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Paraquat and sustainable agriculture

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Abstract: Sustainable agriculture is essential for man's survival, especially given our rapidly increasing population. Expansion of agriculture into remaining areas of natural vegetation is undesirable, as this would reduce biodiversity on the planet. Maintaining or indeed improving crop yields on existing farmed land, whether on a smallholder scale or on larger farms, is thus necessary. One of the limiting factors is often weed control; biological control of weeds is generally of limited use and mechanical control is either often difficult with machinery or very laborious by hand. Thus the use of herbicides has become very important. Minimum cultivation can also be important, as it reduces the power required to work the soil, limits erosion and helps to maintain the organic matter content of the soil. This last aspect helps preserve both the structure of soil and its populations of organisms, and also sustains the Earth's soil as a massive sink for carbon, an important consideration in the light of global warming. The introduction of the bipyridinium herbicide paraquat in the early 1960s greatly facilitated weed control in many crops. Paraquat has the unusual property of being active only by direct spray onto plants and not by uptake from soil in which strong binding deactivates it. Together with its rapid action in light in killing green plant tissue, such properties allow paraquat to be used in many crops, including those grown by low-tillage methods. This paper reviews the ways in which agricultural systems have been and are being developed to make use of these properties, and provides a risk/benefit analysis of the world-wide use of paraquat over nearly 40 years.

Keywords: paraquat; bipyridinium herbicides; soil sorption; bioavailability; deactivation; degradation; sustainable agriculture; risk/benefit analysis; minimum cultivation

1 INTRODUCTION

Sustainable agriculture is the maintenance of cropping systems that neither deplete soil fertility, even over the long term, nor lead to the development of overwhelming pest, disease or weed problems. Such agricultural systems must be reliable and high yielding if the expanding world population is to be fed adequately without bringing yet more virgin land into cultivation. The conservation of virgin areas and their natural vegetation is important in its own right to prevent the further extinction of many specialised species and thereby maintain biodiversity on the planet. Furthermore, both clearing virgin land and intensive cropping systems lead to massive mineralisation of soil organic carbon to carbon dioxide, whose increase in atmospheric concentrations over the past 100 years is believed to be an important contributor to the process of global warming. The use of pesticides over the past 50 years has led to tremendous improvements in both crop yield and quality, and this review considers the role in sustainable agriculture and soil conservation worldwide of paraquat, a herbicide with a wide range of uses.

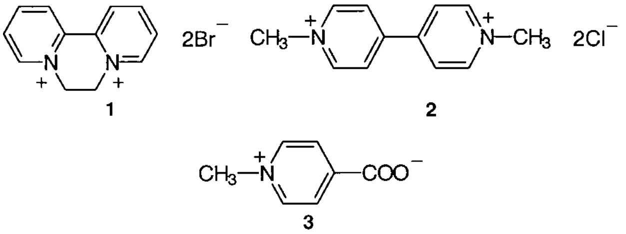

Figure 1. Structures of bipyridinium herbicides (**1**) diquat, (**2**) paraquat, and (**3**) photolysis product of paraquat.

The bipyridinium compounds (Fig 1) were first recognised as herbicides in 1954 following screening by ICI at Jealott's Hill Research Station in the UK. Diquat dibromide (**1**) was the first to be discovered, but shortly afterwards in 1955 paraquat salts were also found to be active. It is interesting that paraquat, synthesised by the reaction of 4,4′-bipyridine with methyl iodide, had been known since 1882 and had been used since 1932 under the name of methyl viologen as an oxidation–reduction indicator. Although related bipyridinium compounds are also active, only diquat and paraquat are commercial herbicides, the latter compound usually being applied as the dichloride salt (**2**).

These bipyridinium salts when applied to plants cause rapid scorching of green tissue following

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exposure to light. The compounds are little translocated within plants, in part because of the rapid desiccation of the green tissues, and so underground parts such as tubers and roots are not affected and usually regrow. Furthermore, these herbicides are strongly and rapidly sorbed by soil, thus being deactivated such that crops can be sown almost immediately into treated soil without risk of phytotoxicity. This strong binding to soil greatly limits any leaching of these herbicides but also reduces their availability for microbial breakdown in the soil water, so that these compounds are persistent in soil though not active therein. Roberts *et al*[1] have recently reviewed the deactivation of the biological activity of paraquat in soil, and Dyson[2] covered aspects of the ecological safety of paraquat in soil. Many aspects of the chemistry of the bipyridinium herbicides, their mode of action and environmental behaviour have been reviewed by Summers.[3] Diquat is especially effective against broad-leaved plants and hence finds particular use as a crop desiccant; paraquat has a broader spectrum of activity and now has the larger market share for the bipyridinium herbicides, being used mainly for weed control but also as a desiccant. This present review concentrates on paraquat, both updating environmental aspects of its use and considering the risk/benefit analysis of paraquat use based on field experience. Safety of use in sustainable agriculture is a prime consideration and these aspects are considered before going on to assess the benefits in different areas of agriculture. Particular emphasis is given to the way in which agricultural systems have been developed to make effective use of the unusual properties of paraquat. These systems include its use in smallholder agriculture, weed control in row and plantation crops, its role in minimum-cultivation techniques and recent developments in its use in direct-seeded rice. Given the nearly 40 years use of paraquat world-wide, it is now timely to appraise its contribution to long-term sustainable agriculture, and to consider what future benefits may be realised in such areas as the conservation of soils and their global management to minimise carbon losses therefrom.

2 PARAQUAT BEHAVIOUR IN PLANTS AND SOIL

2.1 Mode of action

Paraquat has been described as a chemical flamegun, insomuch as it kills the above-ground parts of plants whilst not damaging the roots. Such effects will usually kill annual weeds, but deeper-rooted and rhizomatous weeds will resprout; agricultural systems have been developed to take advantage of these properties. For example, in tropical soils, using paraquat to manipulate the ground cover in plantations rather than to maintain fallow conditions can greatly reduce erosion, since live roots bind the soil together.

The bipyridiniums are non-selective herbicides that require both light and oxygen to cause rapid desiccation of plant leaves following spraying. They appear to act by diverting electrons from the iron–sulfur centres in photosystem I in the chloroplasts. The reduced paraquat species for example then reacts with oxygen to give the superoxide anion O_2^-, which generates hydroxyl radicals either directly or via a hydrogen peroxide intermediate. These highly reactive radicals attack membranes and induce breakdown of cells in the sprayed green tissue. The 'browning' of leaves can be observed within a few hours of treatment under strong light conditions, with complete desiccation occurring after a few days.

2.2 Sorption of paraquat to soil

The paraquat dication is rapidly and strongly bound to soil, with values of the sorption coefficient (K_d) often over 1000 litre kg^{-1}. As leaching is considered insignificant for compounds of $K_d > 10$ litre kg^{-1}, the strength of this binding is notable. Such strong binding also greatly limits the bioavailability of paraquat in soil, so that it is not phytotoxic to plant roots under normal application conditions nor do micro-organisms have ready access to paraquat in the soil water. Thus microbial metabolism of paraquat, which can be quite rapid under culture conditions in the absence of soil, is very slow in soil itself.

Sorption to soil occurs onto both the organic matter and the clay fraction. The latter is especially important in giving strong long-term sorption, and depends on the type of clay present. Thus kaolinite, with a typical non-expanding lattice, sorbs in total about 2500–3000 mg kg^{-1} whereas montmorillonite with its expanding lattice sorbs about 75 000–85 000 mg kg^{-1}. The process of sorption is essentially ion exchange, but greatly enhanced in expanding-lattice clay by the ability of the planar paraquat molecules to become intercalated between the lattice layers and then be held by strong coulombic forces. Though such binding is a reversible process, equilibrating with 1 M NaCl or $BaCl_2$ solutions removed only about 5% of paraquat from montmorillonite; this portion is assumed to be on the outer surfaces of the clay particles.[4,5] In contrast, such treatment removed about 80% from kaolinite and essentially all the paraquat from ion-exchange resins, indicating that it is not cation exchange alone that determines strength of sorption. The paraquat-sorption capacity of several soils was only 10–30% of their total cation-exchange capacity as measured by ammonium ions; it is thought that the much larger size of the paraquat molecule limits entry to many sites.

Knight and Denny[6] used X-ray diffraction to investigate the mechanism of paraquat sorption to montmorillonite. Paraquat was shown to be held between the montmorillonite layers, in so doing expanding the basal layer spacing from approximately 0.96 to 1.26 nm. Given that the thickness of an aromatic ring is 0.34 nm and of a methyl group 0.40 nm, the interlayer expansion of only 0.30 nm caused by paraquat indicates either bond shortening or keying in of the paraquat molecule between the silicate sheets.

For non-ionised pesticides, sorption to soil is primarily by a process akin to partitioning into the organic matter fraction. This approximates to a linear isotherm, such that K_d is largely independent of solution concentration. In contrast, paraquat sorption is mainly on the clay fraction and appears to be more akin to a Langmuir isotherm.[7] The classic Langmuir system has a finite number of primary sorbing sites and, once these are filled, subsequent sorption can occur only by secondary interactions. In the sorption of paraquat by soil, this manifests itself as a very strong sorption up to a certain concentration (the strong adsorption capacity, SAC), beyond which there is weaker sorption up to a limiting concentration at which no more paraquat is sorbed. The SAC typically comprises 10–50% of the total sorbing capacity depending on the soil type, with the latter itself averaging about 50% of the total cation exchange capacity (CEC). Removal of organic matter by hydrogen peroxide slightly reduces the SAC and the maximum paraquat capacity, with a somewhat more marked reduction of the CEC.[8] Even within the region of the SAC, [^{14}C]paraquat can displace unlabelled paraquat from montmorillonite; this indicates that this sorption, though very strong, is none the less reversible.[9]

Soils with a high organic matter content have a high capacity for paraquat sorption, but such sorption is weaker than on the expanding clay lattices. It is thought that, in clay soils, paraquat initially sorbed onto the soil organic matter is redistributed over several days or weeks onto the clay particles on which it is more strongly bound. Paraquat is so strongly absorbed to soils that it is extremely difficult to extract for analysis. The usual method is to reflux with 6 M sulfuric acid, a process so extreme that it is essentially dissolving the soil to leave the solubilised paraquat.

2.3 Persistence of paraquat in soil

As discussed above, the very strong sorption of paraquat in soil limits its availability in the soil water for microbial breakdown[10] and so it is very stable in the sorbed form in soil. An early report[11] from the Weed Research Organisation (UK) indicated that, after six annual applications of paraquat at 4.48 kg ha^{-1} beginning in 1967, essentially all of the applied paraquat could be recovered at the end of this period. However, when this trial was reassessed after 12 years of annual application,[12] the amounts of paraquat found were beginning to reach a plateau. Although the data were somewhat variable, it appeared that about 10% of the paraquat was being lost each year, equivalent to a half-life of about 6.6 years (Fig 2). It was considered possible that the earlier appraisal had been confounded by the use of worn corers that had taken a larger soil volume than expected, and also the later study used an improved analytical method.

A similar trial was conducted by ICI at Goldsboro (North Carolina, USA) with annual applications of paraquat at 1.0 kg ha^{-1} over 11 years to a sandy soil with a low SAC value of 25 mg kg^{-1} as assessed by a wheat bioassay.[1] The amounts recovered from the soil never exceeded 6 kg ha^{-1}, though the cumulative applied amounts were in excess of 12 kg ha^{-1} (the soil contained a small amount of paraquat at the start of the trial). This corresponds to a half-life of about 4.6 years, slightly less than seen in the UK study, which difference might be attributable to the warmer climate in the Goldsboro trial and a lower SAC. No deleterious effects were noted on any of the crops grown (maize, wheat, soybean and bermudagrass), and paraquat residues were not detected (<0.05 mg kg^{-1}) in any of the harvested grains. However, in other plots receiving high rates of paraquat (28, 57 or 114 kg ha^{-1} ie 50, 100 or 200% of the SAC), wheat yields were depressed at the two highest rates. In laboratory incubations, Cheah *et al*[13] observed half-lives of 1.4 and 7.2 years in a Malaysian sandy loam and muck soil, respectively.

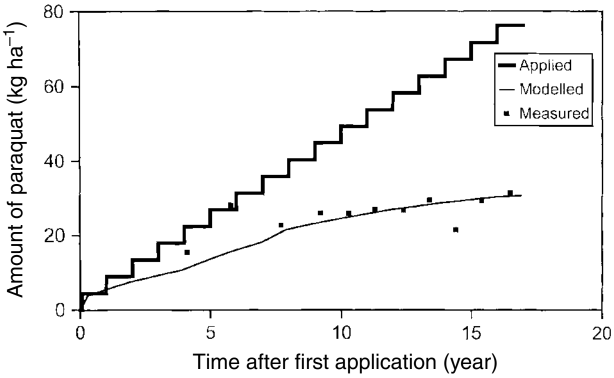

Figure 2. Accumulation of paraquat in soil following annual applications of 4.48 kg ha^{-1} over 17 years at the Weed Research Organisation, Oxfordshire, UK.

These studies used paraquat applied directly to bare or lightly vegetated soil, but in practice the target weeds will intercept a substantial proportion of the sprayed compound, perhaps up to 80%, depending on the amount of growth. Paraquat is quite rapidly broken down by photolysis on surfaces,[3] with such breakdown also occurring in plant tissue to which paraquat is rapidly sorbed.[14,15] Thus the doses reaching soil will be rather less than the amount applied. Such interception by weeds was thought an important factor in the limited accumulation of paraquat in coffee plantations in Costa Rica despite 20 years of annual applications and a low degradation rate in the soils.[16]

The role of sorption to soil in slowing paraquat breakdown has been investigated in a field experiment at Sattahip, Thailand (M Lane, pers comm). Paraquat was applied at two rates, 44.8 or 358 kg ha^{-1}, both of which are greatly in excess of agronomic practice. Breakdown was monitored over nearly 8 years (Fig 3), giving DT_{50} values of 10.6 and 6.5 years for the lower and higher rates respectively. The initial concentrations of paraquat in topsoil resulting from the higher rate application were 132 mg kg^{-1}, in excess of the SAC of this soil, which was 90 mg kg^{-1}. Thus this paraquat was more available in the soil water

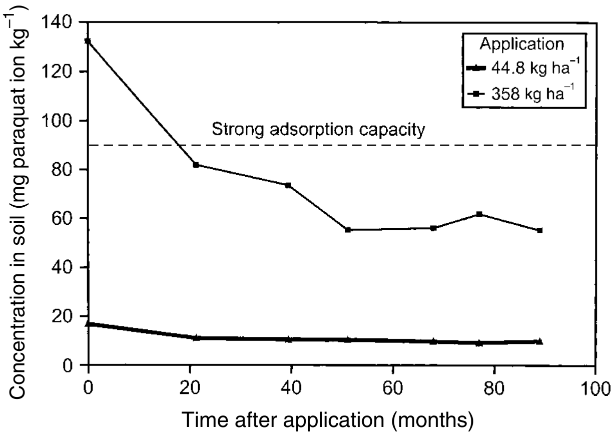

Figure 3. Effect of application rates on the degradation of paraquat in soil at Sattahip, Thailand.

for microbial degradation before its concentration fell below the SAC.

This faster breakdown of paraquat at very high application rates also provides reassurance that the microbial processes involved in its breakdown are not inhibited even at these high concentrations of paraquat in soil. Modelling the accumulation of paraquat resulting from worst-case agronomic practice at this site (two applications annually each of 1.0 kg ha^{-1} with 50% interception by the weed vegetation) gave a plateau concentration of paraquat of 8.8 mg kg^{-1}, ie well below the SAC and so of no biological significance.

A wide range of soil fungi and bacteria has been shown able to degrade paraquat in laboratory cultures.[3] An example is the soil yeast *Lipomyces starkeyi* Lod and Rij which is particularly effective, degrading paraquat rapidly with 50% mineralisation (ie conversion to carbon dioxide) occurring within a few days to a couple of weeks.[17,18] These processes occur in soil, but much more slowly due to the very strong sorption limiting bioavailability of paraquat in the soil water. Recently, Lee *et al*[19] have shown that paraquat can be degraded microbially when sorbed to plant tissues and in light this may occur together with photolysis. The main photochemical degradation product (Fig 1, **3**) is the betaine 1-methyl-4-carboxypyridinium; this is not strongly sorbed to soil and is rapidly degraded by microbial attack yielding methylamine from the methyl moiety and ultimately a variety of other fragments including carbon dioxide, fumarate and succinate.[20–23] Thus paraquat is not intrinsically stable either to photolysis or microbial metabolism but, once in the soil matrix, very strong binding reduces the bioavailability and hence greatly slows breakdown.

3 ENVIRONMENTAL IMPACT OF PARAQUAT

3.1 Criteria for registration of pesticides

The main criteria that a pesticide has to satisfy in the registration process are that there should be no unacceptable (ie only negligible) risks in the following areas:-

1 Exposure of pesticide operators
2 Phytotoxicity to the crop or to following crops
3 Residues in foodstuffs
4 Environmental safety (includes protection of groundwater, effects on soil organisms, effects on beneficial insects and other wildlife, toxicity to aquatic life).

With regard to human exposure, both of workers applying pesticide or people ingesting pesticide residues on foodstuffs, large safety factors (typically at least ×100) are included to allow for any variation between the test animal species and humans, and also for possible variation in sensitivity between individuals. Every relevant aspect of use is specified—permitted crops, formulations and method of application, maximum application rates and their timing, and pre-harvest intervals for edible crops. Thus every practicable step is taken to ensure that a pesticide is safe when used in the way prescribed by the label.

The persistence of pesticides in soil within the registration system currently operated in the European Union is assessed using a tiered approach. If, in laboratory tests at 20 °C using several soils, the disappearance time of half the pesticide (DT_{50}) is greater than 60 days (or $DT_{50} > 90$ days at 10 °C if this represents a climate more typical of the proposed use), then field studies are required. In these, with pesticide application as in typical usage, if the $DT_{50} > 3$ months or $DT_{90} > 12$ months, further tests are triggered to see whether the persistence of the pesticide gives rise to undesirable effects (eg year-on-year accumulation in soil, effects on soil microbial processes). Only if deleterious effects are shown unlikely to occur, given the proposed use pattern, will the registration criterion regarding persistence in soil be satisfied. Thus, though still occasionally a matter of debate, pesticides in soil are assessed not on the basis of persistence *per se* but on the consequences of persistence for those compounds exceeding the DT_{50} or DT_{90} trigger values, of which paraquat is an example.

The possible environmental impact of pesticides has to be viewed in the light of the enormous impact of agriculture itself. Vast areas of forests have been cleared, virgin grasslands ploughed, hillsides terraced and deserts made to bloom. Such changes have, of course, benefited some wildlife, but have had a devastating effect on many more. With the rapidly increasing human population, the pressure on what natural habitat remains, be it an English hedgerow or the Amazon jungle, is intense. The direct effect of modern pesticides on the farmed environment is small; indirect effects, such as the removal of weeds reducing food supplies for some farmland birds, no doubt do occur, but the corollary is that the substantially higher yields of efficient agriculture mean that extra land does not have to be taken into cultivation. Even in efficient agricultural systems, conservation measures can be taken to improve the wildlife value of farmland. Maintenance of soil quality requires that pesticides should only have short-term impacts, primarily on the undesirable organisms, and, if the pesticide persistence is greater than the criteria given above, the bioavailability should be sufficiently low that soil organisms and processes are not adversely affected.

3.2 Bioavailability of paraquat in soil

The ability of a soil to sorb paraquat quickly and so deactivate it has been assessed by a simple bioassay, the Strong Adsorption Capacity—Wheat Bioassay (SAC-WB).[10] In this test, soil slurries are equilibrated for 16 h with paraquat at different rates, and then wheat seedlings are grown for 14 days in the soil solutions from the slurries. The SAC-WB is assessed as the paraquat concentration (mg paraquat kg^{-1} soil) that reduces root growth by 50% (this is achieved by a solution concentration of *ca* 0.01 mg paraquat litre^{-1}). This method thus measures a level at which paraquat residues in soil may pose a risk to wheat, though in practice this is likely to over-represent the risk, since equilibration in the field will usually occur for longer, leading to more complete strong sorption. In such surveys on soils throughout the world, SAC-WB values have generally ranged from 20 to well over 1000 mg kg^{-1}, equivalent to paraquat levels of 70 to 3000 kg ha^{-1} incorporated to a depth of 20 cm.[10] This represents tens to thousands of years of normal usage of paraquat (Table 1),[1] during which time degradation would be occurring; it is also a conservative estimate insomuch as wheat is one of the crop plants most sensitive to paraquat residues, and so most other crops would have a greater margin of safety. Scott and Weber[24] showed that adding organic matter or kaolinite reduced phytotoxicity, with montmorillonite giving the greatest protection due to its strong sorption of paraquat.

In surveys of a large number of Korean orchards which had received paraquat over a period of 26 years up to 1996/97, the highest paraquat concentration in topsoil was 35 mg kg^{-1} with a mean of 7.5 mg kg^{-1}.[25] These soils are primarily kaolinitic with a mean SAC-WB of 254 mg paraquat kg^{-1} soil; desorption tests on soils treated to 255 and 364 mg kg^{-1} released only 0.00035 and 0.07% respectively. It was concluded that the strong sorption of paraquat to these orchard soils made it environmentally safe.

Table 1. Amounts of paraquat in soil required in cause phytotoxicity in the SAC-WB test (adapted from Roberts *et al*[1])

Soil type	SAC-WB values (mg kg^{-1})	Paraquat dication (kg ha^{-1} to 20 cm depth)
Clay	500–5000	1500–15 000
Loam	150–1500	460–4600
Peat	50–150	25–75
Sand	25–250	75–750

3.3 Ecotoxicology of paraquat in soil

As outlined above, paraquat is persistent in soil due to its very strong sorption to clay particles. Less (and usually much less) than 0.1% of applied paraquat will be present in the soil water, and this very limited bioavailability both slows the degradation of paraquat by soil micro-organisms and conversely minimises the possible adverse influence of paraquat on soil-dwelling organisms, whether small or large.

Using the SAC-WB wheat bioassay procedure, the available concentrations of paraquat in soil water are much lower than LC_{50} values (LC_{50} is the concentration that kills 50% of a population) for soil organisms, including soil microbial processes. Thus, for a loamy sand in the UK with a SAC-WB of 120 mg paraquat kg^{-1} soil, the LC_{50} values for three earthworm species were much higher at 500–5000 mg kg^{-1} soil. Given that the SAC-WB value is itself highly unlikely to be reached, there is a large margin to protect soil organisms. Cultivation is itself damaging to many soil organisms; for example, ploughing substantially reduces worm populations, both by direct damage and by exposing them to heavy predation by birds. Thus the use of paraquat to permit low- or no-tillage systems as described below can promote populations of soil-dwelling organisms and so improve soil structure.

Consideration of the effects of a pesticide on larger creatures such as birds and mammals living on farmland is an important part of the registration process. Though paraquat is not applied to crops intended for consumption, none the less fallen grain in stubbles may, for example, receive paraquat if these are sprayed prior to drilling. The dietary LC_{50} for birds is about 1000 mg paraquat kg^{-1} food. Thus birds such as pheasants (*Phasianus colchicus* L) would need to eat about 100 000 grains to take in a lethal dose, equivalent to about three times their bodyweight,[26] and so toxic effects on farmland birds are very unlikely.

Cattle showed no toxic symptoms even when in tests they were allowed to graze on pasture freshly sprayed with paraquat thus exposing them to unusually high concentrations on vegetation of up to 1000 mg kg^{-1}. In additional, the residues in milk and meat were below the limit of detection (0.005 mg kg^{-1}) with the exception that milk contained 0.02 mg kg^{-1} on the day after spraying. Animals rapidly excrete paraquat and so there is no risk of bioaccumulation.[26] Thus, although paraquat is quite toxic to mammals, with for example the LD_{50} for rats and guinea pigs being respectively about 129–157 and 30–56 mg kg^{-1} bodyweight,[27] even under conditions of misuse or accidental exposure no significant effects were observed.

Many studies have assessed the effect of paraquat in aqueous solution on the growth and survival of soil micro-organisms and fungi (reviewed by Summers[3]). Inhibition of fungal or bacterial growth has commonly been observed, but in general only at unrealistically high concentrations of paraquat such as greater than 100 mg paraquat litre^{-1}. A few soil fungi and bacteria were inhibited at 5 mg litre^{-1}, although usually the much lower concentrations that might occur in soil water have not been tested. For example, the SAC-WB bioassay has an LC_{50} of 0.01 mg litre^{-1} and even such low levels would be in excess of those likely to be seen in practice.

In tests in soil, mycelial growth of *Sclerotinia rolfsii* Sacc was only reduced by paraquat at the very high concentrations of 500–1000 mg kg^{-1} soil,[28] whereas concentrations down to 12.5 mg litre^{-1} inhibited growth in solution. In field trials on a sandy loam soil,[29,30] paraquat at concentrations of 10–1000 mg kg^{-1} had little effect on fungal populations and indeed the numbers of bacteria and actinomycetes increased, especially at the higher concentrations. Other authors have reported a similar lack of effect. For example, paraquat either formulated or as technical material had only a transient effect on soil microbial populations when applied at ten times the normal field rate to a calcareous loam.[31] Effects on microbial populations of the long-term repeated use of paraquat were ascribed to the indirect effects of the loss of vegetation cover rather than being a direct response to paraquat itself.[32,33]

In the field, breakdown of barley stubble was not influenced by paraquat treatment at normal rates.[34,35] In another test to see the influence of paraquat on the decomposition of cellulose in soil, paraquat at the very high concentration of 1300 mg kg^{-1} soil did not slow the decomposition of buried cotton wool. If the cotton wool was itself sprayed prior to burial, decay was at times even accelerated. Similarly paraquat, either pure or formulated, did not affect carbon dioxide release from decomposition of wheat straw contained in laboratory bioreactors,[36] nor was there any effect on cellulose decomposition in Japanese soil held under upland conditions or with transitional flooding.[37] These and other reports thus indicate that paraquat is not affecting microbial and fungal processes in soil when used according to normal agricultural practice.

4 PARAQUAT USES AND BENEFITS

4.1 The introduction of bipyridinium herbicides

When paraquat and diquat were first found to be herbicidal, their lack of activity in soil and their lack of selectivity in plants seemed to be disadvantages. However, once the unusual herbicidal behaviour of the bipyridiniums had been appreciated, novel ways of using them in agricultural systems were developed. One of the first major outlets explored was its use in rubber plantations in Malaysia, where field trials were begun in 1959. The inability of paraquat salts to penetrate tree bark ensured safety to the crop, and its rainfastness aided its reliability as a herbicide in a tropical climate; furthermore, because paraquat does not kill roots or rhizomes, such use allows manipulation of the ground flora to favour less competitive species that nevertheless are adequate to prevent soil erosion. Paraquat also finds use as a defoliant and desiccant in several crops. Applied to maturing cotton plants, its rapid action speeds maturation, aids the harvesting of the bolls and provides some weed control for the following crop. This allows earlier planting of the following crop, so improving its yield potential.[38]

A further important potential use was pasture renovation and in 1961 the first 'direct-drilling' trials were started at Jealott's Hill in the UK. Direct drilling requires less energy than conventional ploughing, which can expose soil to erosion and is also damaging to soil invertebrates such as earthworms. However, without control of weeds, direct drilling can be difficult and the crop may suffer from undue competition. Paraquat, exhibiting rapid contact action against a wide spectrum of weeds and with its deactivation by sorption to soil, allowed the development of improved direct-drilling systems in which crops could be drilled only two days after the herbicide application. The rapid action of paraquat and its deactivation by soil thus allow a rapid turnaround from one crop to the next, a feature which is essential for some cropping rotations. Allen[39] has reviewed the earlier work on such agronomic practices and this approach has since been successfully used in minimum-cultivation regimes for many crops.

The way in which these early agronomic uses of paraquat have been extended to a wide range of cropping situations, a process which is continuing, is discussed in more detail below.

4.2 Minimum cultivation

Tilling the soil has been an essential part of agriculture for centuries. For example, inversion ploughing buries weeds and crop trash, and facilitates the making of a seed bed for the succeeding crop. However, in many parts of the world, excessive tillage has left soil vulnerable to wind and rain erosion.[40] The American 'dust bowl' of the 1930s is a famous example of the dangers of ploughing marginal or semi-arid land. Such risks are of course exacerbated if the land is sloping or subject to extremes of climate. Erosion of soil is not merely inimical to sustainable agriculture but also causes other economic losses such as the need to remove sediment from drainage systems and rivers.[41] Such erosion losses are of course very variable, but have been estimated to average about 10 tonne ha^{-1} year^{-1} for cropland soils in the USA.[42] Likewise, in Europe, trials have shown that use of non-inversion tillage in place of ploughing appreciably reduces water erosion and nutrient loss[43] and improves soil structure due to larger populations of earthworms.[44] In their book on no-tillage seeding, Baker *et al*[45] cite the benefits of such systems, which include reduced fuel requirements, improvement in levels of soil organic matter and in soil aeration, preservation of soil structure and soil fauna, and, most important, prevention of soil erosion.

Methods for reducing tillage were proposed in the late 1920s, but management of weeds remained a problem. With the introduction of paraquat in the 1960s, this could be overcome and many such agricultural systems were investigated. Seed drills were developed with improved coulter systems and these facilitated direct drilling. In the USA, Shear and Moschler[46] showed that maize could be drilled without cultivation, using a mixture of paraquat and atrazine to control weeds. This approach allowed farmers in hilly regions to extend their cropping from the valley bottoms up the slopes, which previously had to be left under permanent pasture to prevent erosion. A cropping system was developed whereby rye was direct drilled onto the slopes in autumn, and then, in spring, both rye and weeds were killed with paraquat prior to the direct drilling of maize. Special drills were developed for this purpose, and the technique spread rapidly. Today conservation tillage (a term which includes both direct drilling and minimum tillage) accounts for nearly 60% of the maize area in the USA (32 million ha) and 85% of the soybean area (28 million ha).

Another aspect of minimum cultivation that has recently received increasing attention is the reduced loss of soil organic carbon in such systems. The approximate doubling of carbon dioxide levels in the atmosphere over the past century, and with it the likely consequences of encouraging global warming, has placed premiums on agricultural systems that minimise carbon mineralisation.[47,48] The Earth's soils hold vast reserves of carbon, equivalent to about two to three times more than is stored in all the trees and other vegetation and about twice that present in the Earth's atmosphere. So cultivation systems that reduce carbon losses are important, such losses being greatest from ploughed grasslands and reclaimed forests. Heavy cultivation of soils encourages microbial breakdown of soil organic matter, leading to loss of carbon dioxide by mineralisation; minimum tillage reduces such losses and can allow old agricultural soils to increase their level of soil organic matter. The use of paraquat can aid this process by facilitating the adoption of minimal cultivation.

4.3 Plantation crops and orchards

Paraquat has been widely used in orchards, in plantation crops such as bananas, pineapples, oil palm and rubber, and also in vineyards. Its mode of action does not require the weeds to be in active growth and so, provided the weeds are in leaf, paraquat is effective even when applied in the winter months. The rapid uptake into plant tissue, typically sufficient in 30 min, allows use both in the dry season or at times and places when there is regular daily rainfall. As it is little translocated within plants, any paraquat inadvertently sprayed onto the leaves of the crop will only cause localised scorching from which the plant can soon recover. Also paraquat reaching tree trunks (or the pseudostems of banana plants) does not penetrate into the tissue and so causes no damage. Total control of vegetation in such crops is often not necessary, and strip weeding or ring-weeding around trees may be the preferred option. Even where the crop roots are shallow, paraquat can be used safely because it only acts on green tissues. Removal or reduction of competition by weeds for water and nutrients close to the crop plants usually gives a substantial increase in yield.

Repeated use, as often occurs in vineyards, kills annual weeds and keeps perennial weeds in check. However, in many areas it is desirable to maintain a cover of vegetation on the soil so as to avoid erosion problems, though strongly competitive weeds need to be discouraged. In oil-palm plantations in Malaysia, these competitive weeds tend to be broad-leaved species, (eg *Asystasia gangetica* T Anderson, *Mikania micrantha* Kunth, *Hedyotis verticillata* (L) Lam and *Ageratum conyzoides* L), together with volunteer seedlings of the oil palms themselves. The more desirable species (sometimes called 'soft' weeds) are grasses (*Axonopus compressus* (Sw) P Beauv, *Paspalum conjugatum* Bergius and *Ottochloa nodosa* (Kunth) Dandy). A move away from paraquat to glyphosate in the early 1990s led to the elimination of the grasses and a domination by the broad-leaved weeds together, with problems from the oil-palm seedlings against which glyphosate is ineffective. Reversion of this treatment policy has reduced the occurrence of the problem weeds and encouraged the grasses, and compromise regimes are now being used such as two spray rounds of paraquat alternating with one of glyphosate.[49,50] Lam *et al*[51] observed similar succession of weed flora in trials in rubber plantations when paraquat was replaced by glyphosate.

Banana production is widely practised in the humid tropics, where temperatures optimal for growth and regular rainfall occur throughout the year. Excess water is usually carried away by a network of drainage ditches and canals. However, such conditions can also encourage heavy infestations of pests, diseases and weeds. In order to ensure that banana production was sustainable, a study in Costa Rica compared biodiversity in commercial and low-input plantations, the former having received repeated applications over the previous 5 years of fungicides, nematicides and herbicides including paraquat. More species of beneficial parasitic wasps were recorded in the low-input holdings, but biological control of foliar insect pests was effective in both these and the commercial holdings. Though organic matter levels in the Andisol soils of the region were low, neither soil respiration nor numbers of litter-dwelling invertebrate species were influenced by the pesticide applications. The banks of the drainage systems are often planted with perennial grasses and low-growing trees and shrubs, both to trap accidental spray drift and to reduce erosion during high rainfall. This habitat attracts a good biodiversity of wildlife, including amphibians, lizards and birds. Paraquat can be used to control competing weeds in the plantations, leaving less vigorous perennial species to regenerate and so control erosion; also, being quickly sorbed to soil, it does not contaminate the water courses nor affect their bankside vegetation.

Another example is the use of paraquat as a desiccant in killing pineapple plants prior to replanting the new ratoons. Traditional methods involved cutting the plants at the base and leaving them to dry for 13 weeks before burning them, so clearing the land for the new crop. The application of paraquat to the old plants accelerates the desiccation process, such that the land can be cleared and replanted after 5 weeks.[52,53]

4.4 Smallholder agriculture

One of the earliest potential uses for paraquat was identified in horticulture, a relatively specialised small-scale market. However, this potential was soon extended to smallholder and indeed subsistence farming in developing countries. In Africa, the majority of farmers have less than 2.0 ha of land, and in Asia most such farms are similarly small at between 1.1 and 3.6 ha. One of the most labour-intensive tasks is hand weeding to allow the establishment of crops, and it is often this requirement above all else that limits the area of land that can be farmed successfully.[54–56] Some examples quoted are that seed-bed preparation and subsequent weed control comprise 56–74% of the total labour input in small farms in Nigeria, 16–40% for maize in Africa and 57% for cotton in the Gambia. Such high labour requirements not only limit the area of land that can be farmed by a family but also are such that the weed control achieved, typically by hoeing, on the land farmed may be inadequate to prevent some yield loss.

Another crop system used both in smallholdings and larger farms is the rotation of sugarcane and lucerne. Such farms also often have milk-producing cattle, as in the state of Maharastra in India. Lucerne feeds the cattle, and its nitrogen-fixing roots together with the cattle dung provide the fertiliser for the sugarcane which is the cash crop. Paraquat is used in two ways in this rotation. At about 15–20 days after emergence of the new sugarcane shoots, paraquat in tank mixture with the broad-leaf hormone herbicide 2,4-D is applied; although the paraquat slightly damages the emerging cane shoots, this has the beneficial effect of stimulating tillering. Weeds are controlled for about 45 days, by which time the crop canopy is closing and weeds are no longer able to compete. The second use is on the lucerne, this being harvested every 21 days; paraquat applied to the cut field kills or suppresses the weeds but, as it is not downwardly translocated, does not inhibit regrowth from the lucerne stem base. This complete system allows sustainable production with only low fertiliser input.

Another recent and increasing use of paraquat is in vegetable growing in China. For example, in the Guandong region over one million ha are devoted to high-quality vegetable production, with up to eight crops grown in succession each year. Given this intensity of cultivation, rapid turnaround between crops is essential to maximise production. Paraquat is used to treat weeds and crop trash to facilitate reseeding or replanting, such that the next crop can be sown within a day or so. The Gramoxone formulation of paraquat is now used this way on over 40% of the vegetable area. It can likewise be used pre-planting mixed with butachlor to give residual weed control, or indeed be applied with fertiliser. As the crop develops, paraquat can also be sprayed between the rows to control weeds, the developing crops being protected by use of spray shields. Weeds are killed within 1 or 2 days under these conditions. In these uses, the fast action of paraquat and its rapid deactivation by soil are key factors in saving several weeks per year of turnaround time between crops.

4.5 Direct-seeded rice

Rice growing has traditionally been very labour intensive both in weeding and preparing the land and in planting the rice as seedlings. In Indonesia, a major production system has been irrigated rice in paddyfields, which can grow two crops of transplanted rice a year. Though there is time for a third crop, lack of water usually only permits a poor crop of maize or soybean. However, recent studies have indicated that a third rice crop can be grown if this is direct-seeded, which can be sown earlier and so has a longer growing season to provide a good harvest. This approach requires minimum delay between harvesting the previous rice crop and the direct seeding. Furthermore, as rice seedlings are vulnerable to weed competition, a clean seedbed is required; this is achieved by killing weeds with paraquat prior to minimum cultivation and then direct seeding.

Success in this system opens up the opportunity to explore the use of paraquat in the traditional '*gogorancah*' system of rice growing in other parts of Indonesia. *Gogorancah* is a method of direct seeding rice into non-flooded soil in non-puddled, bunded fields.[57] This requires light tillage in the dry season to 12–15 cm depth, followed by a second tillage at the onset of the wet season. The rice seeds are then planted by broadcasting or dibbling into the moist soil. Some 5–6 weeks after germination, the fields are allowed to flood using natural rainfall. If the rain fails, then after about 10 weeks the rice can continue to be grown as dryland rice. This method avoids the time-consuming task of puddling the soil which delays planting and so can lead to the crop failing to mature if the rainy season is curtailed earlier than usual. Both some traditional and also improved varieties are compatible with this system, being capable of withstanding the change from aerobic moist soil to anaerobic flooded conditions which necessitates the plants growing a new root system to adapt to this change. Several weed species can compete strongly with the rice crop,[58,59] and hand weeding or the use of herbicides such as thiobencarb plus propanil, oxadiazon or glyphosate is necessary to maintain the yield potential. Such production systems have been introduced to Java and Lombok, with hand weeding comprising over 50% of the labour cost. It may be that paraquat can also be applied to the seedbed as a cost-effective herbicide to control weeds before the crop seeds germinate.

Another approach in Indonesia is the increasing production of tidal rice, as in Kalimantan. Here the high spring and neap tides form barriers to river flow, and so fresh or brackish water floods low-lying land for over 150 km inland. Approximately one million ha of tidal rice is grown in these areas, but the potential area is as much as 10 million ha. One problem is that iron pyrites underlies much of this area and, although this does not adversely affect the growth of rice, cultivation leads to soil erosion. The use of paraquat in no-till systems helps minimise erosion, and its rapid action ensures that it is effective on weeds even when they are flooded twice daily. The labour-saving in these systems, together with the fact that paraquat is affordable, means that a family can increase its rice cultivation from 0.5 to 1.5–2.0 ha of land, a very substantial increase in food production and income.

5 CONCLUSIONS

The unique properties of paraquat have maintained the use of this herbicide in many areas of agriculture over a period of nearly four decades. In the early testing and screening for herbicides, the properties of paraquat were not those of prime interest at the time, but scientists soon realised that agricultural systems could be devised around these unexpected properties. Chief amongst these are its rapid action, its lack of effect on roots and rhizomes and its rapid deactivation by strong sorption to soil. This last property is particularly important as it limits movement by leaching or in surface run-off, eliminates any possible ecotoxicological effects and allows rapid reseeding or replanting after the killing of weeds by paraquat.

Of major note is the use of paraquat in conservation tillage systems, which can control erosion in marginal areas as well as bringing other benefits. Paraquat has also found widespread use in orchards and plantation crops, either to control weeds or to manipulate the ground cover so as to minimise competition with the crop. A systematic approach to weed management based on paraquat is currently being developed for vines, olives and top fruit; this will help to maintain soil structural stability by avoiding cultivations and so minimise soil erosion in seasonally dry areas. Its use by smallholder farmers in many of the less developed countries has improved productivity and lessened the time and effort previously required to control weeds by hand. The increasing use of paraquat on tidal rice in Asia is based on its properties of water/rainfastness since there may be only a few hours between inundations. This fastness is not met by other herbicides that might be used in rice. Finally, recent advances in the cultivation of rice, using direct-seeding techniques with minimum tillage and use of paraquat to prepare the seed bed, are opening up new opportunities for food production in south-east Asia. Integrated with other herbicides and often used within conservation management regimes, paraquat has played an important role in improving agricultural production in many areas of the world. The cost/benefit analysis addressed in this paper shows that essentially no deleterious side-effects on non-target organisms have been observed, and that paraquat is ideally compatible with the principles of sustainable agriculture.

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