat under GAP conditions will have no detrimental effects on either crops or soil-dwelling flora and fauna. Any such effects can occur only under extreme use conditions (above the SAC-WB), which do not arise in normal agricultural practice.

Keywords: Paraquat; soil; bioavailability; safety; long-term; degradation; adsorption; crop effects; biomass; earthworms; microarthropods

INTRODUCTION

The herbicide paraquat (1,1′-dimethyl-4,4′-bipyridinium dichloride) has been widely used in agriculture for over 40 years. It is approved for use in more than 100 countries, as a nonsystemic contact herbicide for green vegetation. Paraquat is a total vegetative control herbicide that is very strongly adsorbed to soil and, as a result, biologically deactivated.

Its uses are extremely varied; examples include the protection of soybeans, cereals, and cotton in North America; rice in China; and plantation crops such as oil palm in Malaysia, potatoes and green vegetables in the United Kingdom, and coffee in Brazil. Paraquat is also used in reduced-tillage situations, for example, in pineapple plantations.

The deactivation of the chemical in soil is important because it has allowed the introduction of many precision uses in addition to broadcast applications, examples being the use of hooded sprayers in root and vegetable crops in Brazil, Malaysia, and Ghana as well as in Europe.

Adsorption rapidly reduces the bioavailability of paraquat in the soil environment. There is ample evidence to demonstrate that adsorption is capable of deactivating the equivalent of hundreds or even thousands of paraquat applications over a wide range of soils. This also means that paraquat is effectively immobile in soils with no leaching to ground water.

Although paraquat is characterized by strong adsorption to soils, it also undergoes metabolism and degradation under a

* Corresponding author (e-mail mike.lane@syngenta.com).
† JSC International.
‡ Syngenta Limited.

10.1021/jf011323x CCC: $22.00 © 2002 American Chemical Society
Published on Web 05/18/2002

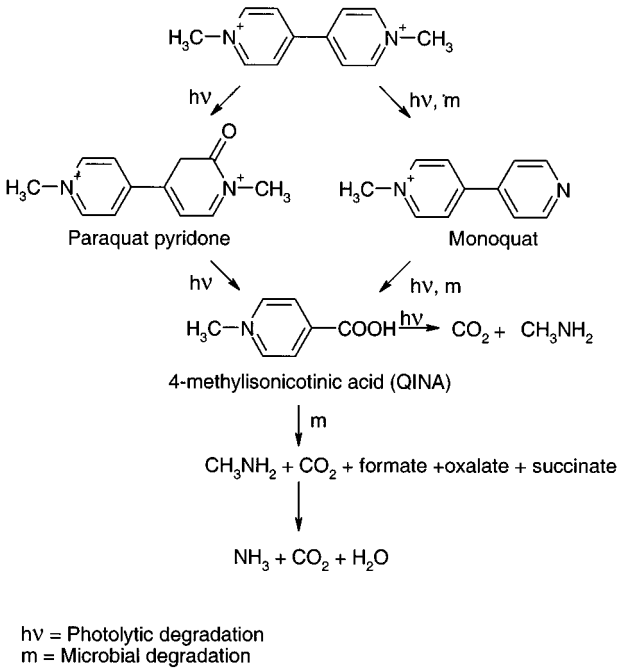

Figure 1. Metabolism and photochemical degradation of paraquat.

range of conditions. Chemically, paraquat is stable in acidic or neutral solutions but is hydrolyzed at pH >12. More relevant to environmental conditions is its rapid photodegradation on surfaces exposed to light, an example being plant surfaces (*1*). Paraquat also undergoes photolysis in aqueous solution at 257 nm to form the *N*-methylbetaine of isonicotinic acid and subsequently methylamine hydrochloride (*2*).

A number of studies have shown paraquat to be intrinsically biodegradable by soil microorganisms, including a variety of both bacteria and fungi (*3*−*6*). Although there are few reports of microbial species capable of metabolizng paraquat as a sole source of carbon (*7*, *8*), there are many examples of co-metabolism in the presence of another carbon source (e.g. see ref *6*). It is likely that degradation occurs via demethylation followed by ring cleavage because $^{14}CO_2$ was released from ring-labeled paraquat (*9*). Appreciable microbial degradation of sorbed paraquat on leaf surfaces has also been observed (*10*).

The photolytic and microbial transformation of paraquat is summarized in **Figure 1** (*11*).

The behavior of paraquat in soil is therefore characterized by strong adsorption that renders the major part of it biologically unavailable, but this fraction is in equilibrium with an extremely small concentration in soil solution that is subject to biodegradation.

Paraquat adsorption and the deactivation of its biological activity in soils have been the subject of many and varied investigations. The purpose of this brief review is to bring together information on the behavior of paraquat in the soil environment with particular emphasis on updating the literature using additional data from laboratory and field investigations in several regions of the world.

NATURE OF PARAQUAT RESIDUES IN SOIL

Paraquat is strongly adsorbed in all types of soil, but its interaction with different soil components such as the clay minerals and organic matter varies. Such interaction was demonstrated in a series of studies conducted in the 1960s (*4*). Typical results (*12*) showed that whereas a soil adsorbed 300 mg/kg of paraquat ion/kg of soil, the clay minerals kaolinite

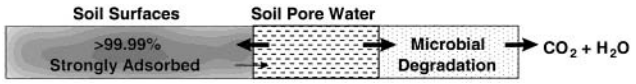

Figure 2. Equilibrium for paraquat between soil and soil solution.

and montmorillonite adsorbed 2500−3000 and 7500−8500 mg/kg, respectively. The greater adsorption to montmorillonite was attributed to the greater surface area of its expanding clay lattice structure compared to that of the nonexpanding clay lattice of kaolinite. Interestingly, at high paraquat concentrations, ammonium ions were found to be capable of partly replacing paraquat in both soil and kaolinite, but to only a very limited extent in montmorillonite. This is presumably due to adsorption occurring via several mechanisms. Other research, for example, that of Knight and Denny (*13*), has provided insight into the mechanisms of paraquat adsorption using X-ray diffraction, and much of this work has been succinctly reviewed elsewhere by Summers (*4*).

The important conclusion from these adsorption studies is that the extent to which any particular soil adsorbs paraquat will be influenced by the amount and type of clay minerals present in soil and, to a lesser extent, the amount of soil organic matter. There is also ample evidence to show that the kinetics of adsorption are important and that the process is biphasic. Initially the majority of the paraquat coming into contact with the soil is rapidly adsorbed, and this is followed by a slower adsorption phase that results in stable equilibrium. This second phase is thought to involve slow diffusion to less readily accessible adsorption sites.

The role played by the different clay minerals and organic matter in the behavior of paraquat clearly depends on several different mechanisms. The primary rapid adsorption of paraquat is via cation exchange, with the positively charged paraquat molecules being attracted to the negatively charged minerals and organic matter in soil. Other processes have also been reported, namely, van der Waals forces, formation of charge transfer complexes, and hydrogen bonding. These processes serve to enhance the adsorption beyond the simple cation exchange reaction. This situation has resulted in the terms "tightly or strongly bound" and "loosely bound" to distinguish the strengths of adsorption (*4*).

Once equilibrium is established (see **Figure 2**), paraquat at typical environmentally expected concentrations is present as a strongly adsorbed residue that is biologically unavailable due to having an extremely low concentration in soil solution. Clearly, methods of analyzing soils for paraquat residues need to take this strong binding into account.

DETERMINATION OF PARAQUAT RESIDUES

Bearing in mind the presence of strongly adsorbed paraquat in soil in equilibrium with a small concentration in soil solution, various approaches to the analysis of paraquat residues in soils have been developed and used.

Chemical extraction is most appropriate for determination of total residues in soil, although early chemical extraction methods did attempt to differentiate between "tightly bound" and "loosely bound" residues. The chemical extraction method most widely used is that developed by Syngenta (*14*). The method involves refluxing soil with 6 M sulfuric acid followed by filtration through a cation exchange resin, which retains the paraquat and some soil constituents. After an acidic wash, the paraquat is eluted from the column with ammonium chloride. The paraquat is then determined by treating an aliquot with sodium dithionite in alkali and measurement of the light

absorption resulting from formation of a free radical. This method results in destruction of the soil in order to release the very strongly bound paraquat residues and is therefore not typical of pesticide analysis. It is possible due only to the stability of paraquat under these very acidic conditions.

Chemical extraction methods provide little or no information on the adsorption status of the paraquat nor do they provide information on the bioavailability of the paraquat in various soils analyzed. For this reason bioassays have also been developed to provide information on the levels of bioavailable paraquat in soil solution.

Bioassays using plants exposed to paraquat in solution have shown that the herbicide is highly active against plant roots, with wheat roots being particularly sensitive (*15*). In view of this biological activity, the availability of soil residues to plants has been the subject of many investigations (*4*, *15*). The availability to plants of paraquat present in soils appears to depend on the nature of the soil, its adsorption capacity, and the concentration of paraquat in soil solution, the latter being available for uptake by roots.

This concept has resulted in development of several different bioassays. For example, Damanakis et al. developed an assay based on the effect of paraquat on *Lemna* (*16*, *17*). This was based on the growth of dry weight of *Lemna*, which was found to be a more consistent response than monitoring chlorosis of *Lemna* fronds by Funderburk and Lawrence (*18*). A breakthrough was achieved, however, by Riley et al. (*15*) with the introduction of the strong adsorption capacity (SAC) bioassay.

A bioassay for paraquat in soils should ideally be a simple but reproducible method for predicting residue levels in any soil that can be reached without harm to plants or soil organisms. These concentrations will vary from soil to soil depending on the soil constituents. In view of the widespread generic use of bioassays, it is important to know whether the capacity of a wide variety of soils to deactivate paraquat applications can be exceeded.

In the remainder of this review, the amount of paraquat that can be rendered unavailable in field soils is determined using the SAC−wheat bioassay (SAC-WB). The SAC-WB procedure (*14*) involves shaking a mixture of soil (10 g) and water (0.2 L) with different amounts of paraquat for 16 h. The mixture is then centrifuged, and pregerminated wheat plants are grown in the supernatant solution over 14 days under appropriate controlled conditions of light and temperature. The maximum root length at each dose level (including a control) is measured and plotted on a dose−response curve. The value of the SAC-WB (expressed as milligrams of paraquat ion per kilogram of soil) is determined as the dose that reduces the growth of wheat roots by 50%. An example SAC-WB dose−response curve generated using these methods is shown in **Figure 3**. The concentration of paraquat in the aqueous phase, which results in this 50% inhibition of root elongation, is ~0.01 mg of paraquat/L.

This assay is based on the initial short-term deactivation of paraquat in soil, because it involves a 16 h adsorption incubation period. As indicated earlier, however, the initial rapid adsorption of paraquat is followed by a slower, further adsorption phase. Consequently, the adsorption capacity for soils with "aged" residues of paraquat will be higher than indicated in the SAC-WB assay. This also explains why, even though the test determines the adsorption capacity at the 50% effect level, effects have not been observed in soils containing paraquat residues up to the SAC-WB level.

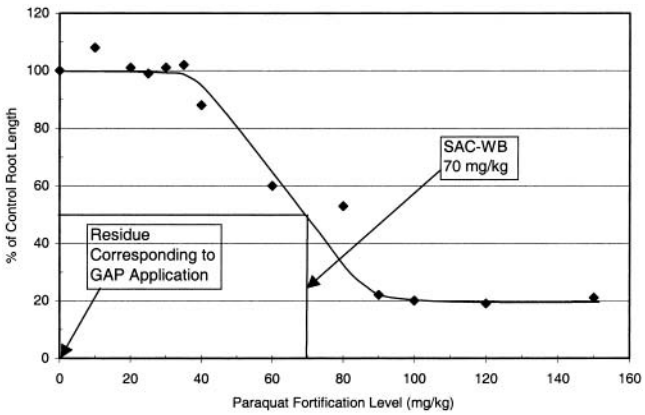

Figure 3. Example SAC-WB dose–response curve with indication of residue levels corresponding to GAP.

DEACTIVATION OF PARAQUAT IN FIELD SOILS

A series of investigations of the field behavior of paraquat has been conducted with various objectives. Initially the aim was to validate the SAC-WB assay under field conditions. Trials were also established to investigate accumulation of residues, any effects on crops, and ecotoxicological effects. The trials conducted are summarized in **Table 1**, and the range of rates used is given in **Table 2**.

Validation of SAC-WB under Field Conditions. Following its introduction, the SAC-WB method has been used as the key reproducible and simple method to determine the capacity of soils to deactivate the biological activity of paraquat residues. Wheat has been used because it is a sensitive plant and also because, as expected for a herbicide, plants are the most sensitive organisms to paraquat residues in soil. The wide use of this assay has shown that SAC-WB values of soils vary considerably (further details are given in the following section).

The SAC-WB method (initially developed in 1974) has proved to be valuable as a laboratory assay for the prediction of residue levels of paraquat in soil that can be reached without causing any harm (i.e., safety thresholds). In parallel with this laboratory work, a series of long-term field trials were initiated in the early 1970s with the initial aim of validating the SAC-WB method under field conditions as a predictor of safe use conditions (*14*).

Soil Dissipation and Accumulation. Once the SAC-WB method was fully validated, trials were also conducted to determine whether the long-term use of paraquat could ever exceed these safety thresholds. For example, trials in Australia provided valuable data to demonstrate that a plateau concentration of paraquat in soil was reached.

Crop Effects and Ecotoxicity. Trials in the United Kingdom, The Netherlands, Australia, the United States, Malaysia, and Thailand were designed to observe any effects on crops and on soil ecology and microbiology.

DESIGN OF AND RESULTS FROM LONG-TERM TRIALS

U.K. Trials. The fate of paraquat in soils has been the subject of extended study in the United Kingdom under a variety of conditions, including treatments that are orders of magnitude in excess of the recommended use conditions, for example, Good Agricultural Practice (GAP). Trials initiated in 1971 at Frensham, U.K., have provided valuable long-term data on the fate and effects of paraquat (*14*). The site had a moderate SAC-WB value (120 mg of paraquat ion/kg of soil), and four treatment levels were used, namely, rates corresponding to 0, 50, 110,

Table 1. Long-Term Paraquat Trials Reviewed in This Paper

country	trial location	date started	single application or multiple	key objective	residues monitored vs time
U.K.	Frensham	1971	single high-rate application (maximum rate = 400% of SAC-WB)	assess effect of high-rate residues on crops, soil ecology, and soil microbiology to determine safety threshold	yes
Australia	Meckering	1971	multiple applications annually at normal rates and 28 times normal rate	effect of high-rate residues on crops	yes
U.S.A.	Goldsboro	1979	multiple applications at normal rates and single high-rate applications up to 200% of SAC-WB	monitoring of effects of residues on crops	yes
The Netherlands	three trials: Valthermond, Wieringerwerf, and Breezand	1986	single applications up to 120% of SAC-WB	monitoring of effects of high-rate residues on crops	no
Malaysia	three trials: one mineral soil (Melaka) and two peat soils (Parit Sulong and Pontain)	1989	single applications up to 120% of SAC-WB for mineral soils and 300% for peat soils	monitoring of effects of high-rate residues on crops, earthworms, and microbial biomass	yes
Thailand	two trials: mineral soils at Rayong and Sattahip	1989	single applications up to 120% of SAC-WB	monitoring of effects of high-rate residues on crops and microbial biomass	yes

Table 2. Soils and Paraquat Application Rates in Long-Term Trials

country	trial	soil type	range of application rates (kg of paraquat ion/ha)	range of application rates[a] (L/ha Gramoxone)	max GAP[b] for single application (L/ha Gramoxone)
U.K.	Frensham	sandy loam	18–144	90–720	5.5
Australia	Meckering	sand	0.25 and 7	annually at 1.25 and 35	1.3
U.S.A.	Goldsboro	loamy sand	1.0	annually at 5	5.0
U.S.A.	Goldsboro	loamy sand	28–114	140–570	5.0
The Netherlands	Valthermond	peaty sand	19–153	95–763	5.5
The Netherlands	Wieringerwerf	sand	100–810	507–4052	5.5
The Netherlands	Breezand	sand	63–504	316–2520	5.5
Malaysia	Melaka	sandy clay loam	12–94	59–469	2.8
Malaysia	Parit Sulong	peat	5–28	27–142	2.8
Malaysia	Pontian	peat	3–33	15–166	2.8
Thailand	Rayong	loamy sand	15–122	77–614	2.8
Thailand	Sattahip	sandy loam	44–358	224–1790	2.8

[a] Assumes 20% paraquat ion per liter. Applications made in a single dose unless stated otherwise. [b] Good Agricultural Practice; values quoted are relevant to GAP applications in countries in which trials were conducted.

and 400% of the SAC-WB value. These ranged from 90 to 720 kg/ha incorporated to a depth of 15 cm, and the residue levels in soils were monitored for 20 years. After the treatments, the trial site was cropped with cereals or a grass lea over the 20 year duration of the trial.

The fate of the resultant paraquat soil residues was followed for 20 years, until 1991. Soil samplings for all of the trials discussed in this review used similar methods. In general, the pattern of soil sampling was 20 cores (~2.5 cm diameter) taken from each replicate of each treatment application. The cores were sectioned into a number of depths (e.g., 0−10, 10−20, and 20−30 cm depending on normal cultivation depth), and the samples from each depth appropriately combined. The resultant samples were analyzed for paraquat soil residues using the methods described previously. Of all the trials performed in this series, this trial has been the most extensively investigated with respect to soil flora and fauna. It therefore forms a useful basis for general discussion of the fate and impact of paraquat residues in soil resulting from high application rates.

Cereal crops (spring barley) were used to monitor for biologically available concentrations of paraquat in soil. During the first six years after application, the highest rate treatments resulted in severe effects on crop yield. Barley is as sensitive as wheat to root uptake of paraquat, but as these rates of application corresponded to 400% of SAC-WB, it is not surprising that such effects were observed. However, 17 years after application, effects on yield in these plots had been reduced to <10%. Yields from all other treatments were similar to, or occasionally above, those in the control (untreated) plots from year 2 onward. No residues were observed in either the barley grain or straw (limits of determination of 0.01 and 0.02 mg/kg, respectively).

Assessment of earthworm populations, using methods similar to those described by Raw (*19*), showed that there were effects on populations and distributions of species at the 110 and 400% of SAC-WB (198 and 720 kg/ha paraquat ion). However, the residues were dissipated to such an extent that by six years after application there were only effects at the highest treatment rate, and these effects were limited to changes in earthworm species with total weights remaining unaffected (see **Figure 4**). These differences were mainly attributed to vegetation changes rather than direct effects on the earthworms. The relatively low populations of earthworms, even in the control samples, one year after application are very likely the result of the severe

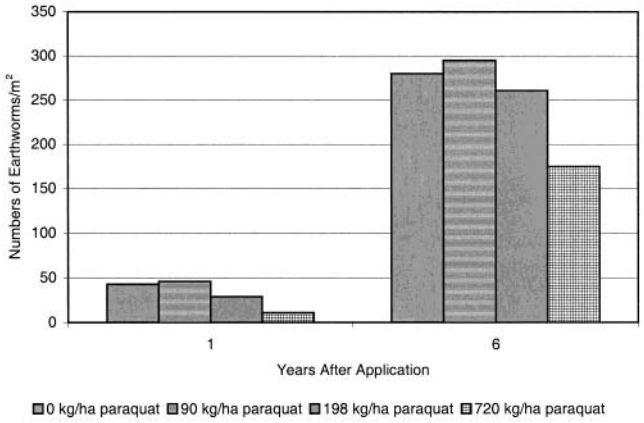

Figure 4. Numbers of earthworms 1 and 6 years after treatment in the Frensham trial.

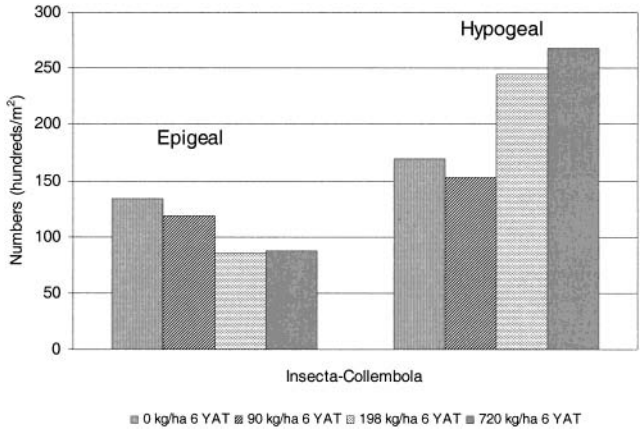

Figure 5. Effect of paraquat on Collembola in the Frensham trial.

cultivation methods required to incorporate the paraquat into the soil after application. Of course, these cultivations were replicated on the control plots, even though no paraquat was applied. Analysis of earthworms from the different treatments for paraquat residues showed that the earthworms did not adsorb paraquat residues from soil.

Microarthropod populations were sampled two months before application and four months, one year, and six years after treatment in direct-drilled barley crops. The only effect directly attributable to the applications made was a reduction in the numbers of some Collembola and Gamasina at the highest rates of application one year after application. These were likely to have been as a result of reduced vegetation rather than from direct chemical toxicity. The Insecta-Collembola data generated six years after application are shown in **Figure 5**. The data are split into the category of surface-dwelling (epigeal) and soil-dwelling (hypogeal) organisms. The apparent increase in populations of hypogeal organisms six years after application at the two highest rates of application (198 and 720 kg/ha) was very largely attributable to a single species (*Cryptopygus thermophilus*). Although there were larger numbers of this species in the highest rate treatments (e.g., an average of 191 individuals/m^2), the populations were not statistically significantly different from those in the untreated plots (e.g., an average of 118 individuals/m^2).

Microbial populations and biomass were assessed seven years after application of the chemical. The treatments caused no major differences in the number of microorganisms, total propagules, algae, bacteria, fungi, and actinomycetes. Biomass was determined by soil ATP determination, and no differences between treatments were found. The only minor change observed was in the plots receiving the highest treatment rate, in which the populations of the yeast (*Lypomyces starkeyi*) had increased slightly. Further extensive investigations were made into indirect measures (e.g., carbon dioxide evolution from soil organic matter, glucose and wheat material, and ammonification and nitrification of lucerne). None of these parameters showed any effects from the paraquat applications.

Residues were shown to be dissipated, although as discussed previously the rate was relatively slow. This is consistent with the concept that the residues were largely adsorbed and therefore not available to the microorganisms for degradation. It was, however, apparent that the rate of degradation increased with increasing rate of application. This is again consistent with the concept that availability of the chemical controls the rate of degradation.

Australian Trials. Dyson et al. (*20*) recently published results from a series of long-term trials conducted in Australia between 1971 and 1983. The trials involved both repeated annual applications and excessive-rate treatments in order to deliberately exceed the SAC-WB value of the soil. These trials were conducted in Meckering, Western Australia, on a soil containing 1.3% organic matter and 4% clay, which had an SAC-WB value of 15 mg/kg of soil, an extremely low figure compared to the typical range of 50−5000 mg/kg. The objectives were to test the validity of SAC-WB values for the prediction of paraquat deactivation in the field and, more importantly, to determine long-term safety.

Two treatment regimes were followed. Normal-rate treatments comprised 24 annual applications of a mixture product ("Spray·Seed") applied at the recommended rate of 0.25 kg of paraquat ion/ha. On separate plots, excessive-rate treatments at up to 7 kg/ha/year were applied from 1971 to 1983 (giving a total of 48 kg/ha) in order to exceed the SAC-WB value of the soil, followed then by annual applications at the normal rate (0.25 kg/ha) from 1983 to 1995. The whole trial was cropped with a wheat−clover rotation until 1978 and a wheat−lupin rotation thereafter.

The normal-rate treatment plots had a maximum paraquat residue in the upper 20 cm soil layer of 1.8 mg/kg, representing only 12% of the SAC-WB value for this soil. Crop yields were not significantly different from those of untreated control plots. Moreover, there were no residues detected in the crops (limit of determination of 0.05 mg/kg).

For the excessive-treatment plots, the maximum paraquat soil residue was 180% of the SAC-WB, which was considerably less than that expected from the quantity applied. This was attributed to the degradation of paraquat (pathways in **Figure 1**). It is important to note that even with the excessive-treatment regime, which exceeded the SAC-WB value, no significant effects on crop yields were observed, with the exception of a higher yield in 1975 due to suppression of wild-oat competition. In addition, there were no effects on crop emergence, root development, crop height, wheat-ear length, or tiller counts. As with the normal-rate treatments there were no residues (<0.05 mg/kg) detected in grain or straw from wheat or lupin crops.

This long-term study at the excessive rate has shown that SAC-WB values derived in the laboratory provide a conservative estimate of the capacity of soils to deactivate paraquat in the field. More significantly, because the trial was conducted in a soil with "low" adsorption capacity (as indicated by a laboratory-derived SAC-WB value), it has clearly shown that repeated long-term annual applications of paraquat according to normal agricultural use did not result in effects on crops.

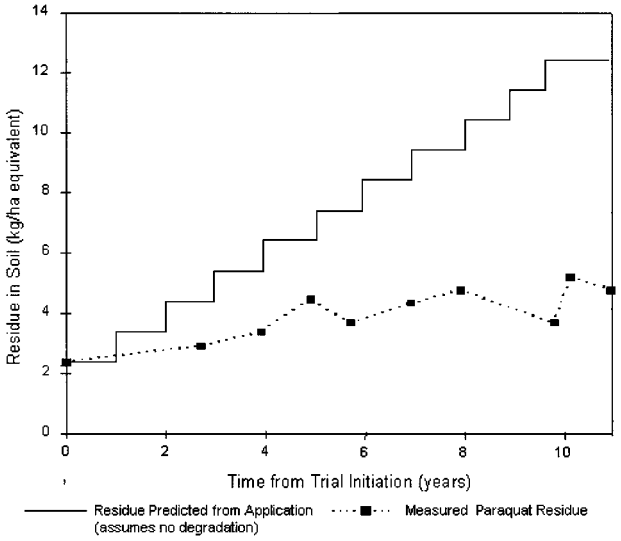

Figure 6. Residue data for paraquat from the Goldsboro trial.

U.S. Trials. Other long-term trials have confirmed that the SAC-WB is equally applicable to soils throughout the world. In trials conducted in Goldsboro, North Carolina, between 1979 and 1991, the soil SAC-WB value was also low, namely, 25 mg of paraquat ion/kg of soil. The trial comprised five paraquat treatments replicated on four blocks, including an annual treatment (1 kg/ha), three single high-rate treatments at 50, 100, and 200% of the SAC-WB value (namely, 28, 57, and 114 kg/ha incorporated to 15 cm depth), and an untreated control. Crops grown were bermudagrass, corn, wheat, and soybean.

Paraquat residues were not detected (<0.05 mg/kg) in any of the grain crops. As in the Meckering trial, the annual paraquat treatment did not adversely affect crop yields, stand counts, plant heights, or grain weights. The only effects noted at high-rate treatments were some significant effects on wheat yields, but these occurred only when residues of paraquat were close to or above the SAC-WB value of the soil.

The Goldsboro trial showed that the residues, following repeated applications, reached a plateau compared with the theoretical accumulation possible (as shown in **Figure 6**).

The Netherlands Trials. In 1986 trials were initiated in The Netherlands with the aim of confirming that the SAC-WB can predict field deactivation of paraquat (*14*). Three sites were selected, one with a peat soil with high organic matter and two with light sandy soils. All soils were agronomically important and had relatively low SAC-WB values (determined in the laboratory). On the basis of the SAC-WB values, each plot was treated with paraquat as Gramoxone at highly exaggerated rates equivalent to 15, 30, 60, and 120% of the SAC-WB value (within a predetermined depth of soil) together with a control. The effect of the resulting residues on the growth of crops was then observed over a five-year period after treatment.

Assessments of crop growth and yield made during the first one to two years after treatment showed that some effects were observed when paraquat residues were present at or close to the SAC-WB value. At the highest treatment rate, in excess of the SAC-WB value, crop effects were marked during years 1 and 2. However, in subsequent years the biological activity of the residues declined to the extent that paraquat residues generally had no significant effect on crop growth unless the SAC-WB value of the soil was still exceeded (see **Figure 7**). In addition to confirming that laboratory-derived SAC-WB values can provide an adequate measure of a soil to deactivate paraquat, the trials provide useful evidence that the bioavailability of paraquat residues declines with time, presumably due to a combination of further adsorption and degradation of the herbicide.

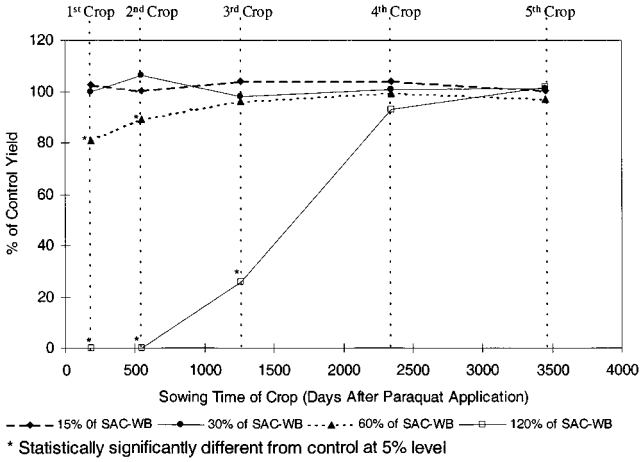

Figure 7. Results from the Valthermond site.

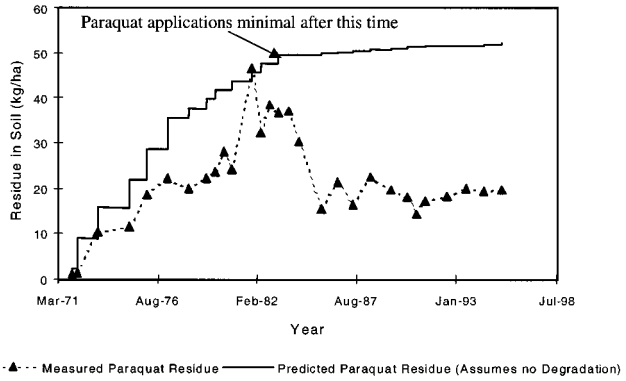

Figure 8. Residue data for paraquat in soil from the Meckering trial.

The overall conclusion drawn from these investigations is that the SAC-WB value provides a conservative prediction of safety thresholds, and this has been validated across a wide range of field soils.

Summary of Field Trials. As described earlier, the long-term trials described here were conducted for several reasons. In some cases (e.g., The Netherlands), the objective was to validate the SAC-WB assay, but many trials have provided valuable information on the long-term dissipation of paraquat in the field following single or repeated applications. Information on effects in crops, earthworms, and microarthropods have also been obtained.

The results of the Meckering, Australia, trial referred to earlier (see **Figure 8**) have clearly shown that there is a decline in the concentration of paraquat with time whether the rate of application was excessive (7 kg of paraquat ion/ha/year) or normal (0.5 kg of paraquat ion/ha/year). This dissipation is assumed to be the result of degradation of paraquat in soil solution and other processes. That the concentration of paraquat in soils not only reached a plateau but also declined provides reassurance that the herbicide can be safely used in the long term.

The results from the Frensham, U.K., trial provided data on the effects of paraquat on soil microorganisms, microarthropods, and earthworms. Soil plots were treated with paraquat at rates of 90, 198, and 720 kg of paraquat ion/ha, equivalent to 50, 110, and 400% of the SAC-WB. The barley crops were direct drilled. Microarthropods were monitored two months before and

four months, one year, and six years after treatment. After seven years of monitoring, these treatments had not resulted in any statistically significant differences in the numbers of microorganisms (total propagules, algae, bacteria, fungi, actinomycetes, and the yeast *Lipomyces starkeyi*) or in the ATP concentration for the 90 and 198 kg/ha treatments. Even for the 720 kg/ha treatment there were only minor statistically significant differences in the numbers of fungi and *L. starkeyi*. It was concluded from these high-rate studies that repeated applications of paraquat to soil will not adversely affect the number or activity of soil microorganisms, especially at recommended application rates close to 1 kg/ha.

Rather different investigations have been conducted in Malaysia, where three trials were performed in 1990 to predict the relationship between the capacity of Malaysian soils to deactivate paraquat in the field and the laboratory-determined SAC-WB values (*14*). Within these trials, treatments were up to 120% of the SAC-WB, and some information on the effects on soil biomass and earthworms was obtained. The microbial biomass values across all treatments were consistent, and the variability observed was well within that expected for such measurements. There were no statistically significant differences between earthworm populations in treated and control plots.

In addition, data are available from U.K. trials on the effects of paraquat on earthworms. When paraquat was applied at high rates (equivalent to more than 100 normal applications), no effects were observed, although at the very high rate of 720 kg/ha there were some effects (up to 35% reduction in total numbers of earthworms) some six years after treatment. On the basis of these data, it can be concluded that repeated applications of paraquat at rates within the GAP will not affect earthworm populations. Similar results were obtained for microarthropods (*14*).

Combining the outcomes from all of these trials, it has been shown that paraquat residues can and do increase in soils receiving repeated applications to reach a plateau. However, such plateau levels have been shown to be well below the concentrations that would be required to markedly affect either crops or soil organisms. The SAC-WB value has been shown to be a conservative estimate of threshold concentrations for effects to occur.

Further work has been conducted to elucidate the contribution of various soil constituents to deactivation and to gain an understanding of whether the SAC-WB is ever likely to be exceeded following the normal use of paraquat.

CONTRIBUTION OF SOIL CONSTITUENTS TO BIOLOGICAL DEACTIVATION

As indicated earlier, the SAC-WB values of soils can vary considerably, depending primarily on the amount and type of clay and, to a lesser extent, the organic matter content. The influence of clay type was initially demonstrated in studies on a limited range of pure clay minerals (*4*). For example, it was shown that montmorillonite can adsorb, and hence deactivate, appreciably more paraquat than kaolinite, due mainly to its larger surface area. However, field soils comprise mixtures of clay minerals and organic matter in organoclay complexes. There has thus been a need to try to relate the SAC-WB values to a wider range of combined soil constituents as they occur in field soils.

Knight and Tomlinson (*21*) demonstrated that removal of organic matter by hydrogen peroxide digestion generally reduced the SAC values (as determined by an early chemical assay technique). On average, 82% (range = 42−100%) of the SAC values of soils could be accounted for by clay minerals, particularly the expanding clay minerals, for example, montmorillonite, illite, and vermiculite, rather than kaolinite (a nonexpanding clay mineral) and allophane (an amorphous clay mineral). Also, in a study by Constenla et al. (*22*), the SAC-WB values of 20 Costa Rican soils (range = 100−>5000 mg/kg) were poorly correlated with clay content and organic matter content, due to major differences in clay mineralogy between soils. For example, the highest SAC-WB value (>5000 mg/kg) for a soil with a modest clay content (31%) was due to the dominating presence of illite. However, the soil with the highest clay content (62%) had one of the lowest SAC-WB values (150 mg/kg) because it contained only kaolinite and the aluminum oxide gibbsite.

In the most exhaustive investigation to date, Rana (*23*) attempted to relate the SAC-WB values of 27 field soils to their individual soil constituents. The soils had their properties and constituents fully characterized, including particle-size analysis, pH, cation exchange capacity (CEC), organic matter content, and clay mineralogy by differential thermal analysis (a quantitative method, which is also able to detect amorphous clay minerals such as allophane). Several hypothetical relationships between soil constituents and properties were evaluated using statistical fitting procedures, from which a number of conclusions can be drawn.

First, soil constituents could account for up to 90% of the variations in SAC-WB values. This is considerably more than could be accounted for using only simple properties of soil alone, such as clay content, organic matter content, and CEC, particularly because widely differing mineralogical profiles from temperate and tropical soils were used in the investigation.

Second, most of the clay minerals (nine in total, including some metal oxide minerals) contributed to the SAC-WB value. However, only a few of these minerals had a contribution that was statistically significant. When statistical significance could not be established, it was due to the presence of only small amounts of these minerals and/or the relatively low SAC-WB values.

Third, correlations occurred between soil constituents, notably a negative correlation between organic matter and individual clay minerals. Hence, organic matter appeared to reduce the SAC-WB value of soils. However, this result is not really surprising, because clay minerals are coated to various degrees with organic films, effectively slowing the rate of adsorption by restricting access to the stronger adsorption sites on clay surfaces. This was illustrated by Damanakis (*16*), who showed in a laboratory experiment that paraquat adsorbed to organic matter would gradually transfer to stronger adsorption sites on clay minerals. Certainly, when clay minerals are not present in peat soils, SAC-WB values indicate a substantial capacity to deactivate paraquat. For example, SAC-WB values for 13 temperate peats ranged from 25 to 560 mg of paraquat ion/kg of soil (*14*), and Lane et al. (*24*) reported an SAC-WB value of 70 mg/kg for a tropical peat.

The overall conclusion from the investigation of Rana (*23*) is that SAC-WB values of other soils can be predicted at an initial screening level. Such predictions will generally be a refinement of (and hence be more precise than) the order of magnitude variations in typical SAC-WB values associated with each broad textural class of mineral soils (see **Table 3**). More importantly, perhaps, the investigation demonstrates that a wide range of clay minerals are capable of deactivating significant amounts of paraquat in field soils. Consequently, the precise details of the clay mineralogy of a particular soil appear to be

Table 3. Range of SAC-WB Values for Different Soil Groupings

soil type	SAC-WB values (mg/kg)	Gramoxone (L/ha to 20 cm)
clays	500–5000	7500–75000
loams	150–1500	2300–23000
peats	50–150	125–375
sands	25–250	375–3750

Table 4. Concentration of Paraquat Ion in the Aqueous Phase of the Soil/Water Slurries

concn of applied potassium (mg/kg)	concn of paraquat in the aqueous phase (mg/L)
0	0.0059
1000	0.0059
5000	0.0064
10000	0.0072
15000	0.0089

largely irrelevant for ensuring that the SAC-WB values will be large enough to deactivate paraquat residues, because typical SAC-WB values are equivalent to hundreds and even thousands of years of paraquat applications.

LONG-TERM SAFETY OF PARAQUAT USE

It is therefore possible to conclude from the trials considered above that paraquat can be safely used over the long term because it is highly unlikely that the SAC-WB values will ever be exceeded. This is apparent from the normally very high SAC-WB values measured combined with the knowledge that residues of paraquat are not accumulated following repeated applications. Also, the residues decline after applications have ceased.

However, it is also important to understand whether there is any potential for release of adsorbed paraquat from soil through a change in the adsorption equilibrium. The possibility that cations introduced into the soil (e.g., from fertilizers) could compete with paraquat for adsorption sites and so shift the adsorption equilibrium between adsorbed and unbound paraquat was investigated in two studies. Malquori and Radaelli (*25*) studied the desorption of paraquat using a variety of clay minerals with various concentrations of paraquat and of so-called "releasing inorganic cations". Paraquat desorption from clay was not detected when its concentration fell below a certain limit, which varied with each type of clay mineral. This concentration was presumed to correspond to the SAC-WB of the clay mineral.

A second investigation (*14*) studied the desorption of paraquat from loamy sand soil. Soil was treated with aqueous solutions of paraquat at concentrations equivalent to 140 mg of paraquat ion/kg of soil, just above the SAC-WB of the soil. To this mixture was added various concentrations of potassium ion (from 1000 to 15000 mg/kg of soil). Paraquat was not desorbed by the steadily increasing concentrations of potassium, confirming that no detectable shift in adsorption equilibrium occurred with the changing chemical conditions. As the results in **Table 4** demonstrate, the addition of potassium to soil/water slurries had no effect on the adsorption of paraquat. It should be noted that an addition of 15000 mg/kg of potassium to soil would be equivalent to ca. 400 years of normal agronomic practice. Similar experiments showed that the converse was true; that is, addition of paraquat at rates up to 200 mg/kg of soil did not have an impact on available potassium concentrations.

It can therefore be concluded that, in agricultural use, paraquat will be released only through the equilibrium between the adsorbed state (typically more than 99.99% of residues present) and the presence of trace levels in soil solution. Paraquat in soil solution is known to be degraded rapidly.

During more than 40 years of use in over 100 countries, covering many and varied agronomic practices, there has been no observation of the reactivation of adsorbed paraquat residues due to desorption.

PARAQUAT USE AND SUSTAINABLE CROP PRODUCTION

The foregoing review has shown that paraquat is essentially biologically unavailable to crops and soil organisms. However, there is a school of opinion that demonstration of the lack of biological effects of a chemical does not provide sufficient reassurance of the absence of some long-term effect. Consequently, it is appropriate to consider whether the presence of "unavailable" chemical (such as paraquat) in soil could affect soil quality.

There are many definitions of "soil quality". The Soil Science Society of America (SSSA) defines soil quality as "The capacity of a soil to function within ecosystem boundaries to sustain biological productivity, maintain environmental quality, and promote plant and animal health" and the Natural Resources Conservation Centre quotes the simpler definition "Soil quality is how well soil does what we want it to do".

The latter goes on to describe the inherent and dynamic qualities of soil. The *inherent* quality is the natural ability of a soil to function. For example, sandy soils drain more rapidly than clay soils. The *dynamic* soil quality is the manner in which soil changes depending on how it is managed.

With this in mind, it is important to consider whether there is evidence to show that paraquat has affected soil quality in the 40 years of its widespread use. There appears to be no such evidence. In fact, since the first use of paraquat in the early 1960s, its use has played a major role in the way many crops are grown throughout the world. It is relevant to note that in all this time paraquat has been shown not to contaminate either ground water or surface water and so meets the water quality criteria laid down in the European Union. This is again a feature of its strong adsorption to all soil types. With the launch of paraquat, the modern concepts of zero tillage and reduced tillage were born (*26*) as a significant approach to address concerns about soil erosion. Nowadays, the role of paraquat in reduced tillage covers millions of hectares of land across the globe, which helps to prevent soil erosion, as well as conserve time and fuel, improve levels of soil organic matter, soil aeration, and soil structure, and help the proliferation of soil fauna.

The continued use of paraquat in agriculture will no doubt provide further data upon which to continuously review its environmental impact.

CONCLUSIONS

During the many years of paraquat usage, many and varied investigations of its environmental impact have been conducted. Much of this information has been published, but some key, long-term field studies have not previously been presented and assessed. It has long been known that the major part (some 99.99%) of a paraquat application within the typical GAP remains strongly adsorbed in soils of a wide variety of textures, in equilibrium with a low concentration in soil solution.

Notwithstanding its strong adsorption, paraquat is intrinsically biodegradable, so the DT_{50} of paraquat in soil solution is short.

The deactivation of the biological activity of paraquat in soils has been investigated thoroughly. It is recognized that determination of total soil residues by severe extraction provides no insight to available paraquat levels. Consequently, the key assay developed for this purpose, namely, the SAC-WB method, has proved to be very valuable for the determination of the adsorption capacity relevant to paraquat for any particular soil. This method has been validated in field soil situations within a series of long-term trials in different regions of the world, most of which are very long-term.

The conclusions from a review of the available data on paraquat are that no effects of paraquat on subsequent crops and soil organisms are to be expected when the herbicide is used according to GAP. In fact, it is clear that either single, very large applications or repeated applications at high rates are most unlikely to result in effects as long as the SAC-WB value for a soil is not reached.

Finally, it is concluded that paraquat can continue to be used safely because it does not impair soil quality and, when used according to GAP, continues to be a valuable tool in reduced-tillage agriculture.

LITERATURE CITED

(1) Slade, P. The fate of paraquat applied to plants. *Weed Res*. **1966**, *6*, 158−167.

(2) Slade, P. Photochemical degradation of paraquat. *Nature* **1965**, *207*, 515−516.

(3) Funderburk, H. H.; Bozarth, G. A. Review of the metabolism and decomposition of diquat and paraquat. *J. Agric. Food Chem.* **1967**, *15*, 563−567.

(4) Summers, L. A. Fate of bipyrdinium herbicides. In *The Bipyridinium Herbicides*; EDS Academic Press: San Diego, CA, 1980.

(5) Dyson, J. S. Ecological safety of paraquat with particular reference to soil. *Planter* **1997**, *73*, 467−478.

(6) Ricketts, D. Paraquat is intrinsically biodegradable. *Book of Abstracts, 9th International Congress of Pesticide Chemistry, The Food−Environment Challenge*; Royal Society of Chemistry and International Union of Pure and Applied Chemistry: London, 1998; Vol. 2, 6A018.

(7) Tu, C. M.; Bollen, W. B. Effect of paraquat on microbial activities in soils. *Weed Res.* **1968**, *8*, 38.

(8) Imai, Y.; Kuwatsuka, S. Characteristics of paraquat degrading microbes. *J. Pestic. Sci.* **1989**, *14* (4), 475−480.

(9) Baldwin, B. C.; Bray, M. F.; Geoghegan, M. J. The microbial decomposition of paraquat. *Biochem. J*. **1966**, *101*, 15P.

(10) Lee, S. J.; Katayama, A.; Kimura, M. Microbial degradation of paraquat sorbed to plant residues. *J. Agric. Food Chem*. **1995**, *43*, 1343−1347.

(11) Ricketts, D. The microbial biodegradation of paraquat in soil. *Pestic. Sci*. **1999**, *55*, 596−598.

(12) Coats, G. E.; Funderburk, H. H.; Lawrence, J. M.; Davis, D. E. Persistence of diquat and paraquat in pools and ponds. *Proc. Southern Weed Conf.* **1964**, *17*, 308−315.

(13) Knight, B. A. G.; Denny, P. J. The interaction of paraquat with soil: adsorption by an expanding lattice mineral clay. *Weed Res.* **1970**, *10*, 40−48.

(14) Unpublished Syngenta data. For further details contact Mike Lane, Syngenta, Jealott's Hill International Research Station, Bracknell, Berkshire RG42 6ET, U.K.

(15) Riley, D.; Wilkinson, W.; Tucker, B. V. Biological unavailability of bound paraquat residues in soil. In *Bound and Conjugated Pesticide Residues*; ACS Symposium Series; American Chemical Society: Washington, DC, 1976; pp 302−351.

(16) Damanakis, M.; Drennan, D. S. H.; Fryer, J. D.; Holly, K. The adsorption and mobility of paraquat on different soils and soil constituents. *Weed Res*. **1970**, *10*, 264−277.

(17) Damanakis, M. A bioassay for the determination of low concentrations of paraquat. *Weed Res.* **1970**, *10*, 77−80.

(18) Funderburk, H. H.; Lawrence, J. M. Mode of action and metabolism of diquat and paraquat. *Weeds* **1964**, *12*, 259−264.

(19) Raw, F. Estimating earthworm populations by using formalin. *Nature (London)* **1959**, *184*, 1661−1662.

(20) Dyson, J. S.; Muller, K.; Roy, W.; Warner, R. Long-term safety of paraquat use on a sandy Australian soil. *Book of Abstracts, 9th International Congress of Pesticide Chemistry, The Food−Environment Challenge*; Royal Society of Chemistry and International Union of Pure and Applied Chemistry: London, 1998; Vol. 2, 8B-014.

(21) Knight, B. A. G.; Tomlinson, T. E. The interaction of paraquat (1:1′-dimethyl 4:4′-dipyridilium dichloride) with mineral soils. *J. Soil Sci.* **1967**, *18*, 233−243.

(22) Constenla, M. A.; Riley, D.; Kennedy, S. H.; Rojas, C. F.; Mora, L. E.; Stevens, J. E. B. Paraquat behaviour in Costa Rican soils and residues in coffee. *J. Agric. Food Chem.* **1990**, *38*, 1985−1988.

(23) Rana, R. K. The effects of soil properties on the biological deactivation of paraquat by adsorption. M.Sc. Thesis, Department of Soil Science, Reading University, U.K., 1998.

(24) Lane, M. C. G.; Ngim, J.; Chia, T. H.; Lam, C. H.; Daorai, A.; Dyson, J. S.; Lim, J. K. Biological activity of high rate paraquat residues in tropical soils. Presented at the 4th International Conference on Plant Protection in the Tropics, Kuala Lumpur, Malaysia, 1994.

(25) Malquori, A.; Radaelli, L. Adsorption and release of diquat and paraquat by some clay minerals. *Sci. Agrairie* **1966**, *36*, 35−44.

(26) Baker, C. J.; Saxton, K. E.; Ritchie, W. R. *No Tillage Seeding−Science and Practice*; CAB International: Oxon, U.K., 1996; ISBN 0 8 5199 10 3 3.

Received for review October 4, 2001. Revised manuscript received March 31, 2002. Accepted April 2, 2002.

JF011323X