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SPECIAL ISSUE
REVIEW
Seventy-five years of synthetic herbicide use in agriculture: Will there be 100?

From sea salt to glyphosate salt: a history of herbicide use in France

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Abstract: Herbicide use has deeply changed weed management and cultivation practices in France as well as round the world. However, the use of herbicides is more and more questioned, so that it appeared interesting to us to take stock of herbicide use in France. Since 1913, it has been possible to reconstruct the marketing and withdrawal of all the herbicidal active substances used in cultivated plots. Developed to compensate for the lack of manpower, chemical weed control started at the end of the 19th century with the use of mineral molecules. While copper sulfate can be considered as the first active substance with which technical experiments were carried out, sulfuric acid was the molecule that saw the greatest development because of its efficiency. The discovery of active substances in the United States and Great Britain during World War II allowed for the development of selective weed control, first for eudicotyledonous plants and then for grasses. In France, a total of 233 active substances have been authorized either alone or in combinations. Active substances have been used for more than 27 years on average, but 2,4-D and MCPA have been used continuously for more than 75 years. The effects of these molecules on the environment and health are responsible for most of the questions about their use. The withdrawal of key molecules could soon call into question the very effectiveness of weed control and perhaps put an end to an agronomic innovation that has been in use for nearly one hundred years.

Keywords: active substance; combination; historical use; chemical weed management; herbicide resistance; HRAC groups; herbicide ban; environmental regulation

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1. Introduction

The history of herbicide use began in France at the end of the 19th century. As in many European countries, various social and economic factors caused a significant decrease of the available workforce for weeding crops from (Bain et al., 2010). As a result, the use of products that destroyed unwanted plants appeared to be one of the crucial solutions for maintaining agricultural production (Fron, 1917). Different pre-existing chemical substances with a potential herbicidal action were tested over time. In non-cultivated areas, sodium arsenite (1907), sodium biphosphate (1920), sodium chlorate and ammonium chlorate (1925) were used to weed paths and yards (Vermorel, 1926). In agricultural areas, from the end of the 19th century, copper sulfate (1896), zinc and iron sulfate (1898), copper and sodium nitrate (1898) and zinc sulfate (1899) made it possible to achieve the first selective weed control (Rabaté, 1927; Vermorel, 1926; Vilcoq, 1899;).

Copper sulfate was identified as a herbicide by a wine grower – Mr. Bonnet – by accident in 1896. It was the first ever solution studied from practical and technical points of view in France to determine efficient doses and the best application periods (Poubelle, 1898). With the aim of managing high densities of weed species belonging to the Cruciferae family – *Sinapis arvensis* and *Raphanus raphanistrum*, broad-leaved and flat-leaved eudicotyledonous plants –, the effectiveness and the cost of treatments were evaluated for the different crops (Fron, 1917). Despite the development of the first horse-drawn sprayers to facilitate the application of copper sulfate, the very high doses to be applied (30-40 kg ha^{-1}) made the use of this solution unattractive and costly compared to other products.

World War I poison gases and toxic dusts (Guérin, 1921) completed this frightening list of attempts to develop "*des poisons des plantes*" (plant poisons) (Rabaté, 1927). These first trials and findings were the subject of numerous communications in national and local agricultural journals. The application of some of these products (sodium bisulfate, sodium chlorate, sulfuric acid) was not without a risk for farmers (Carbonière, 1925); sodium arsenite was first compound to be banned in 1915 because of its harmfulness (Truffaut, 1938). The dangerousness of some of these products may explain the continued use of less effective but more flexible and less dangerous substances such as copper nitrate (Fron, 1917).

On a larger scale, sulfuric acid (1913) and sea salt (1924) were used in cultivated fields to control high densities of broad-leaved weeds such as *S. arvensis*, one of the most troublesome weeds at the time (Rabaté, 1927). In the case of sea salt (Dessaisaix, 1925), 375-600 kg of salt per hectare seemed to provide acceptable control of broad-leaved weeds such as Brassicaceae species, but also of other weed species such as *Chenopodium* sp., *Matricaria* sp. and even perennial species such as *Convolvulus* sp. Improvements in the application procedure, the development of spreading equipment and the low cost of the product allowed it to be used until the 1940's. The first tests with sulfuric acid were carried out at the end of the 19th century but failed. However, sulfuric acid at adapted dilutions was tested in the 1910's by an agricultural engineer who gave his name to the method (Rabaté method; Rabaté, 1911). Sulfuric acid was widely used after 1930 and ranked ahead of the other products. Its larger spectrum allowed for the control of a wider range of broad-leaved weeds. It was applied on winter cereals, but also on flax or alfalfa (Rabaté, 1927) and was still in use after world War II. This active substance was tested all over the world to improve its use and better define its spectrum of action (Aslander, 1927).

At the very beginning, the term 'herbicide' was used as an adjective to describe a tool used for weed control, e.g., "*une faux herbicide*" (a herbicidal scythe) or "un sel herbicide" (a herbicidal salt). In 1910, an advertisement in a horticultural magazine for a product used for weeding paths referred to the product as a "herbicide". The term "*désherbant*", which was widely used in French agronomy books after World War II, is far less used nowadays.

The commercial product Sinox© (DNOC - sodium dinitro-o-cresulate) was the first major organic chemical herbicide developed in France in 1933. This active substance was sold with a particular focus on *S. arvensis* in winter cereals (Truffaut, Pastac, 1943). Sinox© was conditioned to treat half a hectare to make it user-friendly; "*le procédé Truffaut*" (Truffaut process) was marketed by comparing it with sulfuric acid and other widely used molecules. Application doses were determined for different weed species to improve its efficacy. The success of this product was so great that the Truffaut company even warned about its use on other crops such as sugar beet and flax (Truffaut, 1938).

France is an important agricultural country at the world scale, with a highly diversified crop production on just a little more than 28 million hectares. More than 250 crops are grown in mainland France and in the overseas territories. This crop variability (cotton is the only major crop not cultivated in mainland France or its overseas territories) is partly the reason for the diversity and quantity of herbicides being used. The most widely used pesticides in France are herbicides (46%) (Union des Industries de la Protection des Plantes, 2020). More than 29,300 tons of herbicides have been used in France on average per year over the last decade (Ministère de l'Agriculture et de l'Alimentation, 2021a).

The potential end of the use synthetic pesticides by 2050 in Europe (Billen et al., 2021) will mark the end of the herbicide technology that has deeply changed crop production from agronomic and sociological points of view. The use of these substances has led to numerous advances in weed management and has increased yields while reducing the tediousness of weeding. However, the multiple impacts (agronomic, environmental, health, food, etc.) make the use of these substances hardly acceptable for a future sustainable agriculture. Following on from an article published in 2012 (Chauvel et al., 2012), the objective of this work is (i) to provide quantitative and precise data from 1913 onwards on the use of herbicides in France, and (ii) to put forward hypotheses on the consequences of the latest European policies on weed control. The historical approach was considered particularly relevant because it allows comparing the use of pesticides with the evolution of agricultural practices.

2. Materials and Methods

2.1 Sources

A database was built from various sources of information. The registration procedure of herbicides was enforced in France only at the end of 1943 (Ministère de l'Agriculture et de l'Alimentation, 1943). However, it was decided to also consider the most important chemical solutions developed before this period in the cases where reliable information was available in the literature. We were allowed to access the registration forms of new herbicides deposited in the 1940's. These data belong to the French Ministry of Agriculture, Food and Fisheries, and have never been used before. For reasons of confidentiality, we are not allowed to disseminate them and can only use the generic data (name of the active substance, registration date). Moreover, we used rare pesticide compendia edited in France (Maison de l'Agriculture, 1937; Institut National de la Recherche Agronomique, 1957) to complete the database. The database was built using Excel software (Microsoft Excel, office 2019); its analysis (pivot table) was conducted using tools proposed by this same software program.

From 1961 onwards, the database was completed by reviewing the issues of the "Index ACTA phytosanitaire" (phytosanitary Compendium) published by ACTA (Association de Coordination Technique Agricole) (Ministère de l'Agriculture et de l'Alimentation, 2021b) every year, except the issues of 1964, 1968, 1971 and 1976. The "Index acta phytosanitaire" is based on data provided by chemical companies every year. It could lead to an underestimated number of commercial products, but has no influence on the number of active substances (ASs) and little influence, if any, on the number of combinations of active substances (CAs). Only ASs present in the chapter "Selective and non-selective herbicides" in the "Index ACTA phytosanitaire" were retained for the present study. Only uses in cultivated fields were considered. Only ASs clearly used as herbicides at the indicated doses were introduced in the database (sulfosate was considered as a glyphosate salt; therefore, sulfosate and glyphosate were both considered under the name "glyphosate"). Other chemicals such as plant growth regulators (e.g., flurenol*)*, herbicide safeners (e.g., mefenpyr-diethyl) or synergists (e.g., ammonium thiocyanate), were not included in the database. Similarly, ASs or CAs specifically used against algae (e.g., dichlorophen, nabam) and mosses (e.g., calcium cyanamide, quinoclamin) were not retained.

2.2 Nomenclature

The common names of the ASs and chemical families were those approved by the Weed Science Society of America (Weed Science Society of America, 2021). The internet site of the Compendium of Pesticide Common Names completed the data (https://pesticidecompendium.bcpc.org/). The groups of modes of action (HRAC groups) were determined according to the website of The Herbicide Resistance Action Committee (Herbicide Resistance Action Committee; (Herbicide Resistance Action Committee, 2021). Each HRAC group was identified by a number (e.g., HRAC 1: inhibition of Acetyl CoA Carboxylase).

2.3 Data assessment

The variables contained in the database were as follows: AS name, HRAC group, chemical family, absorption route (shoots, underground parts, or both), targeted weeds (broadleaved or grasses), life cycle (annual or perennial). The number of commercial products was also indicated for each year. The database indicates whether each AS can be used only alone, in combination, or only in combination with (an)other AS(s), as well as the authorized crops (thirty-eight major crops were considered; Annex 1). The database currently contains 12,432 lines and 38,025 data (from 1913 to 2021 included), and each line includes the date for an AS or a CA for a given year.

3. Results and Discussion

3.1 Availability of active substances and of combinations of active substances

At least 233 ASs have been registered and used in France since 1913 (Annex 2). At the beginning of the 20th century, weed control was first carried out using mineral herbicides (sulfuric acid, sodium chlorate, potassium chloride). In 1944, only three synthetic pesticides (DNOC), dinitrophenol and trichlorophenol) were potentially used as herbicides. MCPA and 2,4-D were the first two officially authorized synthetic ASs in 1946 for winter cereals. A total of sixteen ASs used as herbicides were identified in 1944 (Figure 1). Twenty-one additional ASs had been registered in the first "Index ACTA phytosanitaire" in 1961 (Ministère de l'Agriculture et de l'Alimentation, 2021b).

Considering the new authorizations and withdrawals, a regular increase of about three new ASs per year was observed between 1960 and 1992 (Figure 1). The number of ASs remained stable in the 1990's until 2002. The maximum number of ASs available in a year was observed in 2002 (138 ASs). The European regulation of pesticides in 2003 caused the number of available ASs to decrease (Figure 1). Today the French supply of ASs (91 ASs in 2021) is similar to that of the mid-1980's.

The first CAs were observed as early as 1925. Initially, the low number of CAs (until 1960) could be explained by the low number and the specificity of the different ASs available at the time (Figure 1). After 1960, the registration of new selective ASs with new modes of action – hence wider efficacy spectra – increased the opportunities to propose new CAs (156 in 2002, Figure 1). At the beginning of the 1980's, weed control solutions based on CAs became dominant and still remain significant today. More than 481 CAs were registered over the studied period.

We were able to estimate the number of commercial products starting from 1961, using data provided by the "Index ACTA phytosanitaire". One hundred and thirty to 800 commercial products were potentially available each year in France (data not shown). The commercial offer still remains very high in 2021, with 722 commercial herbicidal products. Glyphosate alone can be provided in the form of more than 130 commercial products. A significant reduction in the commercial supply of glyphosate-based products due to regulatory constraints is observed in 2022, with only 25 products (data not shown).

3.2 Composition and evolution of combinations of active substances

The combination of different ASs was at first of great interest in the strategies for managing broader spectra of weed species. Marketing strategies now focus on the combination of two or three ASs (Figure 2) in order to

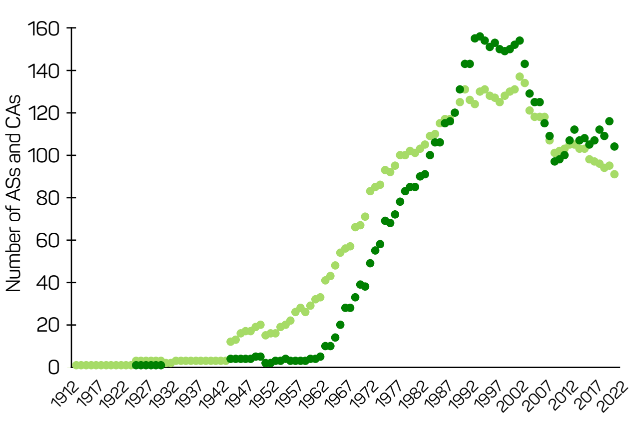

Figure 1 - Number of active substances (ASs ○) and combinations of active substances (CAs ●) registered between 1913 and 2021 considering annual authorizations and withdrawals. All ASs are listed in Annex 2.

control species that have become herbicide resistant (e.g., *Lolium* sp., *Papaver rhoeas*) or naturally difficult to weed by chemical treatment (Umbelliferae). Up to five ASs (MCPA, mecoprop, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), dicamba, ioxynil) have been used in combination to control weeds in ornamental crops.

The current high number of CAs can be explained by new ASs marketed since 2000 that are only marketed in combinations (halauxifen-methyl, beflutamid, oxadiargyl, etc.), and by the obligation to reduce treatment frequency, which can be achieved by combining ASs – generally 2 or 3 – with broad spectra of action. Additionally, the ban of some ASs that were pivotal for weed control in some crops, has led companies to devise new associations that were not considered before.

The database allowed us to highlight the herbicidal molecules most frequently used in CAs over time (data not shown). Dicamba has been the most frequently used AS in CAs since the mid-1960's. Three other molecules have also been used recurrently: 2,4-D, MCPA, and methylchlorophenoxypropionic acid (mecocrop). Group HRAC 4 (auxin mimics) formed the basis of many CAs available to farmers for almost 50 years. From the 2000's onwards, new ASs – diflufenican (HRAC 12), isoproturon (HRAC 5) and ioxinyl (HRAC 6) – have become important in CAs. Finally, over the last 10 years, diflufenican, iodosulfuron-methyl-sodium (HRAC 2) and florasulam (HRAC 2) have been the main ASs used for weed control in crops to manage resistant weed populations. Unfortunately, these data cannot be linked to quantities per hectare.

3.3 Duration of the use of active substances and combinations of active substances

ASs have been used for more than 27 years on average (from 2 to 76 years) (Figure 3a). Twenty-four ASs have been used for more than 50 years, while 2,4-D and MCPA have been used for 76 years. The ASs with the longest duration of use share several characteristics: few cases of resistance, low levels in groundwater, post-emergence treatment and use on many different crops. The use of HRAC 4 ASs should not be questioned in the near future as they are authorized at least until 2030 (European Commission, 2022).

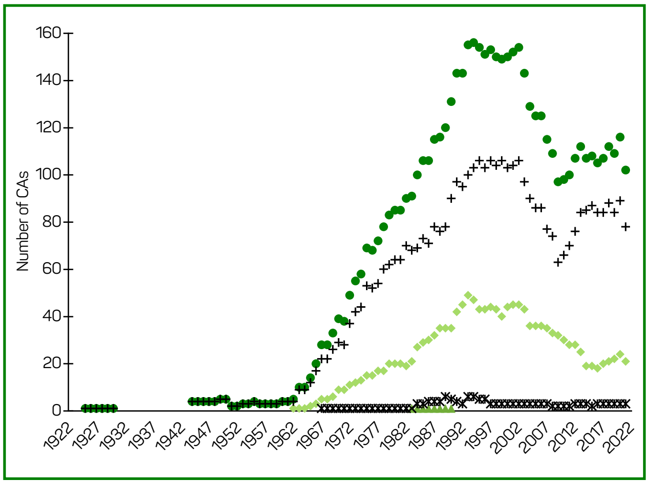

Figure 2 - Number of combinations of active substances (CAs) from 1924 to 2021. +: combination of two ASs; ◇: combination of three ASs; ★: combination of four ASs; ▲: combination of five ASs; ●: total number of CAs.

The period of use of CAs is much shorter – 13 years (Figure 3b). Almost 25% of CAs have been used for less than 5 years. Only four CAs have been marketed for at least 50 years, all based on 2,4-D and MCPA. The shorter use of CAs can be explained by both commercial and agronomic choices.

3.4 Authorizations and withdrawals of ASs and CAs

Thanks to the annual publication of the "Index ACTA phytosanitaire", we monitored the introduction of new

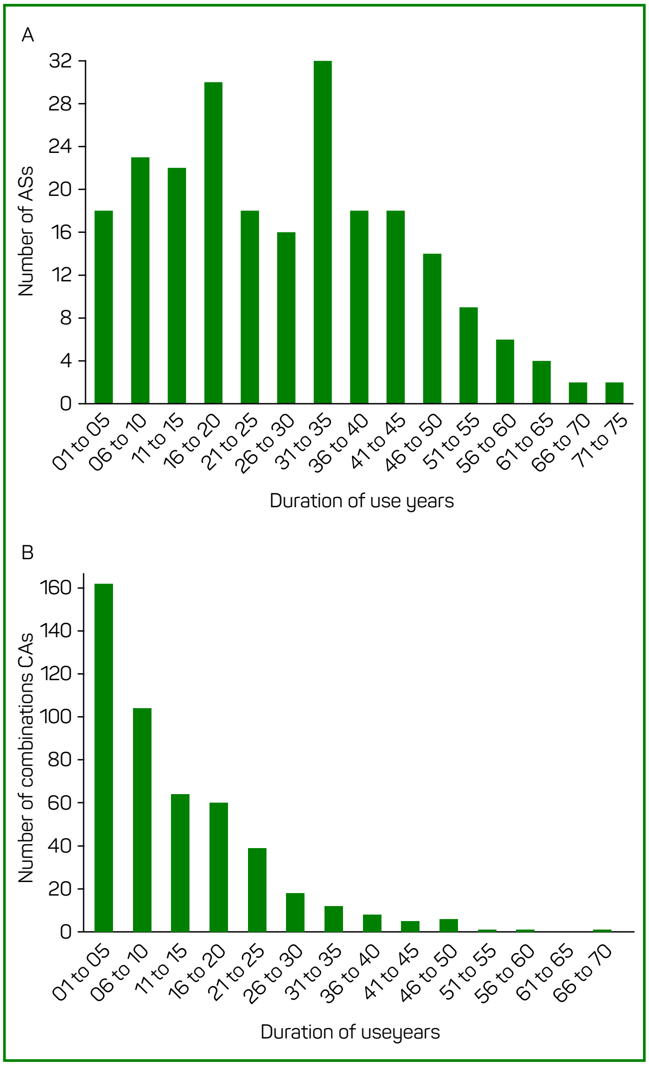

Figure 3 - Duration of use (a) of active substances (ASs) and (b) of combinations of active substances (CAs) sorted by five-year classes. Data were calculated for the active substances and combinations withdrawn before 2021. The data take currently authorized molecules into account.

active substances on the market as well as withdrawals (sales bans) each year. In the large majority of withdrawals, farmers were allowed to use the previously purchased stocks for one year. Until the 1990's, the number of new authorized ASs was higher than the number of withdrawn ASs (Figure 4). Then, from the 1970's, the number of new authorizations decreased regularly, slightly more sharply so since the 2000's. After the early 2000's, the number of new ASs did not offset withdrawals. The high number of withdrawals in the early 2000's is largely due to the re-evaluation of pesticides in Europe that started in 1991. Only seven new ASs have been registered in the last decade.

3.5 Evolution of chemical families and HRAC groups

The increase of the number of ASs was favoured by the development of new chemical families. Herbicide molecules used in France can be classified in 48 different chemical families (Annex 2). The number of families remained limited from 1913 to 1952, but increased afterwards until the 1980's. From 1987 to 2017, at least 40 (40 to 45) chemical families were regularly used, and then the number started to decline.

Knowledge of the modes of action of ASs has become essential for the development of sustainable weed management strategies, particularly to manage herbicide-resistant weed populations. Before 1944, only three groups of modes of action (HRAC 0: unknown; HRAC 6: Inhibition of photosynthesis - PS ll - histidine 215; HRAC 24: uncouplers) were available (Figure 5). The other modes of action appeared over time until 1994, and reached a total of 22 (Figure 5).

Different modes of action have been used in France over long periods of time, from 28 years (HRAC 27) to 76 years (HRAC 4). Seven modes of action (6, 10, 18, 19, 22, 24 and 34) have been withdrawn (Figure 5). HRAC 10 (glufosinate-ammonium) and HRAC 22 (paraquat) were the latest groups to be withdrawn, resulting in a significant reduction in the supply of non-selective ASs. For other groups such as HRAC 5 (inhibition of photosystem II), the number of authorized molecules is now limited to 7 molecules that are used less and less despite their agronomic role in the management of resistant or new grass weed species (chlorotoluron, metobromuron) or in global weed management in crops such as sugar beet (*Beta vulgaris*). The latest authorized mode of action was HRAC 27 (inhibition of hydroxyphenyl pyruvate dioxygenase; Figure 5); the main AS of this group is sulcotrione.

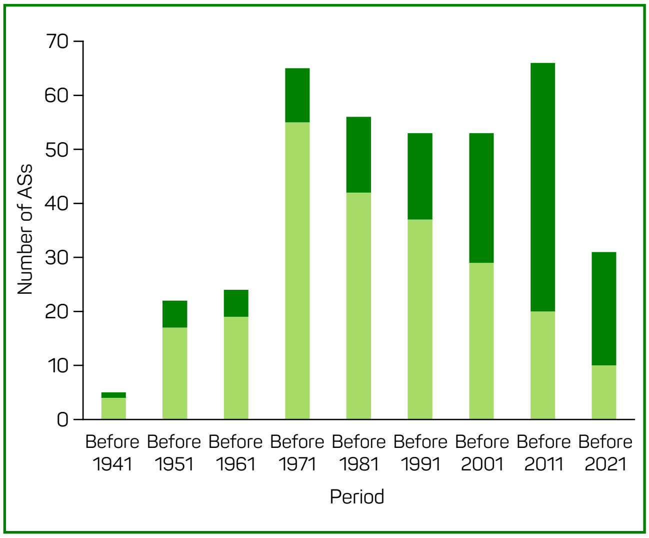

Figure 4 - Number of new active substances (Ass) registered (white) and withdrawn (black) per ten-year period.

3.6 Practical and technical uses of active substances

The field use of herbicides is linked to several characteristics. Among the most important points, the level of specificity (weed spectrum) according to the main botanical groups – eudicotyledonous and graminoid plants – is essential to the choice of the AS.

Historically speaking, ASs such as sulfuric acid, dinitrophenol, MCPA were the main ASs used on eudicotyledonous plants until the 1950's (Figure 6). The marketing of efficient ASs on perennial and annual grass weeds –bardan in the mid-1960's, then flamprop and diclolofop-methyl in the 1970's – made it possible to considerably increase the control of weed species

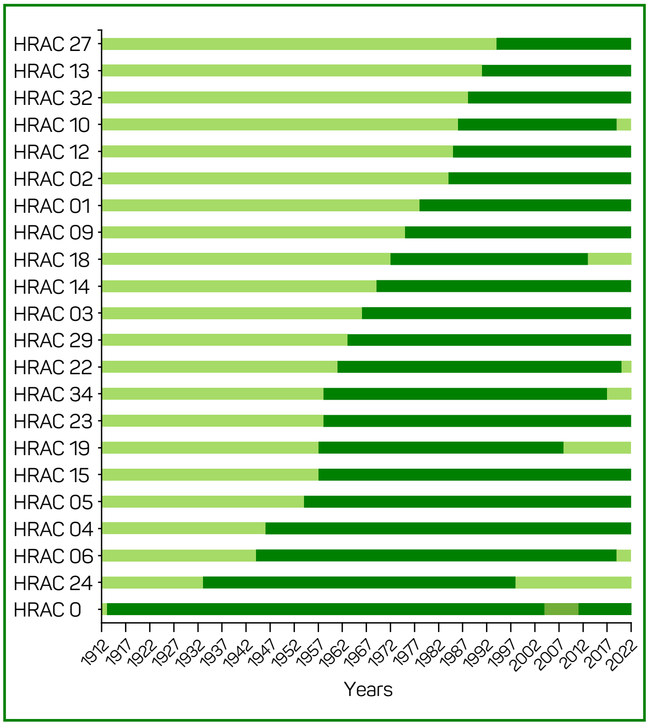

Figure 5 - Registration of the different modes of action over time. The black bars in the histogram indicate how long the mode of action has been used.

such as *Elytrigia repens*, *Avena fatua* or *Alopecurus myosuroides* (Figure 6). Broad-spectrum ASs (efficient on eudicotyledonous and graminoid plants) are currently the group from which the greatest number of ASs has been withdrawn from the market; this contributes to weed control difficulties in the field (Figure 6).

The application period is another major characteristic of ASs. The number of ASs used in pre-emergence or pre-post emergence has declined since 2003 (Figure 7), at least partly explained by the European political willingness to protect water quality. These ASs were sprayed on soils with a low plant cover and often persisted in the environment. Post-emergence ASs, which currently represent two thirds of available ASs (Figure 7), are mainly present in chemical families such as sulfonylureas (HRAC 2: inhibition of acetolactate synthase; 23 ASs in 2021) and aryloxyphenoxy-propionates (HRAC 1: inhibition of Acetyl CoA carboxylase; 10 ASs in 2021). However, these ASs belong to the chemical families most concerned by weed control problems linked to the development of herbicide resistance.

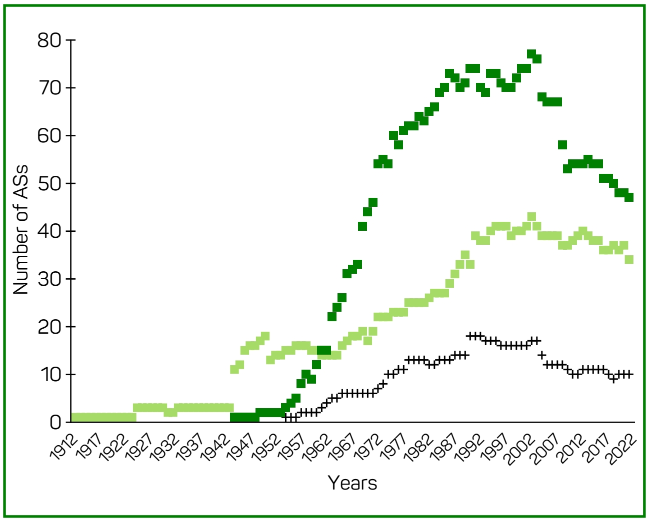

Figure 6 - Time course of the number of registered actives substances (ASs) according to their weed spectrum. ■: broad-spectrum herbicides; +: ASs against graminoid species; ☐: ASs against eudicotyledonous species.

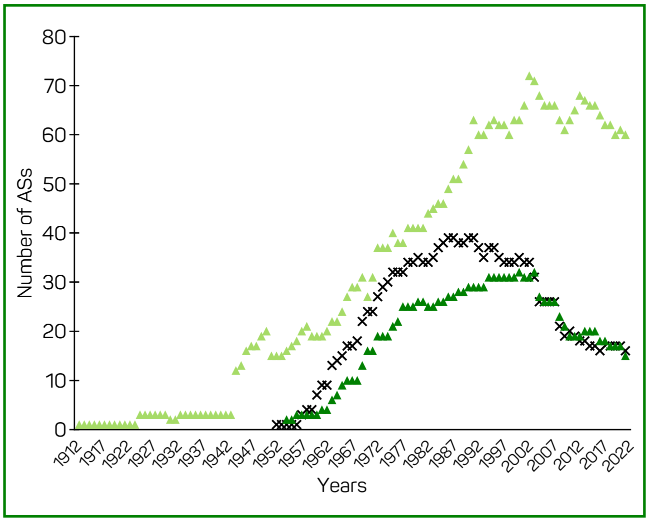

Figure 7 - Time course of the number of available actives substances (ASs) according to their agronomic use. △: pre-emergence ASs; ×: post-emergence ASs; ▲: pre- and post-emergence ASs.

3.7 Herbicide resistance

Herbicide resistance was first observed in France in 1978 (Figure 8) in maize and vineyards, with the classic chloroplastic resistance to triazines (HRAC 5; Gasquez et al., 1982). The first plants resistant to aryloxyphenoxy-propionate (HRAC 1) and then to sulfonylurea (HRAC 2) ASs were identified only one decade later (Figure 8), mainly on *A. myosuroides* and then on various other grassweeds (*Lolium* sp., *Avena* sp.; (Research and Reflection Ring on Pesticide Resistance, 2018). Eudicotyledonous weeds (*Ambrosia artemisiifolia; P. rhoeas*) became a source of acetolactate synthase (HRAC 2) resistance (Délye et al., 2020; Research and Reflection Ring on Pesticide Resistance, 2018). The latest case of herbicide resistance (2019) was by *Lolium* sp. and concerned a new mode of action (HRAC 15: inhibition of very-long-chain fatty acid synthesis). In France, 22 weed taxa resistant to six modes of action have been identified to date, with different

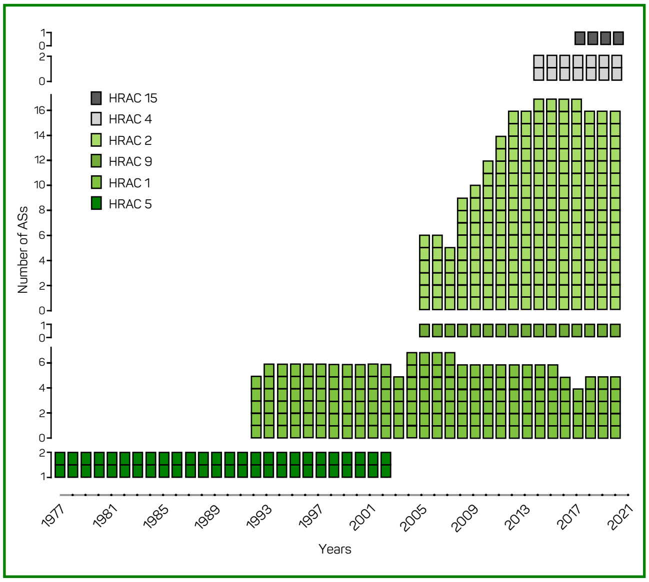

Figure 8 - Number of active substances (ASs) for which resistant weeds have been identified according HRAC groups. HRAC 1: inhibition of Acetyl CoA carboxylase; HRAC 2, inhibition of acetolactate synthase; HRAC 4: auxin mimics; HRAC 5: inhibition of photosynthesis at the level of PSII - Serine 264 binders; HRAC 9: inhibition of enolpyruvyl shikimate phosphate synthase; HRAC 15: inhibition of very-long-chain fatty acid synthesis.

levels of agronomic importance (Research and Reflection Ring on Pesticide Resistance, 2018).

The potential withdrawal of some ASs belonging to chemical families not concerned by herbicide resistance, such as prosulfocarb and propyzamide, has become a major concern for farmers in the management of grass weeds. Hormone-type ASs (HRAC 4) without herbicide resistance still provide effective solutions for farmers to control eudicotyledonous weed species.

3.8 Availability of herbicidal molecules depending on the crop

3.8.1. *Comparison of two crops*

The dataset was used to follow the availability of ASs and CAs crop by crop. From the beginning of the 20th century, winter wheat was the crop on which the first mineral molecules were tested (sulfuric acid, copper sulfate, etc.), and then the first organic molecules (DNOC, 2,4-D, etc.). Then, chemical weeding of wheat was mainly based on numerous CAs from the end of the 1970's (> 80 CAs in the 1990's; Figure 9) and until 2021 (47 CAs). The number of available ASs has been stable since the early 1990's and has remained high (27 ASs; Figure 9) despite EU regulations.

In the case of vineyards (Figure 9), the situation is different. Since the beginning of the 1960's, chemical weed control has been carried out with a lower number of ASs (15 - 20) compared to wheat, and a smaller number of CAs answers to reach less than 20 chemical solutions today. Vineyard is sometimes referred to in France as the first major crop on which no more herbicide could be used in the coming years.

3.8.2. *Diversity of the modes of action for different main crops over time*

A measure of the diversity of ASs used over time can help estimate the possibilities of chemical weed control for a given crop (wheat, maize, rice, rapeseed, soybean, sunflower, potato, sugar beet, carrot, vineyard).

For field crops (wheat, maize, rice, rapeseed, soybean, sunflower, sugar beet, vineyard), the number of ASs increased until 1990-2000 (Table 1). This increase was associated with the enhancement of modes of action (MoA). The number of ASs and MoA still remains high for these crops. However, this diversity has been reduced by the presence of resistant plants that reduce the range of solutions available to farmers in the field.

Rice is a highly developed crop worldwide; its area of production in France is very small (< 14,000 ha), but the number of authorized herbicides is proportionally high (eight ASs in 2021) (Table 1). Weed control of this crop is more complex because of the habitats and botanical proximity of certain weeds with the crop; the use of chemical weeding remains frequent.

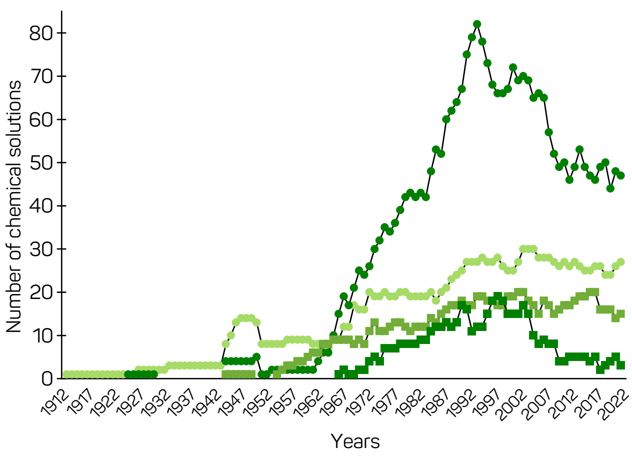

Figure 9 - Time course of the number of available chemical solutions for winter wheat (○: ASs; ●: CAs) and vineyard (☐: ASs; ■: CAs).

For vegetable crops (potato and carrot), AS and MoA availability increased until 2010-2020 (Table 1). The highest MoA/AS ratio was observed for these crops. This situation is interesting for resistance management because it enables farmers to use ASs with different MoAs.

The reduction of the range of solutions seems to be greatest from an overall point of view. However, the authorization of ASs already registered for other crops has made it possible to maintain a certain number of solutions. Nevertheless, this can result in the use of a same mode of action during a rotation despite the use of different ASs; it implies that the same selection pressure is exerted each year, with a high risk of resistance selection.

4. Discussion

This intensive use of pesticides including herbicides is now being questioned by a large part of society. The use of herbicides in France since the 1960's has many consequences on the environment (water and air contamination, reduction of biodiversity in the agrosystems and environments connected to the cultivated fields; (Detoc, 2003); (Schiavon et al., 1995), health (recognition of professional diseases, (Institut National de la Santé et de la Recherche Médicale, 2021) and crop management (herbicide resistance; Research and Reflection Ring on Pesticide Resistance, 2018).

4.1 History of herbicide use

The database used in the present review provides an interesting tool for a better understanding of the historical evolution of herbicide use in France. It makes it possible to replace the history of all these molecules in relation to each other, all together or crop by crop.

Before the 1940's French agronomic research was at the forefront of the development of the first chemical weed

Table 1 - Diversity in terms of numbers of active substances (AS), modes of action (MoA) and chemical families (Family) for ten of the main crops in France over 10-year time steps (* 1984; ** 1965; *** 1963).

		1951	**1961**	**1971**	**1981**	**1991**	**2001**	**2011**	**2021**
Total	AS	15	32	72	101	131	131	105	91
	MoA	4	10	13	16	21	21	20	16
	Family	6	15	25	36	42	44	41	38
Wheat	AS	8	8	16	19	27	27	26	27
	MoA	4	3	7	9	13	13	11	12
	Family	5	4	7	9	13	16	13	15
Maize	AS		2	10	20	22	28	26	25
	MoA		1	4	7	8	10	8	9
	Family		1	5	8	11	15	13	12
Rice	AS		2	6	7	6	9	7	8
	MoA		2	4	4	6	6	4	4
	Family		2	4	4	6	7	6	6
Rape seed	AS		3	4	11	18	18	13	18
	MoA		3	3	5	7	10	8	10
	Family		2	3	8	10	10	9	12
Soybean	AS		-	-	4*	13	11	12	13
	MoA		-	-	3*	4	6	7	7
	Family		-	-	4*	7	7	9	9
Sunflower	AS		2	3	3	12	12	10	13
	MoA		2	2	2	7	6	7	8
	Family		2	2	2	9	9	9	11
Potato	AS		1**	5	6	10	9	12	12
	MoA		1**	2	2	4	5	8	7
	Family		1**	5	5	10	9	11	11
Sugar beet	AS		1***	6	12	17	19	15	15
	MoA		1***	2	5	5	6	5	6
	Family		1***	4	10	10	11	11	11
Carrot	AS	1	3	5	6	8	6	9	13
	MoA	1	3	3	3	5	2	6	9
	Family	1	2	5	4	5	3	8	10
Vineyard	AS		6	8	12	17	20	17	15
	MoA		4	5	9	12	13	11	9
	Family		5	6	10	14	16	14	12

control practices (copper sulfate, sulfuric acid, DNOC). Later on, solutions were brought by research from other countries. The introduction of herbicidal molecules in France more than 70 years ago deeply changed weed management practices. On the one hand, herbicidal molecules greatly reduced the tediousness of agricultural work, which was still largely done by hand or mechanical tools before the advent of herbicides. In the 1960's, herbicidal molecules also enabled the development of new crops (e.g., maize), and the extension of diversified rotations (Sebillotte, 1969) with a better control of perennial weed species. Soil tillage and rotations that allowed alternation of ASs constituted the cornerstone of integrated weed management (Swanton, Weise, 1991; Chikowo et al., 2009). The first congresses '*Journées d'études sur les herbicides*' [Study days on herbicides] organized in France in collaboration with the European Weed Research Society in 1961 and 1963 showed the extent of numerous trials aimed at finding molecules that could meet the needs of each crop. In the mid-1970's, the first herbicides against annual grass weeds were proposed to farmers, and allowed the first efficient chemical control of weeds such as *A. fatua* (diclofop-methyl) and *A. myosuroides* (isoproturon) described as the number-one weed in France since 1960 (Barralis, 1961). Although herbicide resistance was only observed relatively late (1978) in France (Darmency, Gasquez, 1990), changes in the composition of weed communities were quickly observed, particularly when herbicide use was linked to the reduction of soil tillage (Récamier, 1969). Presently, the management of herbicide-resistant grass weed species is a major problem for cereal farmers who do not have sufficient crop diversity in their rotation. *Lolium* sp. is a major problem due to multiple resistances (Duhoux et al., 2017), and some ASs like prosulfocarb and propyzamide have become the last chemical solutions for many farmers. The possible withdrawal of these last ASs would make it almost impossible to implement a weed control strategy solely based on chemical weed control.

Since 2012 and the first publication based on the database (Chauvel et al., 2012), seven new ASs belonging to four HRAC groups have been authorized (Table 2), while 20 ASs belonging to 17 different HRAC groups have been withdrawn. Some of these molecules (diclofop-methyl, isoproturon, oxadiazon) were used on a wide range of crops. No new mode of action has been introduced since 1994.

4.2 The case of glyphosate

The use of glyphosate is now widely questioned by a large part of French society. In France, glyphosate currently represents the symbol of intensive agriculture, which is rejected because of its potential effects on health (Institut National de la Santé et de la Recherche Médicale, 2021). With more than 8,000 tons year^{-1} used in France over the 2018-2020 period (Ministère de la Transition Écologique, 2021), this molecule has become an emblem of the struggle against pesticides to the point that the highly politicised debate leaves little space for scientific arguments. This AS is the only broad-spectrum one still in use today in France after the withdrawal of atrazine (2003), paraquat (2007), amitrole (2016) and glufosinate (2018). Its use remains essential for the management of perennial weed species during the intercropping period and for the management of herbicide-resistant grass weeds. This withdrawal could also completely challenge the development of conservation agriculture in which management of annual grasses and perennial broadleaved plants depends to a large extent on this molecule (Derrouch et al., 2020). Specific studies are still being carried out to try and limit its use by determining maximum authorized annual doses for different crops. All the farms of the INRAE research institute and state agricultural colleges are committed to a complete withdrawal of glyphosate in 2022.

4.3 "Natural" herbicides or bioherbicides

The intensive use of synthetic herbicides is questioned for several reasons (risks for the environment, health). As biocontrol has not had any effective development in the field for the moment, bioherbicides could offer an alternative to synthetic herbicides and a number of potential benefits such as rapid degradation in the environment. Despite efforts to identify effective bioherbicides, few solutions are currently

Table 2 - New actives substances (ASs) authorized during these last ten years (2012-2021). SS: used alone; SA: used alone and in combination; AA: only used in combination. Post: post treatment; pre/post: pre or post treatment. Dicots: eudicotyledonous plants; monocots: graminoid plants.

Active substance	HRAC Group	Registration Year	Treatment	Target weed	Use
Pelargonic acid	0	2012	post	Broad spectrum	SS
Aminopyralid	4	2012	post	All dicots	AA
Pinoxaden	1	2012	post	Annual monocots	SA
Thiencarbazone-methyl	2	2013	pre/post	Annual weeds	AA
Halosulfuron-methyl	2	2017	post	Broad spectrum	SS
Halauxifen-methyl	4	2018	post	Annual dicots	AA
Caprylic acid	0	2020	post	Broad spectrum	SS

available on the market (Cordeau et al., 2016). After having disappeared for more than 40 years, three so-called 'natural' molecules are now authorized in France, and are available to farmers. These new ASs (pelargonic acid, acetic acid and caprylic acid; HRAC 0) are broad-spectrum ASs. Pelargonic acid in particular is presented as a potential alternative to glyphosate. However, many technical adjustments are still necessary (Travlos et al., 2020) before this type of AS can be considered as a real alternative in the field. Moreover, the user cost of this molecule over large areas is still prohibitive.

5. Conclusion: what is the future of synthetic herbicides?

Pesticide use has regularly increased in France since the 1950's: France is the seventh largest pesticide user in the world, and the first one in Europe (https://fr.statista.com/infographie/15061/consommation-pesticides-en-europe-par-pays/). On an amount-per-area basis, it ranks seventh in Europe with 3.7 kg of active substance ha^{-1} year^{-1}. Intense debates are currently going on about the short- and long-term effects of pesticides, and two subjects are particularly taken up by the media: the use of neonicotinoids in relation to honey bees (*Apis mellifera*) mortality and the use of glyphosate. As in the case of triazine herbicides about 20 years ago (Mahé et al., 2020), the debate on glyphosate use is dividing society and the agricultural community. Moreover, it is more particularly the use of all herbicides that is currently being questioned. The French "Grenelle de l'Environnement" in 2007, a national public round table, was conducted to reduce (if possible) by half the use of pesticides over a period of 10 years. The "Ecophyto 2018" plan (Ministère de l'Agriculture et de la Pêche, 2018), which aimed to remove the products considered most worrying, did not /reach the proposed objectives. The effort to reduce the use of pesticides was maintained through the implementation of new plans "Ecophyto II" and then "Ecophyto II+", which aimed at i) a 25% reduction in 2020 based on the optimization of production systems, ii) an additional 25% reduction in 2025, which will be possible through major changes in production systems and the farming sector, and iii) the support of farmer networks towards agroecology. In 2009, the Ecophyto Plan aimed to reduce the use of pesticides by 50% by 2018 in France. Then, this objective was postponed to 2025. In spite of significant fundings, the reduction in pesticide use did not reach the expected level. However, the Ecophyto plan sent a strong signal, which undoubtedly announced the end of the use of herbicides in agriculture as a basic strategy (Guichard et al., 2017).

To measure the evolution of pesticide use, various indexes were proposed, such as the Phytosanitary Treatment Frequency Indicator (TFI: number of reference doses used per hectare during a crop year) or the Number of Dose Units (NODU; Hossard et al., 2017). Thanks to these indicators, a trend towards a decrease in the overall use of pesticides is confirmed with the lowest three-year average for 10 years (- 5.7% between 2017-2019 and 2018-2020) but the interpretation of these tendencies is still debated. Currently, the attention is paid to chloroacetanilide ASs (e.g., metolachlor, metazachlor) which has become an important issue due to the pollution of water resources.

The question today is whether there is still a place for synthetic ASs within the framework of "agroecological agriculture" as desired in France (https://agriculture.gouv.fr/les-fondements-de-lagro-ecologie (Caquet et al., 2019). In 1969, French agronomists considered that the use of these new herbicides would offer the possibility to introduce new crops in rotations (Sebillotte, 1969). More than 50 years later, this same diversification of rotations is considered as one of the best tools to limit the use of chemical treatments (Mahaut et al., 2019). Without being contradictory, these two approaches show the difference that has emerged in the weed management approach. According to the agricultural extension institutes, under favourable conditions, the introduction of mechanical weeding in straw cereals could increase the cost by at least 10€/ha compared to an "all chemical" strategy, the labour time being at least 3 times higher. If soil tillage and other new weed control techniques (robotics, electricity, laser, natural molecules) do not prove sufficiently effective in some agronomic situations, can we still consider keeping certain synthetic molecules for weed management in crops and during the intercropping period? Based on what criteria would it be possible to keep a certain number of strategic synthetic ASs? For certain synthetic molecules such as glyphosate, the question seems to be clear-cut (at least in France), but nothing is clearly explained yet for the other synthetic ASs. The effects of climate change (Ziska, 2020; Storkey et al., 2021) on the dynamics of weed communities or on the development of new species (Chadha et al., 2020) will also certainly influence policy-making. Will it be possible to determine weed species, crops or cropping systems for which the highly regulated use of synthetic herbicides will still be possible for agronomic, health or economic reasons? Agronomic considerations may not always be considered, while it is acceptable that proven health risks take priority over a weed management issue in the field.

Author's contributions

BC and J-PG: Conceptualization of the manuscript and development of the methodology, data interpretation, writing, review editing. CG: Data interpretation, review editing.

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References

Aslander A. Sulphuric acid as a weed spray: historical review. J Agric Res. 1927;34(11):1065-91.

Bain C, Bernard JL, Fougeroux A. [History of crop protection from 1850 to the present day]. Paris: Groupe France Agricole; 2010. French.

Barralis G. [Distribution and infestation status of grass weeds in France]. In: Comité Français de Lutte Contre les Mauvaises Herbes – Columa, editor. [Proceedings of the symposium on herbicides and of the 1st COLUMA conference]. Paris: Comité Français de Lutte Contre les Mauvaises Herbes; 1961. French.

Billen G, Aguilera E, Einarsson R, Garnier J, Gingrich S, Grizzetti B et al. Reshaping the European agro-food systemandclosing its nitrogen cycle: the potential of combining dietary change, agroecology, and circularity. One Earth. 2021;4(1):839-50. Available from: https://doi.org/10.1016/j.oneear.2021.05.008

Caquet T, Gascuel-Odoux C, Tixier-Boichard M, Dedieu B, Detang-Dessendre C, Dupraz P et al. [Interdisciplinary prospective thinking for agroecology]. Paris: Institut National de la Recherche Agronomique; 2019[access Dec 1, 2021]. French. Available from: https://www.inrae.fr/sites/default/files/pdf/20190431_Rapport_final_ARP_AE_diffusion_vf_oct2020.pdf

Carbonière C. [Weeds]. Bull Com Agr Castres. 1925;4:27-8. French.

Chadha A, Florentine S, Javaid M, Welgama A, Turville C. Influence of elements of climate change on the growth and fecundity of *Datura stramonium*. Env Sci Pollut Res. 2020;27:35859-69. Available from: https://doi.org/10.1007/s11356-020-10251-y

Chauvel B, Guillemin J-P, Gasquez J, Gauvrit C. History of chemical weeding from 1944 to 2011 in France: changes and evolution of herbicide molecules. Crop Prot. 2012;42:320-6. Available from: https://doi.org/10.1016/j.cropro.2012.07.011

Chikowo R, Faloya V, Petit S, Munier-Jolain NM. Integrated weed management systems allow reduced reliance on herbicides and long-term weed control. Agric Ecosys Environ. 2009;132(3-4):237-42. Available from: https://doi.org/10.1016/j.agee.2009.04.009

Cordeau S, Triolet M, Wayman S, Steinberg C, Guillemin J-P. Bioherbicides: dead in the water? A review of the existing products for integrated weed management. Crop Prot. 2016;87:44-9. Available from https://doi.org/10.1016/j.cropro.2016.04.016

Darmency H, Gasquez J. [Herbicide resistance in weeds]. Agronomie. 1990;10(6):457-72. French. Available from: https://doi.org/10.1051/agro:19900604

Délye C, Colbach N, Le Corre V. [Herbicide resistance: mechanisms, situation in France and good practices]. Innov Agron. 2020;81:33-49. French. Available from: https://doi.org/10.15454/8j8h-6610

Derrouch D, Dessaint F, Felten E, Chauvel B. [The adoption of direct seeding under plant cover: a smooth transition or a rupture?]. Cah Agric. 2020;29(5):1-6. French. Available from: https://doi.org/10.1051/cagri/2020003

Dessaisaix R. [Destruction of weeds by sea salt]. Jour Agr Prat. 1925;43:334-6. French.

Detoc S. [Groundwater quality and quantity in France]. Hou Blanche. 2003;89(2):102-7. French. Available from: https://doi.org/10.1051/lhb/2003035

Duhoux A, Carrère S, Duhoux A, Délye C. Transcriptional markers enable identification of rye-grass (*Lolium* sp.) plants with non-target-site-based resistance to herbicides inhibiting acetolactate-synthase. Plant Sci. 2017;257:22-36. Available from: https://doi.org/10.1016/j.plantsci.2017.01.009

European Commission – EC. EU Pesticides database. Geneva: European Comission; 2022[access Apr 1, 2021]. Available from: https://ec.europa.eu/food/plants/pesticides/eu-pesticides-database_en

Fron G. [Harmful plants to agriculture: botanical and agricultural characteristics. methods of control]. Paris: Encyclopédie Agricole; 1917. French.

Gasquez J, Barralis G, Aigle N. [Distribution and extension of chloroplast resistance to triazines in annual weeds in France]. Agronomie. 1982;2(2):119-24. French. Available from: https://doi.org/10.1051/agro:19820203

Guérin P. [The action of chlore and certain vapours on french and foreign higher plants]. Ann Sci Agron. 1921;6:10-9. French.

Guichard L, Dedieu F, Jeuffroy MH, Meynard JM, Reau R, Savini I. [Ecophyto, the French action plan to reduce pesticide use: a failure analyses and reasons for hoping]. Cah Agric. 2017;26(1):1-12. French. Available from: https://doi.org/10.1051/cagri/2017004

Herbicide Resistance Action Committee – HRAC. Classification of herbicides according to mode of action. Paris: Herbicide Resistance Action Committee; 2021[access Dec 1, 2021]. Available from: http://www.hracglobal.com

Hossard L, Guichard L, Pelosi C, Makowski D. Lack of evidence for a decrease in synthetic pesticide use on the main arable crops in France. Sci Tot Environ. 2017;575:152-61. Available from: https://doi.org/10.1016/j.scitotenv.2016.10.008

Institut National de la Recherche Agronomique - INRA. [Approval of pest control products for agricultural use]. Paris: Institut National de la Recherche Agronomique; 1957. French.

Institut National de la Santé et de la Recherche Médicale – Inserm. [The effects of pesticides on health: new data]. Montrouge: Institut National de la Santé et de la Recherche Médicale; 2021[access Dec 1, 2021]. French. Available from: https://www.inserm.fr/wp-content/uploads/2021-07/inserm-expertisecollective-pesticides2021-rapportcomplet-0.pdf.

Mahaut L, Gaba S, Fried G. A functional diversity approach of crop sequences reveals that weed diversity and abundance show different responses to environmental variability. J Appl Ecol. 2019;56(6):1400-9. Available from: https://doi.org/10.1111/1365-2664.13389

Mahé I, Gauvrit C, Angevin F, Chauvel B. [What lessons can be learned from the withdrawal of atrazine in the context of the planned ban on glyphosate?] Cah Agric. 2020;29(9):1-9. French. Available from: https://doi.org/10.1051/cagri/2020026

Maison de l'Agriculture (FR). [Practical guide to plant health]. Paris: Maison de l'Agriculture; 1937. French.

Ministère de l'Agriculture et de l'Alimentation (FR). [ACTA Phytosanitary Index 1961 - 2021]. Paris: Les Instituts Techniques Agricoles; 2021b. French.

Ministère de l'Agriculture et de l'Alimentation (FR). [Agreste Graph'Agri 2021: agriculture, forestry, fisheries and agri-food industries]. Paris: Ministère de l'Agriculture et de l'Alimentation; 2021a[access April 1, 2021]. French. Available from: https://agreste.agriculture.gouv.fr/agreste-web/download/publication/publie/GraFra2021Integral/GraFra2021_integral.pdf

Ministère de l'Agriculture et de l'Alimentation (FR). [Law No. 525 of 2 November 1943. Relating to the organisation of the control of pest control products for agricultural use]. *Journal Officiel Lois & Décrets*. Nov 4, 1943 French.

Ministère de la Transition Ecologique (FR). [Glyphosate exit] Paris: Ministère de la Transition Ecologique; 2021[access Dec 1, 2021]. French. Available from: https://www.ecologie.gouv.fr/sortie-du-glyphosate.

Ministère de l'Agriculture et de la Pêche (FR). [Ecophyto 2018 plan to reduce the use of pesticides 2008-2018]. Ministère de l'Agriculture et de la Pêche; 2018[access Dec 1, 2021]. French. Available from: https://agriculture.gouv.fr/ministere/le-plan-ecophyto-2018

Poubelle L. [The destruction of wild mustard]. Semaine Agricole. 1898;890:182. French.

Rabaté E. [Destruction of rwhite charlock with sulphuric acid]. J Agr Prat. 1911;75(1):407-9. French.

Rabaté E. [Weed control]. 2nd ed. Paris: Librairie Agricole de la Maison Rustique; 1927. French.

Récamier A. [Herbicides and the opportunity to eliminate ploughing]. In: COLUMA, editor. Herbicides et techniques culturales; 11-02 -12-02-1969; Versailles (France). Paris (France): FNGPC; 1969. p. 63-106. French.

Research and Reflection Ring on Pesticide Resistance - R4P. Resistance cases to PPPs in France 2018. Paris: Institut National de la Recherche Agronomique; 2018. Available from: www.r4p-inra.fr

Schiavon M, Perrin-Ganier C, Portal J-M. [Water pollution by plant protection products: status and origin]. Agronomie. 1995;15(3-4):157-70. French.

Sebillotte M. [Crop rotation changes in relation to the use of herbicides]. In: Comité Français de Lutte Contre les Mauvaises Herbes – Columa, editor. [Herbicides and cultural techniques]. Paris: Fédération Nationale des Groupements de Producteurs de Coton; 1969. p. 235-99. French.

Storkey J, Mead A, Addy J, MacDonald AJ. Agricultural intensification and climate change have increased the threat from weeds. Glob Change Biol. 2021;27(11):2416-25. Available from: https://doi.org/10.1111/gcb.15585

Swanton CJ, Weise SF. Integrated weed management: the rationale and approach. Weed Technol. 1991;5(3):657-63. Available from: https://doi.org/10.1017/S0890037X00027512

Travlos I, Rapti E, Gazoulis I, Kanatas P, Tataridas A, Kakabouki I et al. The herbicidal potential of different pelargonic acid products and essential oils against several important weed species. Agronomy. 2020;10(11):1-13. Available from: https://doi.org/10.3390/agronomy10111687

Truffaut G, Pastac I. [Powdering of weeds with nitro dyes]. Cr Séances Acad Agric Fr. 1943;29:381-3. French.

Truffaut G. [Control of wild mustards]. Versailles; 1938. French.

Union des Industries de la Protection des Plantes – UIPP. [Our figures: 2020 update]. Paris: Union des Industries de la Protection des Plantes; 2020[access Dec 1, 2021]. French. Available from: https://www.uipp.org/app/uploads/2021/03/Nos-donnees-chiffrees.pdf.

Vermorel V. [Practical manual for weed control]. 2nd ed. Villefranche: Librairie Agricole de la Maison Rustique; 1926. French.

Vilcoq A. [Destruction of harmful cruciferous species]. La Nature. 1899;1368:171-2. French.

Weed Science Society of America – WSSA. List of herbicides: WSSA herbicide site of action (SOA) classification list 2021. Westminster: Weed Science Society of America; 2021[access Dec 1, 2021]. Available from: https://wssa.net/wssa/weed/herbicides/

Ziska LH. Climate change and the herbicide paradigm: visiting the future. Agronomy. 2020;10(12):1-10. Available from: https://doi.org/10.3390/agronomy10121953

Annex 1 - Crops considered in the data base

Crop
Banana
Barley
Carrot
Cereals (other than wheat and barley)
Flax
Fodder grasses
Fodder legumes
Forestry crops
Hops
Intercropping cover
Legumes
Maize
Maize (tolerant)
Medicinal crops
Millet & moha
Miscanthus
Mustard
Orchard
Ornamental crops
Pineapple
Popyseed oil
Potato
Rape seed
Rape seed (tolerant)
Rice
Sorghum
Soyabean
Strawberry
Sugar cane
Sugar beet
Sunflower
Sunflower (tolerant)
Switchgrass
Tobacco
Tropical crops *(other than banana and sugar cane)*
Vegetable crops
Vineyard
Wheat

Annex 2 - Start: first year of registration; End: year of withdrawl; -: still in use

Start	End	Active substances	HRAC	Chemical family
1913	1979	sulfuric acid	0	Non-classified
1925	1930	potassium chloride	0	Non-classified
1925	1958	sodium chlorate	0	Non-classified
1933	1997	DNOC	24	Dinitrophenols
1944	1990	Na Chlorate	0	Mineral salts
1944	1960	calcium cyanamide	0	Mineral salts
1944	1965	Dinitrophenol	24	Dinitrophenols
1944	1960	copper nitrate	0	Mineral salts
1944	1950	zinc nitrate	0	Mineral salts
1944	1950	aluminium sulfate	0	Mineral salts
1944	1950	copper sulfate	0	Mineral salts
1944	1950	iron sulfate	0	Mineral salts
1944	1956	Trichlorophenol	6	Organochlorine
1945	1972	potassium ethylxanthate	0	Carbamate
1946	-	2,4-D	4	Phenoxy-carboxylates
1946	-	MCPA	4	Phenoxy-carboxylates
1946	1962	pentachlorophenol	6	Organochlorine
1947	1950	sodium hyponitrite	0	Mineral salts
1949	1987	2,4,5-T	4	Phenoxy-carboxylates
1949	1991	petroleum-based oils	0	Non-classified
1950	1965	dinoseb	24	Dinitrophenols
1952	1957	seasone	4	Phenoxy-carboxylates
1954	1962	cryptophenol	24	alkylphenol
1954	1979	monuron	5	Ureas
1954	2003	TCA	0	Chlorocarbonic acids
1955	-	MCPB	4	Phenoxy-carboxylates
1955	1961	potassium cyanate	0	Mineral salts
1956	2008	diuron	5	Ureas
1957	2003	dalapon	15	Chlorocarbonic acids
1957	2018	mecoprop	4	Phenoxy-carboxylates
1957	1990	sodium chlorate	0	Chlorocarbonic acids
1957	1961	sodium monochloracetate	0	Chlorocarbonic acids
1957	2007	naptalam	19	Aryl-carboxylates
1957	2003	simazine	5	Triazines
1958	1989	TBA	4	Benzoates
1958	2016	amitrole	34	Triazolocarboxamide
1958	2020	chlorpropham	23	Carbamates
1958	1998	neburon	5	Ureas
1960	2003	atrazine	5	Triazines
1960	1992	chlorbufam	23	Carbamates
1960	1992	cycluron	5	Ureas
1961	-	2,4-DB	4	Phenoxy-carboxylates

Continue

Continuation

Start	End	Active substances	HRAC	Chemical family
1961	1990	di-allate	15	Thiocarbamates
1961	1962	sodium dichloro butyrate	0	Chlorocarbonic acids
1961	2019	diquat	22	Pyridiniums
1961	1969	metam	0	Carbamate
1961	2007	prometryn	5	Triazines
1962	1987	barban	23	Carbamates
1962	1977	pentanochlor	5	Amides
1962	2010	propanil	5	Amides
1963	2020	chloridazon = pyrazon	5	Pyridazinone
1963	1991	chloroxuron	5	Ureas
1963	2010	dichlobenil	29	Nitriles
1963	2003	dichlorprop	4	Phenoxy-carboxylates
1963	1987	di-isopropyl dixanthogen	0	Carbamate
1963	2002	EPTC	15	Thiocarbamates
1963	2018	linuron	5	Ureas
1963	2007	paraquat	22	Pyridiniums
1963	1964	propham	23	Carbamates
1963	-	tri-allate	15	Thiocarbamates
1964	1969	chloramben	4	Benzoates
1964	1980	sulfallate	15	Thiocarbamates
1965	1996	diphenamid	15	Acetamides
1965	2016	ioxynil	6	Nitriles
1965	2009	molinate	15	Thiocarbamates
1965	2000	monalide	15	Anilides
1965	2002	monolinuron	5	Ureas
1965	-	picloram	4	Pyridyloxy-carboxylates
1966	1973	phenyl-carbonate	0	Non-classified
1966	1998	desmetryn	5	Triazines
1966	1985	fenoprop	4	Phenoxy-carboxylates
1966	-	lenacil	5	Uracils
1966	-	metobromuron	5	Ureas
1966	1973	methoprotryne	5	Triazines
1966	2008	trifluralin	3	Dinitroanilines
1967	-	carbetamide	23	Carbamates
1967	1997	dinoterb	24	Dinitrophenols
1968	1969	fluometuron	5	Ureas
1969	2007	bromacil	5	Uracils
1969	2003	chlorthiamid	29	Nitriles
1969	-	dicamba	4	Benzoates
1969	2009	methabenzthiazuron	5	Ureas
1969	2007	metoxuron	5	Ureas
1969	1987	nitrofen	14	Diphenyl ethers

Continue

Continuation

Start	End	Active substances	HRAC	Chemical family
1969	-	phenmedipham	5	Phenylcarbamates
1969	2010	propachlor	15	α-Chloroacetamides
1969	2003	terbutryn	5	Triazines
1970	2008	alachlor	15	α-Chloroacetamides
1970	2003	ametryn	5	Triazines
1970	2011	chlorthal-dimethyl = DCPA	3	Benzoates
1970	-	chlorotoluron	5	Ureas
1970	2002	cyanazine	5	Triazines
1970	2003	cycloate	15	Thiocarbamates
1970	1971	dichlormate	34	Carbamates
1970	1973	phenobenzuron	5	Ureas
1970	-	propyzamide	3	Benzamides
1972	2012	asulam	18	Carbamates
1972	-	bentazon	6	Benzothiadiazinone
1972	1984	benzoylprop-ethyl	23	Arylaminopropionic acid
1972	-	bromoxynil	6	Nitriles
1972	1975	brompyrazon	5	Pyridazinone
1972	1975	isonuron	5	Ureas
1972	-	metribuzin	5	Triazinones
1972	-	napropamide	15	Acetamides
1972	1987	nitralin	3	Dinitroanilines
1972	2015	oxadiazon	14	N-Phenyl-oxadiazolones
1972	2007	terbacil	5	Uracils
1972	1998	terbumeton	5	Triazines
1972	-	terbuthylazine	5	Triazines
1973	1988	butylate	15	Thiocarbamates
1973	1991	secbumeton	5	Triazines
1974	-	benefin=benfluralin	3	Dinitroanilines
1974	1996	difenzoquat	0	Pyrazolium
1974	1978	flamprop	0	Arylaminopropionic acid
1974	2017	isoproturon	5	Ureas
1975	1981	benazolin-ethyl	4	Benzothiazolone
1975	-	ethofumesate	15	Benzofuran
1975	-	glyphosate	9	Glycine
1975	2003	metolachlor	15	α-Chloroacetamides
1975	1979	penoxalin	3	Dinitroanilines
1976	1980	tiocarbazyl	15	Thiocarbamates
1977	2009	butralin	3	Dinitroanilines
1977	1978	cyanatryn	5	Triazines
1977	-	metamitron	5	Triazinones
1978	-	clopyralid	4	Pyridyloxy-carboxylates
1978	-	diclofop-methyl	1	Aryloxyphenoxy-propionates

Continue

Continuation

Start	End	Active substances	HRAC	Chemical family
1978	2002	dimefuron	5	Ureas
1978	1991	ethalfluralin	3	Dinitroanilines
1978	2003	flamprop-M-isopropyl	0	Arylaminopropionic acid
1978	1983	tebuthiuron	5	Ureas
1979	1993	alloxydim	1	Cyclohexanediones
1979	-	dimethachlor	15	α-Chloroacetamides
1979	2003	siduron	5	Ureas
1980	1989	bromofenoxim	6	Nitriles
1980	2007	hexazinone	5	Triazinones
1980	-	pendimethalin	3	Dinitroanilines
1980	2000	tebutam	3	Benzamides
1980	1995	vernolate	15	Thiocarbamates
1982	2002	fosamine-ammonium	0	Organophosphate
1982	-	oxyfluorfen	14	Diphenyl ethers
1982	-	pyridate	6	Phenyl-pyridazines
1982	-	triclopyr	4	Pyridyloxy-carboxylates
1983	-	bifenox	14	Diphenyl ethers
1983	-	metazachlor	15	α-Chloroacetamides
1984	1995	chlomethoxyfen	14	Diphenyl ethers
1984	2015	chlorsulfuron	2	Sulfonylureas
1984	1985	fluazifop	1	Aryloxyphenoxy-propionates
1984	-	oryzalin	3	Dinitroanilines
1984	2003	sethoxydim	1	Cyclohexanediones
1985	-	flurochloridone	12	N-Phenyl heterocycles
1985	2004	quizalofop	1	Aryloxyphenoxy-propionates
1986		fluazifop-P-butyl	1	Aryloxyphenoxy-propionates
1986	2018	glufosinate-ammonium	10	Phosphinic acids
1986	2007	imazamethabenz-methyl	2	Imidazolinones
1986	-	isoxaben	29	Benzamides
1986	-	metsulfuron-methyl	2	Sulfonylureas
1987	-	fluroxypyr	4	Pyridyloxy-carboxylates
1987	1992	haloxyfop-etotyl	1	Aryloxyphenoxy-propionates
1987	-	mecoprop-P	4	Phenoxy-carboxylates
1987	-	thifensulfuron-methyl	2	Sulfonylureas
1988	-	aclonifen	32	Diphenyl ethers
1988	-	dichlorprop-P	4	Phenoxy-carboxylates
1988	-	diflufenican	12	Phenyl ethers
1988	2003	norflurazon	12	Pyridazinone
1988	1995	tralkoxydim	1	Cyclohexanediones
1989	2020	desmedipham	5	Phenylcarbamates
1989	1992	fenoxaprop	1	Aryloxyphenoxy-propionates
1989	2002	triasulfuron	2	Sulfonylureas

Continue

Continuation

Start	End	Active substances	HRAC	Chemical family
1990	-	cycloxydim	1	Cyclohexanediones
1990	-	fenoxaprop-P-ethyl	1	Aryloxyphenoxy-propionates
1990	1992	flamprop-M	0	Arylaminopropionic acid
1990	2007	pretilachlor	15	α-Chloroacetamides
1990	-	propaquizafop	1	Aryloxyphenoxy-propionates
1990	-	prosulfocarb	15	Thiocarbamates
1990		quizalofop-P-ethyl	1	Aryloxyphenoxy-propionates
1991	2003	acifluorfen-sodium	14	Diphenyl ethers
1991	-	amidosulfuron	2	Sulfonylureas
1991	-	bensulfuron-methyl	2	Sulfonylureas
1991	-	clomazone	13	isoxazolidinones
1991	2002	fluoroglycofen-ethyl	34	Diphenyl ethers
1991	2007	fomesafen	14	Diphenyl ethers
1991	2004	quinclorac	4	Quinoline-carboxylates
1991	-	tribenuron-methyl	2	Sulfonylureas
1993	2008	haloxyfop-methyl	1	Aryloxyphenoxy-propionates
1993	-	nicosulfuron	2	Sulfonylureas
1993	-	rimsulfuron	2	Sulfonylureas
1994	2003	cinosulfuron	2	Sulfonylureas
1994	-	clodinafop-propargyl	1	Aryloxyphenoxy-propionates
1994	2008	dimethenamid	15	α-Chloroacetamides
1994	1997	flupoxam	29	Triazolocarboxamide
1994	-	quinmerac	4	Quinoline-carboxylates
1994	-	sulcotrione	27	Triketones
1994	-	triflusulfuron-methyl	2	Sulfonylureas
1995	2015	metosulam	2	Triazolopyrimidine
1997	-	clethodim	1	Cyclohexanediones
1998	2020	flurtamone	12	Pyridazinone
1999	-	azimsulfuron	2	Sulfonylureas
1999	-	carfentrazone-ethyl	14	Triazolinones
1999	-	flumioxazin	14	N-Phenyl-imides
1999	2018	flupyrsulfuron-methyl-sodium	2	Sulfonylureas
1999	-	isoxaflutole	27	Isoxazoles
1999	-	prosulfuron	2	Sulfonylureas
2000	2013	acetochlor	15	α-Chloroacetamides
2000		flazasulfuron	2	Sulfonylureas
2001	2013	cinidon-ethyl	14	N-Phenyl-imides
2001	-	flufenacet	15	α-Oxyacetamides
2001	-	sulfosulfuron	2	Sulfonylureas
2002	-	cyhalofop-butyl	1	Aryloxyphenoxy-propionates
2002	-	florasulam	2	Triazolopyrimidine
2002	-	imazamox	2	Imidazolinones

Continue

Continuation

Start	End	Active substances	HRAC	Chemical family
2002	-	iodosulfuron-methyl-sodium	2	Sulfonylureas
2002	-	mesotrione	27	Triketones
2002	-	pyraflufen-ethyl	14	Phenylpyrazoles
2003	-	dimethnamid-P	15	α-Chloroacetamides
2003	-	mesosulfuron-methyl	2	Sulfonylureas
2003	-	picolinafen	12	Phenyl ethers
2003	-	S-metolachlor	15	α-Chloroacetamides
2004	-	foramsulfuron	2	Sulfonylureas
2004	2015	oxadiargyl	14	N-Phenyl-oxadiazolones
2004	-	propoxycarbazone-sodium	2	Triazolinones
2010	-	beflubutamid	12	Phenyl ethers
2010	-	penoxsulam	2	Triazolopyrimidine
2010	-	pyroxsulam	2	Triazolopyrimidine
2010	-	tembotrione	27	Triketones
2011	-	acetic acid	0	Non-classified
2011	-	pethoxamid	15	α-Chloroacetamides
2011	-	tritosulfuron	2	Sulfonylureas
2012	-	pelargonic acid	0	Non-classified
2012	-	aminopyralid	4	Pyridyloxy-carboxylates
2012	-	pinoxaden	1	Phenylpyrazoline
2013	-	thiencarbazone-methyl	2	Triazolinones
2017	-	halosulfuron-methyl	2	Sulfonylureas
2018	-	halauxifen-methyl	4	Pyridine-carboxylates
2020	-	caprylic acid	0	Non-classified