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Seventy-five herbicide use in agriculture: will there be 100?

Agronomic implications of paraquat ban in Brazil

Alfredo Junior P. Albrecht[a], Leandro P. Albrecht[a], André Felipe M. Silva[b*]

[a] Federal University of Paraná, Department of Agronomic Sciences, Palotina, PR, Brazil. [b] Crop Science Ltda., Maripá, PR, Brazil.

Abstract: Background: Paraquat is a broad spectrum herbicide used particularly in burndown, in pre-plant of row crops and in the pre-harvest desiccation of some crops. In Brazil, paraquat was re-evaluated by Anvisa, leading to a prohibition of production and sales on September 22, 2020, and used until July 31, 2021.

Objective: The objective of this review is to characterize the use of paraquat in Brazil and describe the status in other countries, particularly the agronomic implications of its ban, possible replacements, and scenarios.

Review: The use of paraquat is important for weed management in different production systems. Owing to its toxicity, its use has been re-evaluated in several countries. For pre-harvest desiccation of soybeans, diquat, glufosinate, and some combinations with Protox inhibitors are highlighted as alternatives to paraquat. For pre-harvest desiccation of common beans, diquat, saflufenacil, and glufosinate could be used; however, only glufosinate could be used for wheat. For managing broadleaves weeds, glufosinate, saflufenacil, carfentrazone, and diquat are effective alternatives. Diquat may be less effective in controlling *Conyza* spp. resistant to paraquat. For grasses control, glufosinate, in addition to ACCase inhibitors and possible mixtures, may be helpful. Although pre-emergent herbicides are not classified as desiccant herbicides, they contribute to weed management. The adoption of herbicide-tolerant crops, mechanical control, and cover crops can be added as agricultural practices for integrated weed management.

Conclusions: Due to the ban on paraquat, challenges arise, and the most often suggested replacements are glufosinate, diquat, and Protox inhibitors; however, grass control will be of greater concern.

Keywords: Bipyridylium; weeds; pre-harvest; herbicides

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* Corresponding author:
<afmoreirasilva@alumni.usp.br>

1. Introduction

Paraquat is a non-selective, broad-spectrum, photosystem I electron diversion (group 22), which can be used in burndown applications (Zobiole et al., 2018; Kalsing et al. 2020), in the pre-harvest desiccation of some crops (Bellaloui et al., 2020; Pereira et al., 2020), in interrow application (Costa et al., 2013) and in non-agriculture areas (e.g., under electric transmission lines, railways, and roadsides). However, it has been banned in several countries (Camargo et al., 2020; Kim, Kim, 2020; Tsai, 2020).

Paraquat is highly toxic to mammals (Baltazar et al., 2013a) and has moderate to high acute oral toxicity, high acute inhalation toxicity, and low dermal toxicity. Moreover, it has severe ocular and moderate skin irritant potential (Kim, Kim, 2020). Once ingested, paraquat causes highly acute toxicity in humans, and survival depends on the amount consumed and the time until treatment begins (Gil et al., 2008). Studies have suggested an association between exposure to paraquat and Parkinson's disease (Tamano et al., 2019; Tangamornsuksan et al., 2019). Given its toxicity, paraquat was used for suicide or attempted suicide in Asian countries such as South Korea and Taiwan. Due to the ban on the molecule in these countries, suicidal rates were reduced (Kim, Kim, 2020; Tsai, 2020). There is no specific antidote for paraquat poisoning (Kumar et al., 2016).

In Brazil, the Anvisa promote a re-evaluation of paraquat from 2008 to 2017 due to its high toxicity (Agência Nacional de Vigilância Sanitária, 2017). In 2017, after the review, paraquat was temporarily banned. Due to lack of alternatives for replacement of paraquat in the field, the decision was revised, and a usage restriction was issued from September 22, 2017, to September 22, 2020, when paraquat was permanently banned (Camargo et al., 2020). However, although with several restrictions, stocked paraquat use was allowed in the 2020/21 growing season (until July 31, 2021) (Agência Nacional de Vigilância Sanitária, 2020a).

As of September 22, 2020, with the ban on the production, commercialization, and the use of paraquat as of 2021, Brazil is experiencing a substantial agronomic impact due to the extensive use of paraquat in the production systems. Thus, this study aims to characterize the previous use of paraquat in Brazil, the situation in other countries, and particularly the agronomic implications of its ban in the country, possible replacements, and impact.

2. Paraquat: mode of action and historical aspects

Paraquat and diquat are bipyridylium herbicides with photosystem I electron diversion mode of action. They have contact action, limited translocation and rapid leaf absorption, with a broad spectrum of weed control (Bromilow, 2004; Rodrigues, Almeida, 2018). Herbicides in this group act as false electron acceptors in photosystem I, producing reactive oxygen species. Plant death occurs due to the destruction of fatty acids in thylakoids and other membranes by producing free radicals, which cause, necrosis, and finally, plant death. Symptoms can be observed within a few hours after application, under bright light conditions, and plant death can occur in up to one day (Bromilow, 2004; Hawkes et al., 2014). Paraquat has a high sorption coefficient (Koc) (Amondham et al., 2006; Muhamad et al., 2011). This strong bond significantly limits its bioavailability in the soil; therefore, it is not toxic to plant roots under normal application conditions, that help explain lack of effectiveness on weeds at pre-emergence. Although it is not bioavailable for roots in the soil, due to its high Koc, paraquat has a half-life of approximately six years (Pateiro-Moure et al., 2009) and with low degradation by microorganisms (Roberts et al., 2002). These aspects can prolong its persistence in the soil and contaminate other environments, such as water bodies (Huang et al., 2019). Regarding the vapor pressure, it has a negligible value at room temperature, practically non-volatile (Sartori, Vidrio, 2018).

Bipyridylium compounds were first recognized as herbicides in 1954 in the United Kingdom by the Imperial Chemical Industries (ICI) (Cronshey, 1961; Funderburk, Lawrence, 1964; Akhavein, Linscott, 1968). Diquat was the first to be discovered. In 1955, paraquat salts were also considered active. Paraquat, a known chemical since 1882, has been used since 1932 under the name of methyl viologen as an oxy-reduction indicator (Bromilow, 2004).

Paraquat was vital to establish the non-till system in agriculture, one of the primary conservation grain production systems. The non-till system was initially developed by ICI and partners, which involved paraquat and the use of special equipments to drill in non-tilled soils. No-till and paraquat were introduced in the United States in 1960, with the first reports of commercial use of no-till between 1962 and 1966 (Ekboir, 2003). In Brazil, the technology began to be tested in the 1970s, with the first experiments carried out in Londrina (state of Paraná) and Passo Fundo (state of Rio Grande do Sul), between and 1972-1974, using paraquat (Wiles, Hayward, 1981). After the first studies, between the end of the 1970s and the beginning of the 1980s, other herbicides, mainly glyphosate, were used, and paraquat use declined in no-till (Ekboir, 2003; Bolliger et al., 2006).

The development and adoption of the no-till system are essential for conserving soils in areas of grain crops in Brazil, generating agricultural, environmental, and social benefits (Freitas, Landers, 2014). Therefore, paraquat is of great importance to implement the system. In addition, the increase in the use of paraquat in pre-sown burndown application in the 1990s became one of the main uses of this herbicide. It is effective for weed control and desiccation of previous crops (Neves et al., 1999; Argenta et al., 2001).

With the adoption of transgenic crops tolerant to glyphosate, the consequent increase in the use of this herbicide, and its application in post-emergence on these crops, glyphosate-resistant weed biotypes have been observed. Thus, other herbicides have become even more critical to reduce the selection pressure for new resistant biotypes and for their control. Therefore, paraquat use increased for pre-sowing burndown of soybeans and other crops, as an alternative or combined with glyphosate, to control grasses such as *Digitaria insularis* (Marochi et al., 2018) and broadleaves such as *Conyza* spp. (Cesco et al., 2019), both of which can be resistant to glyphosate.

3. Overview of paraquat use in Brazil and other countries

As previously mentioned, paraquat was banned on September 22, 2020; however, products in stock could be used in the 2020/21 growing season, with restrictions (Agência Nacional de Vigilância Sanitária, 2020a). A total ban was implemented on July 31, 2021, and paraquat could not be used in any crop or region in Brazil.

Nowadays, paraquat is banned in more than 50 countries worldwide, including China, South Korea, the European Union, and the United Kingdom. In other countries such as the United States, Australia, Colombia, Chile, Uruguay, and Japan, paraquat is under re-evaluation and/or use in strictly controlled use (Baltazar et al., 2013b; Camargo et al., 2020; Kim, Kim, 2020; Tsai, 2020).

Paraquat was banned in South Korea in 2012. One of the reasons for the ban was many number of suicides by ingesting paraquat. The paraquat ban significantly impacted agricultural practices and was replaced mainly by glyphosate, glufosinate, and some Protox inhibitors. Although there was a reduction (46.1%) in the total number of suicides from pesticide ingestion (with the paraquat ban), there was an increase in suicide attempts with other pesticides (Kim, Kim, 2020) demonstrating the complexity of this topic.

In Sri Lanka, the most rigid restrictions on the use and import of paraquat were established in 2008, with a definitive ban in 2014 (Marambe, Herath, 2020). The decision to ban paraquat did not generate significant arguments because detailed studies were performed on its health risks, which led to this decision. Due to the restrictions, there has been a considerable increase in the use of glyphosate, which was banned in Sri Lanka in 2015. The ban on glyphosate in Sri Lanka has impacted agricultural practices and discussions. In contrast to paraquat, many researchers and farmers claim that the studies that led to the glyphosate ban were not scientifically proven and conclusive.

With the ban of paraquat in Brazil, it is necessary to understand the situations in which it is used, the implications of its prohibition, and alternatives to its use. In Brazil, paraquat is one of the most used pesticides.

According to *Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis* – Ibama (2022), in 2019, paraquat was the seventh most commercialized pesticide (16,398.14 t active ingredient – a.i.) and the fourth most commercialized herbicide, behind atrazine, 2,4-D, and glyphosate, which was the most commercialized with 217,592.24. More than 10,000 tons of a.i. paraquat have been sold each year since 2015 until 2019, with an increase, particularly in recent years. In 2020, there was a lower sale of paraquat (8,120.21 t a.i.) since it was banned from 22 September. Further information on the pesticides sales in Brazil between 2011 and 2020, particularly paraquat, is presented in Table 1. These data reinforce the importance of paraquat in Brazilian agriculture; therefore, it becomes even more essential to characterize the use of paraquat in the country, the implications of its ban, and the alternatives for its replacement.

4. Pre-harvest desiccation

Paraquat is widely used for pre-harvest desiccation in various crops, such as cotton, rice, potatoes, sugarcane, maize, and soybeans (Rodrigues, Almeida, 2018; Ministério da Agricultura, Pecuária e Abastecimento, 2022). A complete list of crops with herbicides registered for pre-harvest desiccation are presented in Table 2. In this method of use, paraquat was applied at the physiological maturity of the crops (Rodrigues, Almeida, 2018), as it is a contact herbicide with very limited translocation, application at the appropriate stage ensures non-accumulation in food. The maximum residue limits, in mg kg^{-1} of paraquat, was 0.5 for rice, 0.2 for cotton, potatoes, and 0.1 for sugarcane, maize, and soybeans, respectively (Agência Nacional de Vigilância Sanitária, 2020b).

Table 1 - Sales of pesticides, total of herbicide and paraquat in Brazil in the period 2011-2020.

Year	Pesticides	Herbicides	Paraquat	
	tons (ai)	tons (ai)	tons (ai)	L (cp)*
2011	419,528.63	221,329.57	4,275.38	21,376.88
2012	476,554.86	298,872.07	5,249.54	26,247.69
2013	495,772.60	303,573.23	6,792.69	33,963.45
2014	508,556.84	294,915.53	8,404.76	42,023.79
2015	521,525.40	314,452.55	10,536.60	52,683.01
2016	541,861.09	322,755.10	11,638.19	58,190.94
2017	539,944.95	315,573.38	11,756.39	58,781.97
2018	549,280.44	338,838.14	13,199.97	65,999.84
2019	620,537.98	369,578.94	16,398.14	81,990.70
2020	685,745.68	413,833.41	8,120.21**	40,601.05**

c.p.: commercial product

* Estimate based on a concentration of 200 g ai L^{-1}.

** Ban of paraquat sales on 22 September 2020.

Source: adapted from IBAMA (2022).

Pre-harvest desiccation of soybeans can standardize plant maturity, predict harvest, control weeds, and minimize the loss in grain quality (Boudreaux, Griffin, 2011; Toledo et al., 2012; Lamego et al., 2013). In addition to paraquat, other herbicides have been used for this purpose. Some studies have reported the efficacy of glufosinate (Delgado et al., 2015), diquat (Finoto et al., 2017; Araújo et al. 2018), carfentrazone (Pereira et al., 2015), saflufenacil (Zuffo et al., 2020) and flumioxazin (Carvalho, 2017). Zagonel (2005) observed equivalent efficacies for the application of diquat (200 g a.i. ha^{-1}), paraquat (200 g a.i. ha^{-1}), and glufosinate (200 g a.i. ha^{-1}) for the desiccation of soybean without reducing yield. In addition, some combinations of glufosinate with protox-inhibiting herbicides, such as carfentrazone, flumioxazin, and saflufenacil, can be promising for pre-harvest desiccation in soybeans. For the use of protox-inhibiting herbicides in this modality, attention must be paid to the moment/stage of application, considering the growth habit of soybeans, avoiding the anticipation of products with pronounced and rapid contact effects.

Although paraquat has no registry for pre-harvest bean desiccation in Brazil, this herbicide was occasionally used for this purpose by farmers. The effectiveness of paraquat in this modality has been highlighted in several studies (Pinto et al., 2014; Goffnett et al., 2016). Saflufenacil has been evaluated in some studies; in general, it is a good defoliant; however, it can interfere with the quality of seeds or bean yield (Goffnett et al., 2016; Castoldi et al., 2019; Silva et al., 2020), requiring adequate positioning to achieve the expected performance. Other options for paraquat include glufosinate (Soltani et al., 2013; Goffnett et al., 2016; Castoldi et al., 2019), diquat (Soltani et al., 2013; McNaughton et al., 2015) and flumioxazin (Soltani et al., 2013). Therefore, diquat and glufosinate, particularly, should have increased in the pre-harvest desiccation of beans.

Paraquat has not been registered in Brazil for pre-harvest desiccation of wheat; however, the effectiveness

Table 2 - Herbicides registered in Brazil for application pre-harvest.

Herbicide	Crops with registration
Paraquat*	Cotton, rice, potato, sugarcane, maize, and soybean
Glufosinate	Potato, sugarcane, barley, peas, bean, chickpea, lentil, soybean, and wheat
Diquat	Potato, bean, and soybean
Saflufenacil	Cotton, potato, bean, sunflower, and soybean
Carfentrazone	Cotton and sugarcane
Flumioxazin	Bean and soybean

Source: adapted from Rodrigues and Almeida (2018) and MAPA (2022).

* Banned on July 31, 2021.

of paraquat in pre-harvest desiccating of wheat has been observed in some studies (Krenchinski et al., 2017; Perboni et al., 2018). However, desiccation in this crop is a very complex treatment. The efficiency, quality of seeds, and productivity can be affected by the stage of application, herbicide, and cultivar, among other elements. Krenchinski et al. (2017) reported that reductions in wheat yield were found for desiccation with glufosinate, paraquat, glyphosate, clethodim, and diquat; only the carfentrazone did not reduce yield in both locations of the experiments.

Only glufosinate at a dose of 350 g a.i. ha^{-1} has a registration for wheat desiccation (Rodrigues, Almeida, 2018; Ministério da Agricultura, Pecuária e Abastecimento, 2022). Other studies provide evidence of its potential safety. The application of glufosinate (400 g a.i. ha^{-1}) pre-harvest, at the milky to soft dough grain, soft dough to hard dough grain, or hard grain did not reduce wheat yield, even without any residue in grains for application in the hard grain stage (Perboni et al., 2018). Thus, this herbicide will continue to be used to manage pre-harvest desiccation in wheat to achieve standardization objectives, weed control, quality improvement, and reduction of yield losses.

Among the other crops in which pre-harvest desiccation is usual, the possible scenarios in potato crop (*Solanum tuberosum*) are worth mentioning. The herbicides glufosinate, saflufenacil, and diquat are effective for this purpose (Ferebee et al., 2019) and are registered in Brazil (Ministério da Agricultura, Pecuária e Abastecimento, 2022). These herbicides should be considered good alternatives to paraquat in the desiccation of potato plants.

5. Weed management

Paraquat is a contact herbicide that rapidly affects susceptible weeds and controls a broad spectrum of weeds. In the recent history of paraquat and Brazilian agriculture, the primary use of paraquat is in burndown on pre-sowing of several crops. In weed control, in advance of soybean, the main agricultural crop in Brazil, paraquat is predominantly used in applications immediately before or immediately after sowing soybeans. Paraquat is widely used in off-season management and is more used in the second or third sequential application. The last one before or immediately after sowing, it is used alone or combined with a pre-emergent herbicide (Figure 1). Table 3 presents the direct and possible substitutions in systems involving soybeans.

Paraquat is widely used to control species such as *Conyza* spp., in Brazil and other countries, during the off-season and in pre-sowing, after the application of glyphosate plus other herbicides (Santos et al., 2015; Zobiole et al., 2018; Cesco et al., 2019; Flessner, Pittman, 2019; Soltani et al., 2020). In recent years, there has been a reduction in the effectiveness of paraquat in controlling *Conyza* spp. in Brazil. Cases of *Conyza sumatrensis* biotypes resistant to paraquat have been reported, and some biotypes have multiple resistance to paraquat and other herbicides (Pinho et al., 2019; Zobiole et al., 2019; Albrecht et al., 2020a).

There are 72 cases of weed biotypes resistant to paraquat worldwide (Table 4), in which *Conyza bonariensis*, *C. canadensis*, and *C. sumatrensis* represent 21 cases of biotypes resistant to this herbicide (Heap, 2022). In addition to the cases in Brazil, *C. sumatrensis* is reported to be resistant to paraquat and multiple herbicides in Paraguay (Albrecht et al., 2020b). These reports indicate that the performance of paraquat is decreasing because of its repeated use and increases selection pressure, highlighting the need for its replacement in the management of resistant weeds.

Thus, for the management of *Conyza* spp., even without paraquat banning, it would be necessary to use alternative herbicides in the pre-sowing burndown of soybeans. The ban on paraquat reinforces the need for the characterization and configuration of new management. Therefore, glufosinate has been highlighted (Eubank et al., 2008; Frene et al., 2018; Tahmasebi et al., 2018; Albrecht et al., 2020c; Cantu et al., 2021). Saflufenacil can also be used as an alternative for the control of *Conyza* spp. (Zimmer et al., 2018; Hedges et al., 2019). Some studies have indicated a synergistic effect of combinations of saflufenacil and glyphosate in the control of *Conyza* spp. (Dalazen et al., 2015; Piasecki et al., 2020), or even combined with the glufosinate mentioned above, in the control of other species that are difficult to control, such as *Amaranthus palmeri* (Takano et al., 2020a). These and other studies indicate that glufosinate and saflufenacil are important alternatives to paraquat in pre-sowing burndown, in the managing *Conyza* spp. and other weeds, particularly broadleaves, including the combination of these molecules, is very effective.

The synergistic effect of mixtures, such as glufosinate and protox-inhibiting herbicides, such as saflufenacil and carfentrazone, is a possible replacement for paraquat. Due to the paraquat ban, mixture is necessary for weed resistance management. Weeds proved to be resistant,

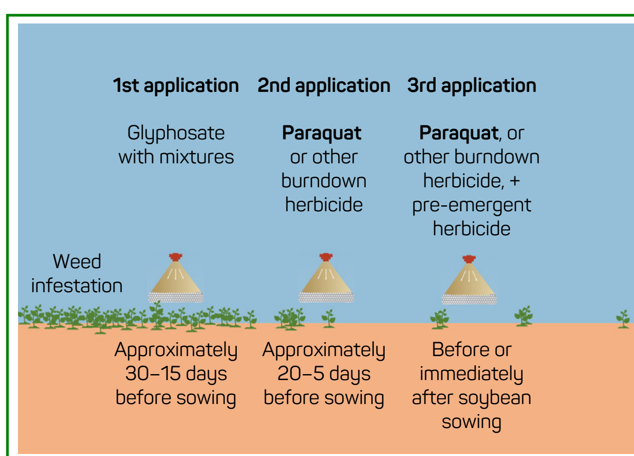

Figure 1 - Exemplification of applications in burndown soybean pre-sowing.

Table 3 - Herbicides for potential use in soybean pre-sowing burndown, to replace paraquat, for weeds that are difficult to control in Brazil.

Weed	Herbicide	References supporting the indication
Conyza spp.	Glufosinate	Oliveira Neto et al. (2010), Frene et al. (2018), Tahmasebi et al. (2018), Albrecht et al. (2020c)
	Diquat[1]	Gitsopoulos et al. (2018), Pinho et al. (2019), Zobiole et al. (2019), Albrecht et al. (2020a)
	Saflufenacil[2]	Dalazen et al. (2015), Zimmer et al. (2018), Cesco et al. (2019), Hedges et al. (2019), Piasecki et al. (2020)
Digitaria insularis	Glufosinate	Melo et al. (2012), Gemelli et al. (2013)
	ACCase[3]	Correia et al. (2015), Cassol et al. (2019), Vilela et al. (2019), Bianchi et al. (2020)
	Glyphosate[4]	Correia and Durigan (2009), Bianchi et al. (2020)
Eleusine indica	Glufosinate	Ulguim et al. (2013), Alcantara et al. (2016)
	ACCase[5]	Ulguim et al. (2013), Alcantara et al. (2016), Vilela et al. (2019)
	Glyphosate[4]	Ulguim et al. (2013), Minozzi et al. (2017)
Lolium spp.	Glufosinate	Schneider et al. (2015)
	Glyphosate[4]	Christoffoleti et al. (2005), Pereira et al. (2017)
	ACCase[5]	Roman et al. (2004), Christoffoleti et al. (2005), Pereira et al. (2017)
	ALS[6]	Trusler et al. (2007), Pereira et al. (2017)
Amaranthus spp.	Glufosinate	Sarangi et al. (2019), Takano et al. (2020a)
	Diquat	Dudic et al. (2020)
	Saflufenacil[2]	Sarangi et al. (2019)
	Glyphosate[4]	Norsworthy et al. (2008), Sarangi et al. (2019), Dudic et al. (2020)
	ALS[6]	Norsworthy et al. (2008), Chahal et al. (2018), Sarangi et al. (2019)
	Carfentrazone	Legleiter and Bradley (2008), Norsworthy et al. (2008)
	Flumioxazin	Norsworthy et al. (2008)
Spermacoce spp.	Glufosinate	Gallon et al. (2019), Kalsing et al. (2020)
	Saflufenacil[2]	Fadin et al. (2018), Gallon et al. (2019)
	Carfentrazone	Martins and Christoffoleti (2014)
	Flumioxazin	Fadin et al. (2018), Carbonari et al. (2020)
	ALS	Ramires et al. (2011), Martins and Christoffoleti (2014), Fadin et al. (2018)
Richardia brasiliensis	Glufosinate	Gallon et al. (2019), Kalsing et al. (2020)
	Diquat	Sharpe and Boyd (2019)
	Saflufenacil[2]	Vitorino et al. (2012), Gallon et al. (2019)
	Carfentrazone	Monquero et al. (2001), Gallon et al. (2019)
	Flumioxazin	Monquero et al. (2001), Gallon et al. (2019)
	ALS	Gallon et al. (2019), Kalsing et al. (2020)
Commelina spp.	Glufosinate	Brito et al. (2017), Ferreira et al. (2017)
	Diquat	Rodrigues and Almeida (2018)
	Saflufenacil[2]	Castro et al. (2017), Santos Junior et al. (2019)
	Carfentrazone	Maciel et al. (2011), Ferreira et al. (2017), Krolikowski et al. (2017)
	Flumioxazin	Silva et al. (2019), Carbonari et al. (2020)
	ALS	Maciel et al. (2011), Ramires et al. (2011)
Ambrosia artemisiifolia	Glufosinate	Barnes et al. (2017), Ganie and Jhala (2017)
	Saflufenacil[2]	Vink et al. (2012), Van Wely et al. (2014)
	Carfentrazone	Vink et al. (2012)
	Flumioxazin	Niekamp and Johnson (2001), Barnes et al. (2017)
	ALS	Van Wely et al. (2014), Ganie and Jhala (2017)
Andropogon bicornis	ACCase	Azevedo et al. (1999)

[1]When there is no paraquat-resistant. [2]Preferably associated with glyphosate. [3]Herbicides from the group of ACCase inhibitors, in the case of *D. insularis*, especially clethodim, haloxyfop and quizalofop when rhizomatous. [4]When there is no resistance to glyphosate. [5]Herbicides from the ACCase inhibitor group when there is no resistance to them. [6]ALS-inhibiting herbicides, when there is no resistance to them, in the case of *L. multiflorum*, especially imidazolinones and sulfonylureas.

Table 4 - Reported cases of weed species biotypes resistant to paraquat, diquat, and multiple, worldwide (March 2022).

Weed	Paraquat	Paraquat and diquat	Multiple
Alopecurus japonicus	1	-	-
Amaranthus blitum ssp. *oleraceus*	1	-	-
Bidens Pilosa	1	-	-
Convolvulus arvensis	1	-	-
Conyza bonariensis	3	1	1
Conyza canadensis	5	-	2
Conyza sumatrensis	5	1	3
Crassocephalum crepidioides	1	-	-
Cuphea carthagenenis	1	-	-
Eleusine indica	6	-	4
Epilobium ciliatum	2	-	-
Erigeron philadelphicus	1	-	-
Gamochaeta pensylvanica	2	-	-
Hedyotis verticillata	-	-	1
Hordeum murinum ssp. *glaucum*	-	2	-
Hordeum murinum ssp. *leporinum*	1	1	-
Ischaemum rugosum	1	-	-
Landoltia punctata	-	1	-
Lepidium virginicum	-	-	-
Lolium perenne ssp. *multiflorum*	-	-	2
Lolium rigidum	1	-	3
Mazus fauriei	1	-	-
Mazus pumilus	1	-	-
Mitracarpus hirtus	-	1	-
Poa annua	2	-	-
Sclerochloa dura	1	-	-
Solanum americanum	2	-	-
Solanum nigrum	3	-	-
Solanum ptycanthum	1	-	-
Vulpia bromoides	-	1	-
Youngia japonica	1	1	-

Source: adapted from Heap (2022).

demand more sophistication in chemical control, and strategies for integrated weed management.

Another potential substitute for paraquat in pre-sowing burndown is diquat, mainly for the managing of broadleaf weeds (Travlos, Chachalis, 2010; Gitsopoulos et al., 2018). However, to control *Conyza* spp., in plants with high resistance to paraquat, these herbicides have the same mechanism of action and the same chemical group (bipyridylium); therefore, the performance of the control was below the required level. For grasses such as *Digitaria insularis, Eleusine indica,* and *Lolium multiflorum*, diquat is not an excellent alternative for management. Generally, diquat has low efficacy but can be increased when combined with adjuvants; however, it still has unsatisfactory levels of control (Gitsopoulos et al., 2014). Its combination with ACCase-inhibiting graminicides and others still needs to be better elucidated for consistent application in the field.

Glufosinate, which can control *Conyza* spp. and other weeds, is also effective in the control of *Digitaria sanguinalis* (Aulakh, Jhala, 2015), *D. insularis* (Melo et al., 2012; Gemelli et al., 2013), and *L. multiflorum* (Schneider et al., 2015) and is promising for use in other grasses, when at an adequate stage for control or management in sequential applications. ACCase-inhibiting herbicides are prominent in managing these grasses (Correia et al., 2015; Vilela et al., 2019), in addition to ALS inhibitors and contact herbicides (Silva et al., 2017).

Paraquat is important for the control of grasses, particularly *L. multiflorum* (Pereira et al., 2017). However, when it was no longer an option, and considering the cases of resistance to glyphosate and ACCase inhibitors, in Brazil, of *D. insularis* (Carvalho et al., 2011; Takano et al., 2020b), *E. indica* (Vidal et al., 2006; Takano et al., 2017), and *L. multiflorum* (Roman et al., 2004; Vargas et al., 2016), the possibilities are becoming scarce. Therefore, combining herbicides and other tactics in grass management during pre-sowing is a requirement.

The combination of chemical control with mowing effectively controls *D. insularis* as an alternative, particularly for perennial plants (Correia et al., 2015; Raimondi et al., 2020). All possible control strategies must be used and associated with the diversification of production systems. Therefore, mechanical control practices, such as mowing or mechanical weeding, are potentially more requested in the field.

Diversifying tactics and observing the requirement for herbicide combinations within chemical control will demand greater technical accuracy applying such practices in the field. An example of these emerging challenges, whether in the replacement of paraquat or another herbicide due to resistance, is the need to avoid incompatible and antagonistic mixtures. The benefits of mixtures of herbicides can be significant and synergistic, which is desirable; however, problems can become more and reoccur. The low performance of combinations of herbicides with an immediate contact effect, such as diquat, with systemic herbicides, has been reported (Wehtje et al., 2008). In addition, there is antagonism between ACCase inhibitors and synthetic auxins (Underwood et al., 2016; Webster et al., 2019; Bauer et al., 2021) or between ACCase inhibitors and ALS inhibitors.

Although they are not classified as burndown herbicides, pre-emergent herbicides contribute to managing weeds, such as *D. insularis* and *Conyza* spp. The use of these herbicides has already been recommended even without the ban of paraquat. Due to the cases of resistance and its prohibition, pre-emergent herbicides have become more significant. Therefore, the pre-emergent herbicides are considerable in control, diminishing emergence flows from the soil seed bank, contributing to the prolongation of the period before interference in the crop and is essential in the management of resistance (by reducing the pressure of selection).

To control *D. insularis* and other grassy weeds, the herbicides s-metolachlor, flumioxazin, imazethapyr, sulfentrazone, clomazone can be used (Drehmer et al., 2015), with effective control in management systems with cover crops (Marochi et al., 2018). In addition, the initial growth-inhibiting herbicides, such as pendimethalin and trifluralin, or commercial premixes, such as flumioxazin/imazethapyr, sulfentrazone/diuron, and imazapic/imazapyr, can be used for weed control. In the case of grasses, pre-emergent herbicides are essential alternatives in the rotation of mechanisms of action to avoid the possible selection pressure for resistance and to help preserve the few herbicide molecules still effective in the post-emergence of some species.

To manage *Conyza* spp. and other eudicot weeds, herbicides can be highlighted, either with action in pre- or post-emergence, ALS inhibitors (cloransulam, chlorimuron, diclosulam, imazethapyr, imazapic) (Braz et al., 2017; Cesco et al., 2019). In addition, pre-emergent protox-inhibiting herbicides, such as flumioxazin and sulfentrazone (Zimmer et al., 2018). Furthermore, some commercial premixes are already available to the producer or soon available, such as sulfentrazone/diuron, imazethapyr/flumioxazin, saflufenacil/imazethapyr, among others (Albrecht et al., 2020c). Moreover, non-chemical measures, such as cover crops and straw formation, should be highlighted for the management of *Conyza* spp. (Campiglia et al., 2015; Guareschi et al., 2020), and other weeds.

New herbicide-resistant crops technologies must be included in the management strategy. The technologies Enlist E3™ (tolerance to 2,4-D, glyphosate, and glufosinate), Roundup Ready™ 2 Xtend™ (dicamba and glyphosate), Liberty Link® GT27™ (glufosinate, glyphosate, and isoxaflutole) will bring options for weed management in the pre- or post-emergence stages of the crop. For maize, combining technologies with the possibility of using glyphosate, glufosinate, haloxyfop, and 2,4-D will be useful. All these herbicides, in different situations, with various transgenic events (current and to come), can be used with other tools, providing alternative management in the absence of paraquat.

Therefore, replacing paraquat with another herbicide is not always possible, with equivalent results and similar costs. The use of herbicides that require more significant investment and the need for herbicide mixtures, with action in pre- or post-emergence, will be a routine in many scenarios, particularly in the absence of paraquat, single or multiple resistance to herbicides is identified in the target population. Possible increases in the cost of herbicides are justified because of potential losses due to weed interference. Herbicide-tolerant transgenic crops can be used as auxiliary tools, allowing the inclusion of new herbicides, including post-emergence of the crop, generating specific compensatory effects due to the lack of paraquat and resistance management. However, there will never be nor have there been single solutions, and it is increasingly necessary to include other controls, such as cultural and mechanical. In integrated weed management, the combination of control strategies within good agricultural practices is vital.

6. Conclusions

Paraquat has been widely used herbicide, with many notable advantages and benefits. Nevertheless, its banning forces new approaches, caused by necessary adjustments in the positioning of substitute herbicides in pre-harvest desiccation and weed management. The substitutes for pre-harvest desiccation of different crops are diquat, glufosinate, and protox-inhibiting herbicides. For weed management, there is higher diversity, including glufosinate, diquat, saflufenacil, and numerous possible mixtures. However, the most significant challenge is finding alternatives for grasses weed control.

Author's contributions

AJPA and LPA: conceptualization, writing of the manuscript, and final approval. AFMS: Writing of the manuscript and critically reviewing the literature and formatting as per journal's format.

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Conflict of Interest

The authors declare no conflict of interest.

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