Review

A historical review of the use of pesticides in Colombian agriculture

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Abstract: The growing production and use of multiple types of pesticides in the agri-food sector has caused strong concern on the part of many organizations worldwide, which question the degree of safety and quality of the products being supplied to the population. Colombia, a geographically privileged country with extensive areas of agricultural use, is not apathetic to this situation. Therefore, this review article aims to give a citrus and updated vision of the use of pesticides worldwide and subsequently in the Colombian agricultural sector. As a result, a sector that is currently growing and contributing to the national economy was identified. However, with a strong tendency to use pesticides to maximize production yields and minimize associated costs. Currently, many pesticide residues are identified in transitional and high value crops, such as vegetables and fruits. This causes chronic and/or acute intoxication scenarios in populations that meet these substances. Finally, academia and the public sector seek to update knowledge that promotes the regulation and management of this type of substances, promoting the transformation of the sector towards organic and regenerative agri-food models that prohibit the implementation of pesticides for pest and disease control.

Keywords: agriculture, agri-food sector, analytical methods, Colombia, pesticides residues

1. Introduction

Agriculture currently fosters the development of the economies of many nations, since it contributes to the domestic production of goods and services, the generation of employment and food security and sovereignty [1]. That said, agricultural systems produce annually an average of 11 billion tons of food and many non-food products such as natural fibers (32 million tons) and timber (4 billion m^3) [2]. Additionally, in economic terms, it is estimated that the gross value of agricultural production exceeds 3.5 trillion USD, being one of the sectors with the highest monetary movement for both developing and developed countries [2]. It generates economic, social and environmental value throughout the life cycle chain of agricultural products [1,2].

However, the growing pressure on the sector to meet the food needs of the human population in the coming years has meant that agri-food systems are not environmentally sustainable [2,3]. Consequently, modern agriculture is based on conventional practices that implement the use of chemical fertilizers and pesticides, monoculture, genetic modification of high-yielding crops and opportunities for technological innovation [4, 5]. These intensivist and not very resilient practices generate a high level of impact on the use of

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natural resources, especially soil, water, biosphere and biodiversity in the areas geographically surrounding the crop zones [5].

This impact has been intensified by the deplorable management of chemical substances, especially pesticides [3,6]. Since traditional agriculture visualizes the application of these substances as a solution for the control of diseases from vertebrate, invertebrate and pathogenic organisms that may affect food production [7]. Since between 20% and 40% of crops are lost due to diseases caused by these organisms [3]. As a result, the agricultural chemical industry invested 74.95 million USD worldwide in 2012, of which 45% was directed to the production of fungicides [7]. These products are so widely used that the market classifies them according to their application function, target organisms and chemical nature [7,8].

Additionally, the uncontrolled use of pesticides, the lack of regulatory processes, product counterfeiting, resistance mechanisms by living organisms and pathogens, and the impact on environmental and human health [3,6,7,8,9] have caused a strong discussion because of the associated costs that the use of these substances may entail [8]. Since, in most of the research on pesticides and their impact on agroecosystems, a strong direct and indirect effect on different socio-environmental matrices is evident [7,10,11]. Therefore, the objective of this article is to provide a critical review of the use of pesticides in the Colombian agricultural sector, identifying their history and dynamics of use, instrumental techniques for the identification of these substances and the effects caused using these agrochemicals.

2. Pesticides.

2.2. History of pesticides.

Humanity has made many efforts to increase agricultural production systems, it has always encountered some soil problems such as loss of fertility, erosion, and some pests. To mitigate pests, the use of pesticides has been a highly effective option with these systems, as they are effective and simple to use [12]. This use has caused an imbalance in ecosystems such as the resistance it generates to some pests and the appearance of new ones, environmental pollution in general and the loss of natural regulation that ecosystems have [12]. Efforts have been made to promote good agricultural practices where this use of pesticides in the environment must be carried out under controlled and specific conditions, follow national and international standards and apply the quantities and dose limits in accordance with the regulation, thus it is sought that the pests are controlled and also mitigate the secondary effects on the species and the environment by their application, however when the recommendations of good agricultural practices are not followed, surely there will be an imbalance in the ecosystem affecting the species and environment [13].

In accordance with the "Code of Conduct for the Distribution and Use of Pesticides" established by The Food and Agriculture Organization of the United Nations (FAO) in 2010, pesticides are defined as any substance intended to prevent, destroy, attract, repel or combat any pest, including species of unwanted plants or animals, during the production, storage, transport, distribution and processing of food, agricultural products or animal feed, or that can be administered to animals to combat ectoparasites [14]. The term includes substances intended to be used as plant growth regulators, defoliants, desiccants, agents to reduce fruit density or germination inhibitors, and substances that are applied to crops before or after harvest to protect the product against deterioration during storage and transportation [15,16]. The term does not normally include fertilizers, nutrients of

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plant or animal origin, food additives or medicines for animals" [14]. Therefore, the objective of pesticides is to exterminate certain species [16].

Using chemicals to eradicate pests and preserve crops is as old as agriculture. The Romans and Greeks burned sulphur for fumigation. In the 16th century certain heavy metals were used, and at the beginning of the 19th century Europe began to frequently use compounds with lead, copper, mercury, ground tobacco (nicotine which is a recognized pesticide) [17,18]. These were called first-generation pesticides (basically insecticides), which are very persistent in the environment but are not very effective. [19,20]. In the 20th, the need to increase agricultural production and crop growth was seen due to the growth of the world population, thus came industrialized practices and the need to explore new forms and varieties of pesticide production [3].

After the two world wars, the development of pesticide synthesis arose due to the need to search for new chemical products for this purpose. These synthetic pesticides, known as the second generation and were primarily insecticides [17,18], are more effective for the eradication of pests but much more polluting. Thus, 1,1,1-trichloro-2,2-bis (4-chlorophenyl) ethane DDT was synthesized, this was the first of its generation and basically arose from the need to protect soldiers from malaria in the second World War, its great properties were explained by Paul Müller in 1939 [17,18]. By 1945, commercialization also included other organochlorine pesticides (OCP) and their use spread throughout the world, encouraging the search for other selective substances with pesticide properties [17]. During the 1960s, routine analyzes of pesticide residues emerged in different agro-food and environmental matrices because of the excessive use of pesticides and the risk to human health and the environment, these methods had to be adapted according to the emergence of the industrial introduction of new pesticides [17,18].

Glyphosate, one of the most sold and commercialized pesticides, was introduced on the market in the seventies and eighties, in addition to the introduction of new families of pesticides such as imidazoles, triazoles, pyrimidias that are fundamentally more selective, less harmful towards others [18,21]. Species but were not exempt from resistance; other new families also appeared in the 1990s (i.e, triazolopyrimidine, spinosyn, strobilurin, azolone, etc.) that even improved later [17,18]. To this day, pesticides are possibly the most studied chemical compounds from an environmental point of view, due to this, many countries have established strict regulations for their use, commercialization and in addition to analysing food products to verify the correct application according to with the established regulations [18,22].

2.2. Toxic and legal aspects of pesticides.

Given the new introductions of pesticide families to the market and those that were already in the past, the classification of pesticides becomes complex. The most common classifications are by their specific function, toxicity, specific action and chemical family [21,22,23]. As an example, the United States Environmental Protection Agency (EPA) classifies pesticides according to their specific function, which is today a broad classification of use - as algaecides (to kill algae and / or slow their growth), antimicrobials (to control germs and microbes), disinfectants (to control germs and microbes), nematicides (to control or eliminate pests on plants), fungicides (to eliminate fungal problems such as : mold and rust), herbicides (to eliminate or inhibit plant growth unwanted), insecticides (to kill and control insects), growth regulators (to disrupt insect growth and reproduction), rodenticides (to kill rodents), and wood preservatives (which are resistant to insects, fungi, and other pests) [23].

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On the other hand, the World Health Organization (WHO) classifies them according to their toxicity (see Table I.) according to the mean lethal dose (LD_{50} in mg / kg) and the mean lethal concentration (LC_{50}). present in organisms and in relation to their body weight [14,24,25]. From a commercial point of view, they are classified according to their destination into pesticides for domestic use, phytosanitary, livestock, environmental, food industry and for personal hygiene [26]. According to their presentation or method of use, they are classified into gases or liquefied gases, fumigants and aerosols, powders with a particle diameter of less than 50 µm, solids and preparations in the form of tablets, liquids, or baits [27].

Table 1. WHO recommended classification of pesticides by hazard [24], [25].

TOXICOLOGICAL CATEGORY	DANGEROUSNESS	DL_{50} FOR RATS (MG/K) BODY WEIGHT)	
		ORAL	DERMAL
Ia	Extremely hazardous	<5	<50
Ib	Highly hazardous	5-50	50-200
II	Moderately hazardous	50-200	200-2,000
III	Slightly hazardous	Over 2,000	Over 2,000
U	Unlikely to present acuate hazard	5,000 or higher	

Source: World Health Organization (WHO), (2019).

When pesticides are classified according to their composition, reference is made to inorganic compounds (arsenical, mercury derivatives), carbamates, coumarin derivatives, urea derivatives, dinitro compounds, OCP, organophosphate pesticides (OPPs), organonitrogen pesticides (ONPs), organometallics, pyrethroids, thiocarbamates, triazines, botanical compounds (rotenone, nicotine), among others [27].

In addition, to protect consumers, regulatory organizations and countries have taken steps to standardize the amount of pesticide residues identified in products marketed for human consumption [28]. These limits are referred to as *"maximum residue limits (MRLs)"* and are aligned with good agricultural practices [29]. As a result, the WHO and FAO defined Codex Alimentarius MRLs, evaluating the toxicology of pesticides and their residues, as well as testing residue data obtained in supervised trials and in uses consistent with international good agricultural practices [29,30]. The tests include data from supervised trials, carried out with the highest recommended, self-registered and/or registered use concentration in the country [29]. It is worth mentioning that MRLs are not toxicological limits or that they are established considering their tolerable daily intake [29,30]. This value refers to a threshold limit of identification of pesticides probably not harmful to the consumer but clarifying that occasional consumption of such products with concentrations above the MRL may not cause harm (although extremely high concentrations may cause an acute effect in some people); in contrast, continued exposure may cause chronic effects [28,29].

This proposal has acquired importance in the international context due to its recognition within the Agreement on Sanitary and Phytosanitary Measures of the World Trade Organization [29], and therefore, should be taken as a reference when analysing pesticides in any food source. In general, MRLs are not unique for each pesticide or product. They generally range from 0.01 to 10 mg/kg depending on the food product [29,30]. These levels are constantly studied and, if necessary, modified or prohibited, especially when children are involved as a vulnerable population [29,31].

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3. Analytical methods for the analysis of pesticide residues in agri-foods.

Separation and identification techniques is one of the most important aspects in any analytical method. That is why the conditions of the analytes, the sample pre-treatment methods and the instrumentation must be considered to obtain the appropriate limits of detection (LODs) and quantification (LOQs) in accordance with current legislation and achieve the levels of reliability and reproducibility of the analyses [32,33]. For pesticide residues, the most widely used techniques in laboratories around the world are gas chromatography (GC) and liquid chromatography (LC), while capillary electrophoresis (CE) has been applied to a much lesser extent [32,33]. In fact, the first two are frequently found in any analytical laboratory dedicated to the routine analysis of pesticides. With the instrumental developments of GC over time, this technique has positioned itself as one of the most widely used techniques for the analysis of thermally stable and low polarity pesticides due to the relatively high volatility of many pesticides, the relatively low cost of the instrumentation compared to LC or CE and the easy maintenance of the equipment [32,33].

As for conventional detectors, these have been widely used, especially for the analysis of specific groups of pesticides. an example of this are the nitrogen-phosphorus detectors (NPD) and the flame photometric detector (FPD) for the analysis of OPPs and ONPs [34,35] respectively, and the electron capture detector (ECD) for OCPs [36] due to its high level of sensitivity and its selectivity that minimizes matrix interference. The flame ionization detector (FID) has also been widely used, but less frequently, due to its almost negligible selectivity [37]. On the contrary, GC coupled to mass spectrometry (MS) soon gained prominence in the identification and quantification of pesticides due to its much-desired confirmatory capacity, in addition to its greater selectivity and greater or comparable sensitivity, which are essential, especially when it comes to the analysis of highly complex matrices [38].

Initially, GC-MS instrumentation used single quadrupoles (Qs) that only allowed to solve coelution or partial overlap problems through the single ion monitoring (SIM) mode. Subsequently, other analysers were introduced, such as the ion trap (ITs), the triple quadrupole (QqQs) and the time of flight (TOF), followed by the Q-TOF and Q-orbitrap, among others, which placed the detection of MS at a higher level. level: the highly desired tandem MS (MS/MS) [39]. These more advanced analysers provide higher structural selectivity by performing consecutive structural fragmentations of analytes in Multiple Reaction Monitoring (MRM) mode. GC-MS/MS also provides a better signal-to-noise ratio (S/N) and therefore improves the sensitivity of the method and reduces the matrix effect [40]. An important evolution in the last decades has been with fast gas chromatography, providing better resolution, shorter analysis time and lower costs compared to conventional GC [40].

An important evolution in the last decades has been with fast gas chromatography, providing better resolution, shorter analysis time and lower costs compared to conventional GC [40]. Better results have been obtained with advances in detector injection systems, heating/cooling systems, and ionization techniques that have allowed chromatographic separations in less time [40]. It is a technique that on average achieves separations between 1-3 min, there are hyper-fast separations of 60 s [40]. Complementary to all advances in this technique, microbore columns have also been found to reduce band broadening and increase column efficiency with reduced i.d. [40]. Another approach is the low-pressure approach which achieves improved S/N ratios and consequently better LODs because of the narrower peaks caused by the increased linear velocity achieved by short

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micro perforation columns [41,42], in addition to achieving lower elution temperatures and allowing high-boiling and thermally labile compounds to be eluted at a moderately low temperature [43]. These fast GC methods are not compatible with MS detection, Q [40]. All these chromatographic approaches combined with the rapid treatment of samples are the ones sought to achieve more and better analyses, especially in the analysis of multiple residues in different agri-food matrices[41,43,44]

Liquid chromatography (LC) is mainly used for the analysis of high molecular weight, very polar and/or thermally labile compounds [45,46].This technique is known as a complement to GC for pesticide analysis. Reverse phase (RP) and pre-columns (C8 or C18) with mobile phases composed mainly of water and methanol (MeOH) or acetonitrile (ACN), using ultraviolet light (UV) or diode array (DAD), have been developed in detection systems is the MS, the MS/MS that is the most used for the analysis of pesticides when it is coupled to HPLC [47,48]. This technique has evolved to the miniaturization of columns to reduce analysis times, the consumption of mobile phase that makes this technique more expensive than GC [44], [49], the decrease in sample dilution and consequently improves the sensitivity [49]. This has given way to capillary and nano LC (CLC and nano-LC), which have led to modification of the instrumentation [50,51]. The reduction of the diameter of the stationary phase particles has led to the introduction of ultra-high-performance LC (UHPLC) [52,53].

Sub 2 μm particles are currently marketed that provide a high separation power for groups with a high number of pesticides [48,54].Another strategy that has been introduced to improve LC performance is the introduction of core-shell particles, which have a solid core 1.2 to 4.5 μm in size surrounded by a porous layer (shell) 0.2 μm in size. or 0.5 μm [55]. These particles also allow to overcome the limitations of the use of large amounts of organic solvents and the long analysis time in HPLC, as well as the high back pressure and frictional heating of UHPLC [56]. In fact, more and more analytical methods, including those dedicated to pesticide analysis, are developed using this type of column, especially those with the smallest sizes [48, 53]. MD-LC multidimensional liquid chromatography is also an alternative to conventional LC separations when extremely complex samples as well as many compounds need to be analyzed [57,58].

For the analysis of pesticides, other techniques have also been used, such as EC, specifically capillary zone electrophoresis (CZE) when they are charged, and micellar electrokinetic chromatography (MEKC) when they are in their neutral form [59,60]. In both cases, the selectivity and resolution of their separation are directly controlled by different buffer additives, i.e. solvents, complexing agents, polymers, etc. Among other separation modes, capillary electrochromatography (CEC) applications with packed or open tubular columns are also highlighted for separations of charged or uncharged pesticides [61,62]. As for the detectors, conventional ones such as (UV, DAD) have been used and the use of coupling with MS has also been developed, although with some limitations since there is no exit vial, nor an electrode to close the electrical circuit. Several interfaces have also been successfully applied, the most common approach being ESI-assisted with a liquid shell [63,66]. When MEKC is to be used, either non-volatile background electrolytes or the application of the partial fill technique should be used [67,68]

Another technique to highlight for the analysis of pesticides is supercritical fluid chromatography (SFC) -considered as a hybrid of GC and LC- also coupled to MS [69,71], which is currently awakening in different fields as a result of the production of more robust and reliable instrumentation that has improved its reproducibility, robustness, specificity, and sensitivity [72,73]The use of supercritical fluids as mobile phases (i.e. supercritical carbon dioxide, the most common) allows rapid separations of pesticides of wide

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polarity due to the use of high flow rates with little or no consumption of organic solvents, which can be used as co- solvents [69,70].

4. Agriculture in Colombia.

3.1. Sociodemographic description.

Colombia is a country located in the northwestern tip of South America, with a land continental shelf extension of 1,141,748 Km2 and 988,000 Km2 of maritime continental shelf; it is the fourth largest country in the region and the twenty-sixth largest in the world [74]. The bordering countries and regions are Panama (northwest), Antilles Sea (north), Venezuela and Brazil (east), Pacific Ocean (west) and Peru and Ecuador (south) [74,75]. Its administrative division is made up of 32 departments, 1 capital district (Bogotá) and 1,122 local administrative entities (1,103 municipalities, 18 non-municipalized areas and the island of San Andrés and Providencia) [74]. Geographically, the country is in the intertropical zone of the equator and is crossed by the Andes Mountain range and the Amazon plain. Additionally, its relief has landscapes of valleys and plains, peripheral mountain systems and central mountain systems [74,75,76]. This results in climatic zones depending on the altitude at which it is located and the behavior of rainfall [74].

On the other hand, according to Departamento Nacional de Estadistica (DANE) and the last population census conducted in 2018, the country has a population of approximately 48,258,494 inhabitants (inhab); which represents a population density of 42 inhab/km^2 and a population growth rate of 6.5% [74,77]. Internally, Colombia is experiencing a displacement of settlers to urban centers seeking to improve their living conditions. This means that 77.1% of the population is in urban centers and municipal capitals, while 7.1% in populated centers and 15.8% in dispersed rural areas [77]. Additionally, the total population is distributed in 13,480,729 households with an average of three persons per household [77].

3.2. Agriculture in Colombia.

As mentioned above, agriculture has played an important role in the economic development of nations [14,78]. Colombia, due to its privileged geographical location, water wealth, availability of natural resources and climate has contributed to the development of the agricultural sector, as an important economic sector [79]. This has positioned the country among the seven nations with high agricultural potential, as well as its potential role as a global pantry that will respond to the increase in demand for agricultural products [78,80]. For this reason, the country has focused the efforts of multiple governmental portfolios on the design and implementation of strategies and activities that dynamize this economic sector to meet domestic and globalized expectations [78]. As a result, the different social, economic and political sectors have established objectives of equity, poverty reduction, economic growth, redefining the rural sector, providing environmental services, combating hunger and reducing poverty [2,78,79].

Now, according to data collected in the national agricultural survey conducted in 2019 by DANE, the production of agricultural products is made up of agro-industrial and agri-food derivatives with a production rate of 63,248,462 t and 42,208,363 t respectively, among which we can highlight coffee, oil palm, sugar cane, cocoa, soybeans and cotton [81]. Additionally, fruit products, tubers, cereals, vegetables and legumes and forest plantations had a production of 6,712,167 t, 6,404,514 t, 4,423,183 t, 3,051,481 t and 448,154 t respectively [20]. As a result, the country has excelled in exotic agri-food production dynamics that include tropical fruits such as pineapple, papaya, mango and passion fruit and a variety of avocado, a product known worldwide for being healthy and contributing to a balanced diet [20].

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However, the sector has presented a volatile behavior in the last twenty years, compared to the first years of the beginning of the century. [79,82]. According to figures provided by the World Bank compiled in the report entitled "development of Colombian agriculture" (2014), in 1965 agriculture contributed 25% of the Gross Domestic Product (GDP) compared to 6% in 2012 [79]. In addition, during the period 1990 - 2011, the behavior of the volatilized agricultural GDP showed a downward trend, with figures below the average for Latin America and the Caribbean [79]. Consequently, the national government has sought to minimize the difficulties in terms of agricultural productivity, access to markets and quality standards that allow the sector to recover to figures of the 1970s (20% contribution to GDP) [82].

Allowing for encouraging results in the framework of the economic reactivation following the pandemic caused by the SARS-CoV-2 virus with an increase of 3.8% of agricultural GDP [83] focusing its activities on increasing the cultivation areas and export of products derived from permanent and transitory crops such as vegetables, fruits, sugarcane, flowers and others [83,84]. This increase monetarily represented a total of $8,947 billion pesos in the agricultural crop's subsector, the largest recorded between 2019 - 2021 and an increase in transitory crop products and permanent crop products [84,85]. This recovery has generated that by 2021 the agricultural sector will be one of the best performers in the international market, with a percentage of product distribution of 18.6%, only surpassed by the marketing of fuel products and products of the extractive industry (55.7%), fuels, mineral lubricants and related products (54.7%) and manufactures (21%) [74,82].

3.3. Pesticides in Colombia.

As mentioned above, the multiple geographical, climatological and hydrological conditions, among other environmental and vegetative characteristics, have made the use of pesticides in Colombia a daily practice in most of the country's production areas [86, 87]. This has caused the imprudent use of this type of substances, which have more than 100 active ingredients used for the reduction and/or elimination of micro and macro-organisms, to unleash a series of toxicological consequences on human health, environmental degradation and costs associated with the acquisition of the products that are of concern to governmental organizations [86,87]. The producers' lack of knowledge about the handling and management of pesticides maximizes the problems of deterioration of different environmental matrices (air, water and soil), intoxication due to chronic or acute exposure, bioaccumulation of pesticides in the food produced and the increase in associated costs, considering that about 14% of the total costs are associated with the purchase of pesticides for small and medium farmers [86,87,88,89].

The use of pesticides dates to the 1970s, when the demand for products such as corn, cotton, potatoes, rice was more intense worldwide, 90% of pesticides were used in these crops and especially OCPs pesticides such as dieldrin, aldrin, endrin, heptachlor, hexachlorobenzene, toxaphene, and DDT [90,91]. Due to problems generated using DDT, its use was prohibited in the country in 1986, and the remaining product was stored and disposed of by the Ministry of Social Protection in containers in different areas of the country, together with the prohibition of import, commercialization and use of other persistent pesticides, basically OCPs [90,91,92]. According to the reports of the Instituto Colombiano Agropecuario (ICA), in 2015 the country reached a production of 50.9 million liters and 24.5 million kg of pesticides [92], with herbicides being the most produced in the country such as OPP, carbamates and pyrethroids [93].

However, multiple investigations have focused their study objective on the identification of pesticide residues in multiple regions of the Colombian territory and in high value crops such as vegetables, tubers, cereals, fruits, among others [87,88,89]. It concluded in the identification of residues of pyrimethanil, tebuconazole, carbofuran, chlorothalonil and OPPs in the departments of Cundinamarca, Boyacá and Huila [94]; also, in 2016, residues of malathion, anzinphosmethyl, fenchlorphos, chlorpyrifos, phorate, dementon, methylsulfon and disulfoton were identified in tropical fruits grown and marketed in the department of Bolivar [95]. Similarly, in other studies conducted during 2019 to 2022, residues of chlorpyrifos, iprodione and lindane were found in fruits distributed in different supermarkets in the city of Bogotá D.C. [96,94,95,97,100]. In the supplementary material (see Table S2) shows a greater number of pesticide residues identified in different regions of Colombia [14,24,86,87,89,101,102].

2.2. Toxic and legal aspects of pesticides in Colombia.

Currently, governmental, regulatory and academic institutions have worked together to identify the toxicological aspects, health effects to which different population groups in the country are exposed and analytical methods (see Table S3) [103]. As a result, guidelines have been updated to minimize the use of chemical substances and improve the health conditions of farmers, food safety and the conservation of agroecosystems. However, the situation is alarming considering the high volume of pesticide application in conventional crops [101,103].

Table S3 Some examples of the application of GC-MS and GC-MS/MS and LC-MS and LC-MS/MS for the determination of pesticides in food samples from Colombia.

Number of multiclass pesticides	Matrix	Sample preparation	Analysis technique	Analyser	LOQ	References
21	Junca Onion	SPME	GC-MS	NPD	0.11-7.15 µg/kg	[104]
201	Tropical fruits and vegetables	QuEChERS	LC-HRMS	QqQ	0.1- 1 µg/kg	[105]
13	Coffee	SPME	GC-MS	Q	0.7- 5 µg/kg	[106]
48	Annona cherimola and gulupa	QuEChERS	GC-MS/MS	QqQ	5 µg/kg	[107]
50	Exotic fruits	QuEChERS	GC-MS	Q	1 µg/kg	[108]

This results in scenarios of chronic and/or acute intoxication in the population centres that are exposed to this type of substances. In the study entitled "Intoxication by pesticides: Casuistry of the Hospital Universitario del Caribe and the Clínica Universitaria San Juan de Dios de Cartagena", a high number of patients intoxicated by pesticides through oral ingestion, dermal contact and/or inhalation were recorded. Chlorpyrifos insecticides as the active agent were the most frequently identified (14%) in the first health care centre.

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Meanwhile, in the second health care centre, a greater number of patients were identified as having been poisoned by insecticides with the active agent propoxur (17.7%) [93]. Likewise, case studies have been identified that have sought to determine the relationship between the ingestion, inhalation and/or dermal contact of pesticides or pesticide residues and their effects on human health. One of the most striking cases is the genetic and embryonic affectation to which intoxicated persons are exposed [86,109]. Identifying cases of affectation of cytogenetic characteristics in blood lymphocytes in children exposed to pesticides in rural areas of the department of Cordoba [110]. In addition, studies that focus their objective on the identification of cognitive affectations in school-age children who were exposed in prenatal and postnatal stages to pesticides in rural areas of the city of Bogotá [70].

However, the Ministerio de Agricultura y Desarrollo Rural, together with organizations such as the ICA, have provided a greater volume of information that makes it possible to have updated lists of pesticides used in Colombia, commercial laboratories, trade names, toxicological category and other data necessary for the proper handling, management of these substances and analytical methods [90, 111, 112]. Additionally, the new paradigms of organic, regenerative and ancestral agriculture have encouraged the modification and adaptation of agricultural models. This has led to the issuance of resolutions that allow the acquisition and management of the organic food seal, allowing a 43% decrease in the use of pesticides in Colombia in the last 20 years, thus increasing the number of vegetables, exotic fruits, flowers and other agricultural products abroad [110,113].

5. Conclusions

Pollution from the indiscriminate use of pesticides has been a cause for concern because that these pollutants can have on human health and the environment. In recent decades, the use of pesticides has increased to increase the global production of agri-food products and meet the global needs in production, in addition to the great variety of new pesticides introduced to the market.

Colombia, a country that is identified as one of the agricultural pantries for the world due to its variety of agro-food products that it produces, thanks to the diverse climates, thermal floors and water resources that characterize it. Therefore, the use of various pesticides is common in agricultural practices, especially OPPs, OCPs as shown above and following the Codex Alimentarius legislation to establish MRLs for pesticides in food.

Regarding the analytical methods applied, most of the works have used GC and LC as the main techniques in the qualification of agro-food pesticides produced in Colombia, although very few studies were found proportionally to what the country produces and exports.

Finally, it should be noted that it is important to continue with these analyzes of pesticides in agri-food products in Colombia, to follow a rigorous control over the pesticides that are currently being used and to take special care of those that have been prohibited according to the legislation, since as evidenced, there are not many works that show these analyzes and controls by departments of the country to keep track.

Supplementary Materials: The following supporting information can be downloaded at: Table S2: Identification of some pesticide residues by Colombian departments; Table S3: Some examples of the application of GC-MS and GC-MS/MS and LC-MS and LC-MS/MS for the determination of pesticides in food samples from Colombia.

Author Contributions:

Riaño- Herrera, D.A.: Methodology, writing—original draft preparation, investigation, data curation, visualization. Fuentes-Molina, N.: Methodology, writing—original draft preparation, writing—review and editing, visualization. Varela-Martínez, D.A.: Conceptualization, methodology, investigation, writing—review and editing, supervision, project administration.

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