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Problems of pesticide residues in grains

La problemática de los residuos de fitosanitarios en granos Problemática dos resíduos de fitossanitários em grãos

Palladino, C.¹; Pareja, L.²; Pereyra, S.³; Pérez, C.⁴

¹Universidad de la República, Cenur Litoral Norte, PDU Abordaje Holístico al Impacto de los Agroquímicos, Paysandú, Uruguay

²Universidad de la República, Cenur Litoral Norte, Departamento de Química del Litoral, Paysandú, Uruguay
³Instituto Nacional de Investigación Agropecuaria (INIA), Sistema Agrícola-Ganadero, Fitopatología, Colonia, Uruguay
⁴Universidad de la República, Facultad de Agronomía, Departamento de Protección Vegetal, Paysandú, Uruguay

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Horacio Silva Universidad de la República, Facultad de Agronomía, Paysandú, Uruguay Received 24 Jul 2032 Accepted 25 Jul 2023 Published 11 Sep 2023 **⊠** Correspondence

Cintia Palladino cpalladino@cup.edu.uy

1. Introduction

Farmers use various pesticides to control pests, weeds, and diseases in order to meet the demands in terms of yields and quality of agricultural products. The use of pesticides in Uruguay has increased steadily since 2000⁽¹⁾. The total number and amount of active substances imported increased from 3.9 to 10.6 thousand tons between years 2000 and 2020. Within plant protection products, herbicides had the highest increase, from 2.1 thousand tons in 2000 to 9.5 thousand tons in 2020⁽¹⁾. Similar trends are observed worldwide⁽²⁾.

The intensity of pesticide's uses in the country quadrupled between years 2000 and 2020, from 2.58 to 8.03 kg/ha. The same trend was observed in countries of the Southern Cone of South America, while the intensity of use is decreasing in the European Union $(EU)^{(2)}$.

This downward trend in the EU countries has been a consequence of a more restrictive use of pesticides, including an increased number of active ingredients bans. They are currently implementing a Green Pact to tackle the threat of climate change and environmental degradation. The aim of this treat is to transform the EU into a modern, resource-efficient, competitive economy. The specific goals are to reduce the use and risks of chemical pesticides in 50% by 2030⁽³⁾.

Currently, Uruguay is a few steps behind this agreement, but several strategies are underway to improve the registration and use of pesticides. The most powerful tool available today is the Integrated Pest Management (IPM), which is an approach to pest and pathogen control that combines sustainable tools with reduced use of pesticides. IPM aims not to eradicate pests, but to manage them below economic damage threshold⁽⁴⁾. For IPM success, it requires an evolutionary perspective, which is currently lacking. Also, it requires compatibility and optimization of tools and strategies used simultaneously⁽⁴⁾.



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In order to implement IPM programs we need to correctly identify the pest (in the wide sense) and understand its biology to decide when and how to monitor, and the type of management practice to use. In addition, decision support tools should be used to determine when chemical intervention is necessary. These chemical strategies need to be managed according to good agricultural practices (GAPs)⁽⁵⁾ in order to minimize residues in grains. Although in many cases the presence of residues on and in crops and crop products is unavoidable, even when applications have been made according to recommended procedures and GAPs⁽⁶⁾.

Pesticide residues are any specified substance present in food, agricultural commodities or feeding stuff. The term includes any derivative of a pesticide, such as conversion products, metabolites, and reaction products, as well as impurities considered to be of toxicological significance⁽⁷⁾.

In Uruguay, pesticide residues are regulated according to the *Codex Alimentarius*⁽⁸⁾, which establishes maximum residue limits (MRLs) for different commodities and pesticide combinations. Pesticide MRLs are the maximum residue concentrations of the active ingredient or metabolites of a pesticide in an agricultural product, expressed in milligrams of chemical per kilogram of product (mg/kg) or parts per million (ppm)⁽⁷⁾.

For exports, the MRLs of the country to which the product is exported will apply, while in the case of imports or domestic market MRLs of the Codex are followed. In the absence of MRLs, the General Division of Agricultural Services (DGSA) follows Resolution N° 514/022⁽⁸⁾. This regulation takes into account the recommendations of tolerances established by regional or international bodies of recognized technical authority, such as the National Agrifood Health and Quality Service from Argentina (SENASA), the National Health Surveillance Agency from Brazil (ANVISA), the Ministry of Health and the Under-secretariat of Public Health of Chile, the European Community Regulation 396/2005 and its amendments, and those published by the Department of Agriculture of the United States of America (USDA)⁽⁸⁾.

It is important to note that MRLs for pesticides are not toxicological limits but toxicologically acceptable limits, based on GAPs and representing the maximum amount of a residue that may be found in an agrifood as a result of the use of certain pesticide. The MRL compliance ensures that they do not cause acute or chronic toxic effects⁽⁷⁾. In order to set MRLs, a food risk assessment must be carried out, taking into account the most critical pesticide management and expected residues in agrifood, the toxicity, and the diet of each community. Therefore, Uruguay should carry out local studies that include the most critical management in agriculture and the diet of the population to have national MRLs.

2. Local studies for the determination of fungicide residues in cereal grains

Pesticide residues determination, presented in this article, was performed at the laboratory of the Departamento de Química del Litoral in Dr. Mario A. Cassinoni Experimental Station of the CENUR Litoral Norte, University of the Republic, Uruguay. The validated methodology consists of a citrate buffered-solid-liquid extraction protocol previously optimized for each type of grain. The pesticides were separated and analyzed by high performance liquid chromatography coupled to mass spectrometry, using a triple quadrupole analyzer.

One of the group's first works dates back to 2015 when the control of Fusarium head blight (FHB) in wheat was evaluated using fungicide mixtures: epoxiconazole, metconazole, tebuconazole, carbendazim, widely used in Uruguay. This study was repeated in 2017 with similar results. At that moment, fungicide management strategies studied rendered no food safety problems related to fungicides.

On the basis of this background, a study on the presence of fungicides residues in cereal grains was carried out. Samples were taken from 89 barley farms located in the barley production area in the country's north coast. Each grain sample was analyzed for fungicides residues used to control the main diseases, FHB and Ramularia leaf spot (RLS). Residues of the following fungicides were detected in the harvested grains: chlorothalonil, azoxystrobin, carbendazim, epoxiconazole, fluxapyroxad, isopyrazam, pyraclostrobin, trifloxystrobin, and prothioconazole, but their concentrations were below the EU and Codex MRLs. Data generated in this work confirmed that current commercial fungicide management strategies for FHB and RLS met the MRLs. Although the results represent a sample of the producers and the diagnosis is only related to the climatic conditions of 2017/18 growing season, these results are very valuable for barley grain production in Uruguay⁽⁹⁾.

In the same direction, another study was assayed to evaluate the control of RLS with fungicide mix-



tures in the field in different barley production areas, and in three growing seasons. The selected mixtures of fungicide were reported to be effective against RLS: epoxiconazole + fluxapyroxad + pyraclostrobin, azoxystrobin + isopyrazam, prothiconazole + trifloxystrobin + chlorothalonil. The timing of application was chosen simulating different epidemics: Z33, Z47 and Z33+Z47⁽¹⁰⁾. The aim of this work was to verify the compliance with MRLs in RLS management with fungicides and strategies widely used in barley production in Uruguay. The main results showed variability in the frequency of residues detections along the different experiments, depending on the environmental conditions during the growing season.

When results were analyzed for the different managements evaluated, azoxystrobin, epoxiconazole, fluxapyroxad, isopyrazam, pyraclostrobin were found at Z47 and/or Z61 applications, and the treatments with more than two applications showed a higher detection of fungicide residues. Although the frequency of detection was associated with higher residue levels, the treatments evaluated in this study did not exceed EU and *Codex* MRLs.

Further studies have been carried out in wheat to evaluate the control of FHB with fungicides in different locations and growing seasons. The fungicide mixtures used in one of the studies were prothiconazole + tebuconazole, and epoxiconazole + metconazole. The results showed compliance with EU and Codex MRLs, even though some of the applications were made when the crop was at the watery milky stage (Z75)⁽¹¹⁾. In another study, epoxiconazole and metconazole were evaluated at Z61, Z65 and Z71, and also showed no residues above the EU and Codex MRLs⁽¹²⁾. Another study to assess the most critical situation for Stripe Rust control in wheat was carried out to test different application times (Z30, Z49, Z65, Z71, Z73, and Z83), and two droplet sizes, large and small, with the fungicide mixture epoxiconazole + fluxapyroxad + pyraclostrobin. The results showed that the detection of residues was associated with the application with the shortest time to harvest, and no difference was found between both droplet sizes. Nevertheless, all treatments evaluated complied with the MRL regulations.

The results of these studies confirmed that the food safety situation for fungicides on cereals is favorable, as there are no MRLs violations. However, re-evaluation will be required if there are changes in the management of chemicals or if MRLs are re-adjusted.

Our results highlight the importance of carrying out local studies, as the degradation curve of an active ingredient may differ depending on the agroclimatic production area. This is because residues are conditioned by weather conditions, among others.

These studies will allow the most critical agronomic practices to be identified and re-evaluated as MRLs change, as well as to identify agronomic practices for winter cereals that meet the current and future requirements of high-value markets, prioritizing economically and environmentally sustainable production.

Keywords: cereals, pesticide use intensity, maximum residue limit, pesticide residue in grains

Palabras clave: cereales, intensidad de uso de fitosanitarios, límites máximos de residuos, residuos de fitosanitarios en granos

Palavras-chave: cereais, intensidade de uso de produtos fitossanitários, níveis máximos de resíduos, resíduos de produtos fitossanitários em grãos

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