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Review Article

Monitoring of Organophosphorus Pesticides in Brazilian Food

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Abstract

The accumulation of agrochemicals in agricultural products is a major concern since the plants act as intermediates in the transport of soil, water, and air contaminants to humans and fauna. The assessment of pesticide residues in food has become a priority objective, ensuring the quality of food and protecting consumers against possible risks. Brazil has legislation on pesticides, but monitoring is still far from other countries, as is the case in the USA and Europe. Therefore, it is necessary to establish better practices for the evaluation of pesticide residues in food.

Introduction

The monitoring of pesticides in the environment is a very important tool in the characterization and management of environmental risks resulting from the use of these products under real conditions [1], as well as a form of measurement in minimizing the potential risk of contamination by pesticides in humans [1,2] and to assist in compliance with legislation [3]. According to the Brazilian Federal Decree No. 4,074 of 2002, the monitoring of pesticides can also be part of the evaluation process in the registration of new products, or yet the re-evaluation of products in use [4].

The monitoring and evaluation of the impacts in the use of pesticides should be seen as vital activities, ensuring the sustainability of the agricultural production systems that use pesticides, in addition to ensuring compliance with regulations [5], to assure that the applications of pesticides be made according to the proposed good agricultural practices (GAP) [5-7], resulting in a safe product for the consumer [6,8]. If GAP is applied efficiently, the number of pesticide residues will be below the corresponding to the maximum residue level [8]. The monitoring of pesticide residues acts as an essential practice in guaranteeing food safety [7-11] and preventing contamination through the food chain [10,11]. According to Masiá et al. [3]. There are three important pillars in legislation to ensure the pesticide and veterinary drug residues control through the food chain:

a. Authorized Products,

b. Maximum Residue Limits (MRLs) and

c. Analytical Methods' Guidelines.

Both the government and the private sector have come to attach greater importance to the analysis of pesticide residues, where there is increasing pressure to improve analytical performance, requiring increased efficiency by reducing the cost and time of analyzes [12]. Monitoring of chemical residues in food is necessary to ensure that human exposure to pesticides [1,2,12,13], mainly through dietary intake, does not exceed tolerable levels [13]. According to WHO, on average, 30% of the diet consists of fruits and vegetables [14,15], being consumed mainly raw or semi-processed [14], and consequently, they are expected to contain higher levels of pesticide residues [14-16] in comparison with other food groups of animal origin [15]. It is impossible to eliminate pesticide residues from the vegetables' internal parts, due to the pesticide's ability to penetrate inside of the leaves and pulps [17,18].

A prerequisite for obtaining high-quality results in a monitoring and surveillance program is the development of sensitive [16,19,20], selective, and reproducible analytical methods and techniques [19]. The analytical methodologies should accurately identify and quantify the concentration of any substance, generally at very low levels, to control and monitor pesticide residues [21], and they should be able to determine the number of possible compounds in an analysis, where multi-residue methods have become more popular because they can determine a wide range of compounds [22].

In a joint initiative, FAO and WHO created the Codex Alimentarius through expert groups that established the Acceptable Daily Intake (ADI) and MRLs for each pesticide, where Codex Alimentarius has so far established MRLs for some 218 pesticides (and for numerous combinations of pesticides/commodities) available in a public database [3]. Thus, in establishing programs to monitor pesticide residues in food for several consecutive years, it is possible to know the profile of existing residues, and thus to promote quality assurance, focusing on the education of farmers, control of the sale of agrochemicals, integrated management of pests and increase of organic agriculture [23].

Many countries routinely carry out pesticide residue management programs on vegetal and animal origin, cereal grains and baby foods [23,24], where each country determines its form of monitoring [25,26]. The food monitoring programs implemented in Brazil are carried out by the Ministry of Agriculture and Livestock and Supply (MAPA), and the Ministry of Health through the National Agency of Sanitary Surveillance (ANVISA) [23], and have been implemented since 2001 with the objective to evaluate food quality and implement actions to control pesticide residues [27,28]. There are currently two monitoring of residues of pesticides in food of plant origin, with the objective of evaluating compliance with national MRLs: National Plan for the Control of Residues and Contaminants in Products of Vegetable Origin (PNCRC/VEGETAL) [29], coordinated by MAPA and the Program on Pesticide Residue Analysis in Food (PARA), coordinated by ANVISA [14,27]. Among the two, the PARA is the one that has the greatest coverage both in the states (including Ceará) and in the analyzes, quantities, and types of samples analyzed [23,27].

However, when compared to international control programs, the PARA in Brazil does not estimate the reality of chronic exposure due to consumption, not generating consistent data for comparison over a period [23]. The summary of the results of the PARA on the ANVISA website is periodically published [27,30], and those of the PNCRC are published in the official government daily (DOU) [27,31].

Multi-Residue Methods

Due to many pesticides on the market, the use of methods capable of analyzing many agrochemicals in a single analysis is currently the most common approach [32-36]. In the multi-residue method, different active ingredients of pesticides are simultaneously analyzed in the same sample, being able to detect several metabolites [37].

In the last decades, the analysis of pesticide residues, with significant analytical developments, was well achieved, in many cases; the sample preparation and analytical detection were the focus, this has allowed MRLs to become increasingly stringent in food products [9]. The development of multi-residue methods allowed the analysis of a large number of substances with a high percentage of recovery (accuracy) of the analytes and the removal of the possible interferents of the sample, besides good precision, robustness, reduction of technical work and the use of solvents [12,38,39].

In recent years, the tendency has been for analytical methods to become faster [40-42] and simple [40,41], but at the same time detect lower levels [40,41,43], besides being more sensitive [41,43] and more accurate in the identification and quantification of analytes in complex matrices (e.g. food products) and that are reliable [41]. The use of multi-residue methods emerges as a more common and efficient way of performing pesticide residue analyses on hundreds of different compounds, and it is possible to measure a range of MRLs of 0.01 to 10 mg.kg-1 [33]. The multi-residue method is the most recognized and used technique for monitoring pesticide residues in food, being adopted by countries such as Germany, Australia, Canada, the United States, the Netherlands, among others [17,18,37].

Both sample preparation and calibration strategies are important aspects that should be considered in multi-residue methods, in order to determine recommendations that balance data quality, as well as time and financial investments [40]. Rapid multi-residue analysis methods are essential to simplify and minimize the costs of sample preparation [42,44] by reducing consumables and waste generated [44]. The multi-residue method favors rapid and efficient monitoring [17,18,37], due to the increase in laboratory productivity [17,18,37,45] by significantly reducing the analysis time, reducing costs [37].

The diverse nature and structure of pesticides require different pretreatment approaches by increasing the work of analysis and decreasing laboratory productivity [46]. Thus, in some cases, it is still necessary to develop simple residue methods for the analysis of a pesticide or some pesticides from the same chemical family [33]. The QuEChERS method changed the mode of multi-residue analysis [41,47-50], as it proved suitable for large-scale residue analyzes in a broad variety of matrices [41,44,47], ensuring exact results, accurate and low detection limits for a wide variety of compounds [50,51]. This pretreatment method is very flexible [52,53] and extensively applied in the determination of various pesticide residues in agricultural products [35,46,52,54-56]. There is a need to develop rapid methods for multi- residue determination of the most commonly used pesticides to monitor pesticide residues in food and ensure not only food safety but also compliance with GAP [7,52].

Maximum Residue Limits (MRLs)

Different guidelines have been established around the world, restricting the pesticide residues in food, as a way to ensure the safe consumption of food by the population[24,46,57,58], so governments and agencies fixed MRLs [2,8, 4,50,57-60], that are specified by each country's federal legislation for each analyte and matrix [62,63]. The legislation also establishes the interval of the safety of each active pesticide ingredient for each crop [61].

The MRL is the maximum amount of pesticide or related residues (metabolites and coadjutants) that remains officially in food, due to the correct application in a specific phase, from its production to consumption [2,3,14,23,61]. Therefore, MRL values represent the maximum concentration of pesticide residue that is legally allowed in food products [2,64], and thus, can be legally marketed. The MRL is expressed in parts of the pesticide (by weight), or their residues per million parts of feed (by weight) (ppm or mg.kg-1) [4].

MRLs limit the types and amount of pesticides that may be legally present in food, according to standards set by various regulatory bodies, to minimize consumer exposure to harmful or unnecessary pesticide ingestion around the world [2,61,64], as well as promoting BPA in the use of pesticides [64]. MRLs are not toxicological limits because they do not represent the maximum amount of active substances that can harm the health of consumers [14]. For the MRL of a certain active ingredient in a food to be correctly established, in addition to the proposed safety interval, it is necessary to take into account the soil and climatic conditions, pests present in the environment, indications of dose and form of application, and this set of factors called GAP [65]. For a product and similar products in the country that there are no limits established, the MRLs by the Codex Alimentarius are used [23]. After demonstrating that the residues are safe for consumers, and based on the rigorous assessment of each legally authorized pesticide [3], the MRLs are established for each pesticide and required for each food crop, taking into account the ADI [65], being the MRL used as the basis for the calculation of exposure and food risk assessment [23].

In Brazil, ANVISA is responsible for establishing MRLs [61,63,66,67] by using toxicity data from each compound [14,23,63], but only natural vegetable crops (in natura) MRLs are established [67]. Each one of the active ingredients with authorized use in Brazil has its respective monograph containing a compilation of information (common name, chemical name, use class, toxicological classification, authorized agricultural crops, and MRLs in force) [30]. For Lemos et al. [14] a value above the MRL of a pesticide does not necessarily imply that there is a health risk, which could be assessed by other parameters such as the ADI. Lemos et al. [14] warn that in a study with statistically significant samples, many samples exceeding the MRL may indicate a potential health risk and need for health risk assessment. Thus, analytical methodologies for the determination of toxic substances in food should be able to quantify residues at very low concentrations, as well as to identify them unequivocally, ensuring that the MRLs are respected [24].

Acceptable Daily Intake (ADI)

The ADI is a safety parameter used to establish the MRLs [23,37,65,68]. The ADI is the maximum amount that is taken daily throughout life, does not present a significant health risk compared to current knowledge, and it is expressed in milligram (mg) of the pesticide per kilogram (kg) of body weight (mg kg-1 b.w.) [37,65]. It is obtained using toxicological studies [23].

In the same way as the MRLs, the ADI is stipulated for each pesticide, based on studies of the pesticide's physicochemical, metabolic, pharmacological and toxicological properties of pesticides [37,65] from laboratory animal studies and performed with procedures recognized at the international level [65]. In Brazil, ANVISA is the agency responsible for establishing the ADI of each pesticide active ingredient for each crop [66]. In Brazil, the ANVISA website provides the IDA values from the authorized monographs of each active ingredient (IA) [30], already the values in the international scope [69,70,71] can be obtained from their respective websites [69,70,71].

In a study conducted by Gerage [72], in the Northeast region, of the 283 pesticides considered in the research, 62 compounds exceeded the IDA value established by ANVISA, among these compounds the OPPs chlorpyrifos and disulfoton was found. In another research done by Meira [73], in schools in São Paulo, in which of the 272 pesticides studied, nine were above the IDA by ANVISA (most were very toxic), with four compounds in the organophosphorus (OPPs) group (acephate, diazinon, pirimiphos-methyl, and terbufos). The toxic effect of a pesticide can be potentiated in view of the simultaneous exposure to other pesticide residues that have the same toxic action mechanism, being necessary to take into account the exposure to multiple residues of pesticides present in the different foods eaten during a meal, during the day or throughout life [37].

Program on Pesticide Residue Analysis in Food (PARA)

The strict inspection of residues in food by appropriate state agencies or other institutions is considered of great importance, since pesticides are one of the most dangerous groups of chemical compounds, due to their toxic properties, persistence in the environment, and ability to bioaccumulate [74]. With the objective of structuring a service to evaluate food quality and implement waste control actions, in 2001 the Project for the Analysis of Pesticide Residues in Foods was developed, which became a program through the Resolution of the Collegiate Board of Directors - RDC nº 119 of May 19, 2003, and was developed annually under the National Health Surveillance System (SNVS) [17,18,37,75].

The creation of the PARA allowed the country to have a clearer understanding of the levels of pesticides present in its agricultural products [76]. According to the PARA of 2016 [37], the program counts on the participation of 27 Federative Units involved in the sampling and taking of actions after the dissemination of the results, where the analyzes are carried out by four Central Public Health Laboratories and by a private laboratory contracted by bidding process.

The PARA periodically monitors various in natural foods by investigating the presence of pesticides, and thus promoting the health of the Brazilian population [66]. It is possible with PARA to verify if foods commercialized in retail have levels of pesticide residues within the MRLs established by ANVISA published in a monograph specific to each pesticide by checking whether the pesticides used are properly registered in the country, and have been applied only to the crops for which they were authorized [17,18], besides estimating the exposure of the population to pesticide residues in plant foods and, consequently, assess the health risk of such exposure [18]. In this way, the PARA helps food safety [18,37], preventing acute or chronic intoxications that may arise from undue dietary exposure to pesticides [18,61], making it possible to diagnose the use of pesticides in foods of plant origin covered by the program [17,18].

The choice of food monitored by PARA is based on the consumption data obtained in the Consumer Expenditure Survey (POF) [17,18,23,37] performed by the IBGE [37], the availability of food in the supermarkets of the different units of the Federation [17,18,37], and in pesticides with the highest detection rate in food [37]. The sampling schedule is approved in advance by during the national meetings of the PARA [17,18,37]. Brazil is at the top of the use of pesticides, mainly in the production of commodities. The PARAs confirm residues of unapproved substances are found in foods consumed daily by the Brazilian population and in amounts greater than those approved by law [23,27]. The PARA also shows that the use of banned pesticides in Brazil persists, such as chlorpyrifos [17,37,75,77]. A factor to be considered is that residues of some non-recommended and restricted-use pesticides can also be found in fruits and vegetables due to indirect sources such as adjacent crops, soil and irrigation water [78]. The PARA recommends that consumers purchase certified and traceable food to farmers and adopt GAPs to reduce the consumption of pesticide residues and prevent health damage [17,18,37].

In the extraction of pesticides, the Mini-Luke modified and QuEChERS methods have been used. The analytical method of multi-residues or specific methodologies previously validated is applied for sample analysis [37]. According to the PARA of 2016 [37], of the irregular detections per chemical group, the analyzed samples that presented pesticides from the OPPs group, of the 4,824 studied, 3,088 were regular and 1,736 irregulars, representing 35.98% detections. The bell pepper has presented a high index of unsatisfactory results, with samples containing pesticides not authorized for culture, where the presence of organophosphates was verified [17,37,75,77,79]. Of the three pesticides with the highest number of irregular detections in the last PARA (2016), two were organophosphates (acephate and chlorpyrifos). Grape was the sample with the highest number of irregular detections with acephate (pesticide detected in 18 of the 25 monitored foods), while tomato sample presents mostly chlorpyrifos (its use is not authorized for this crop) [37].

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