

Book of Abstracts

ONLINE

8th LATIN AMERICAN PESTICIDE RESIDUE WORKSHOP

LAPRW

Food and Environment

May 18-20

20
21



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CHAIRSPERSON'S FOREWORD

With these final words, to close the 8th Latin American Pesticide Residue Workshop (LAPRW2021), I want to express that we have been pleased and honored to have you as participants, who have believed in this project and who have given support to the organization of this online event.

It was a great challenge to host the LAPRW online in this so particular year, in a completely unprecedented way compared to what we have usually done so far at this important Latin American meeting. This is the first time that this workshop is held amidst a very difficult global situation, using advanced communication tools that allowed us to continue with the organization and gather the highest number of participants of the scientific and professional community associated with pesticide residues ever recorded in the history of this event.

I want to express my gratitude to the authorities of the Ministry of Agricultural Development of Panamá for their contribution and continuous willingness to cooperate. I am grateful to the founding members of the scientific committee, who relied on me and on María Rosa Repetti, co-chairperson of the workshop, and gave us the opportunity to perform this task; also to the organizing committee, for their constant, collaborative and proactive work, and always accepting the challenges with a positive attitude. We thank the sponsoring companies; whose support is essential to make this type of events possible. I am also grateful to the lecturers and professors who unselfishly and always cooperatively have accepted our invitation to share with us the latest advances in their research and work.

It should be noted that we intended to offer an important platform for the students, who have made a great effort to present their works through this virtual modality, thereby making a creative and valuable contribution to this event. Via the various planned activities, it was possible to exchange knowledge, experiences, and keep up-to-date with all participants from the Latin American community both from the academic and government institutions and regulatory authorities. Thus, we intended to express both the state-of-the-art in pesticide residues research in Latin America and, as we always do, to maintain the connection with and between all the participants.

The three days of the workshop included a program of actual topics lectured by excellent scientists in the area, as well as enriching poster presentations and outstanding virtual stands of the sponsors, who have greatly collaborated once again for the goals of our workshop. I hope that this event fulfilled the expectations of the more than 600 participants from 34 countries of 3 continents, who we thank again for their support.



Brenda Checa
President of LAPRW 2021

ACKNOWLEDGMENTS

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Time (UTC/GMT-5) Panamá	18 May 2021 Tuesday	Time (UTC/GMT-4) New York	Time (UTC/GMT+2) Madrid
8:00–8:45	LOGIN	9:00–9:45	15:00–15:45
<<<<<<<< Poster and Vendor Exhibition open all day >>>>>>>>>>>>			
8:30–9:00	Opening	9:30–10:00	15:30–16:00
9:00–9:30	Lecture 1 "Further improvements in LC-HRMS for the analysis of pesticide residues in food" Amadeo R. Fernandez Alba	10:00–10:30	16:00–16:30
9:35–10:05	Lecture 2 "Practical approaches to improving efficiency of GC-MS/MS and LC-MS/MS pesticide residue analysis" Katerina Mastovska	10:35–11:05	16:35–17:05
10:10–10:40	Lecture 3 "Green solvents in extraction of multi-pesticide residues in food" Sara Cunha	11:10–11:40	17:10–17:40
10:45–11:05	Vendor Session 1 "Validation of a much faster clearance method for pesticides in food extract using a combined target and non-target approach using Bruker impact II QTOF" Noud van der Borg BRUKER	11:45–12:05	17:45–18:05
11:05–11:15	BREAK	12:05–12:15	18:05–18:15
11:15–11:45	Lecture 4 "Pesticide exposure assessment of the general population through human biomonitoring" Hans Mol	12:15–12:45	18:15–18:45
11:50–12:20	Vendor Session 2 "New developments for multiresidue pesticide analysis using high resolution mass spectrometry LC-QTOF" Victor Mondragón AGILENT	12:50–13:20	18:50–19:20
12:25–12:55	Lecture 5 "Determination of multiclass contaminants using modern chromatographic techniques in livestock products, milk and dairy" Lucia Pareja	13:25–13:55	19:25–19:55
13:00–13:20	Vendor Session 3 "LPGC - The fast way to speed up your multiresidue pesticide analysis for foods!" Jana Hepner INNOVATEK/RESTEK	14:00–14:20	20:00–20:20
13:20–13:45	LUNCH BREAK	14:20–14:45	20:20–20:45
13:45–14:15	Lecture 6 "A high-throughput method for analysis of pesticide residues in hemp and hemp products" Nicolás Michlig	14:45–15:15	20:45–21:15
14:20–14:35	Short Oral Presentation 1 "Improving analytical performance for simultaneous determination of pesticides and mycotoxins in olives" Bárbara Reichert	15:20–15:35	21:20–21:35
14:35–14:50	Short Oral Presentation 2 "Determination of glyphosate, AMPA and glufosinate in honey. Comparative tests on the sample preparation stage" Luisina D. Demonte	15:35–15:50	21:35–21:50
14:50–15:05	Short Oral Presentation 3 "What happened with pesticide residues in minimally processed foods? The case of strawberries" Fiamma Pequeño	15:50–16:05	21:50–22:05
15:05–15:30	Questions and Discussion	16:05–16:30	22:05–22:30
15:30–17:00	Poster Session 1 <i>AUTHORS OF EVEN NUMBERED POSTERS PRESENT</i> (posters accessible for all 3 days)	16:30–18:00	22:30–0:00
17:00–18:00	Red de Latino America y el Caribe (RALACA) Meeting (in Spanish) - all participants are invited	18:00–19:00	0:00–1:00

21 May 2021 Friday

Time: **9:00–11:00 (Panamá)** - 10:00–12:00 (New York) - 16:00–18:00 (Madrid)

COURSE 1

“On the future of data sharing in food safety: current practice and vision of the European Food Safety Agency”

Paula Medina and Jane Richardson
EFSA-RALACA

Time: **11:30–13:30 (Panamá)**: - 12:30–14:30 (New York) - 18:30–20:30 (Madrid)

COURSE 2

“Sample preparation and analysis the QuEChERSER way”

Steven Lehotay

Time: **14:00–17:00 (Panamá)** - 15:00–18:00 (New York) - 21:00–0:00 (Madrid)

COURSE 3

“Challenges for the QA/QC System in a pesticide residue analysis lab”

Antonio Valverde, Jairo A. Guerrero Dallos and Horacio Heinzen

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May 18-20

Oral Presentations

Workshop
June

LECTURE 1

FURTHER IMPROVEMENTS IN LC-HRMS FOR THE ANALYSIS OF PESTICIDE RESIDUES IN FOOD

Amadeo R. Fernández Alba

LECTURE 2

PRACTICAL APPROACHES TO IMPROVING EFFICIENCY OF GC-MS/MS AND LC-MS/MS PESTICIDE RESIDUE ANALYSIS

Katerina Mastovska

LECTURE 3

GREEN SOLVENTS IN EXTRACTION OF MULTI-PESTICIDE RESIDUES IN FOOD

Sara Cunha

LECTURE 4

PESTICIDE EXPOSURE ASSESSMENT OF THE GENERAL POPULATION THROUGH HUMAN BIOMONITORING

Hans Mol

LECTURE 5

DETERMINATION OF MULTICLASS CONTAMINANTS USING MODERN CHROMATOGRAPHIC TECHNIQUES IN LIVESTOCK PRODUCTS, MILK AND DAIRY

Lucia Pareja

LECTURE 6

A HIGH-THROUGHPUT METHOD FOR ANALYSIS OF PESTICIDE RESIDUES IN HEMP AND HEMP PRODUCTS

Nicolás Michlig

LECTURE 7

PESTICIDES APPLIED TO DIFFERENT CROPS AND RISK ASSESSMENT FOR WET AREAS

Yolanda Picó

LECTURE 8

INFRARED SPECTROSCOPY FOR A BETTER UNDERSTANDING OF THE FATE OF PESTICIDES IN SOILS

Rai Kookana

LECTURE 9

INTENSIVE AND EXTENSIVE AGRICULTURE AS SOURCES OF PESTICIDES IN ARGENTINEAN PAMPEAN ECOSYSTEMS

Damián Marino

LECTURE 10

PROGRAMMING, ATTENTION AND MONITORING OF THE NATIONAL PESTICIDE AND PLANT WASTE MONITORING PROGRAM

Jocelyn Cedillo

LECTURE 11

DIRECT, SENSITIVE AND BROAD SCOPE MULTIRESIDUE ANALYSIS IN WATER VIA ONLINE SPE-HRMS

Julio César España

LECTURE 12

MEDICINAL HERBS: ADVANCES IN BRAZILIAN LEGISLATION AND DEVELOPMENT OF A MULTIRESIDUE, MULTICLASS METHOD FOR PESTICIDES AND MYCOTOXINS ANALYSIS

Marlos Zorzella Fontana

LECTURE 13

FOODEX2 AS A TOOL TO FACILITATED EXPOSURE ASSESSMENT TO PESTICIDE RESIDUES MONITORING DATE

Sofía Ioannidou

LECTURE 14

PESTICIDE RESIDUE CONTROL IN THE EUROPEAN UNION

Carmen Ferrer Amate

LECTURE 15

APPLICATIONS OF THE US_EPA COMPTOX CHEMICALS DASHBOARD TO SOURCE PESTICIDES DATA

Antony Williams

LECTURE 16

PROBABILISTIC TECHNIQUES APPLIED TO DIETARY RISK ASSESSMENT FOR PESTICIDE RESIDUES

Darío Maggioni

LECTURE 17

MONITORING PROGRAM FOR PESTICIDE RESIDUE ANALYSIS IN FRUITS AND VEGETABLES IN PANAMA 2015-2019

Samuel Hernández

LECTURE 18

DIETARY RISK ASSESSMENTS CONDUCTED JMPR TO SUPPORT THE MRL SETTING BY THE CODEX ALIMENTARIUS

Eloisa Dutra Caldas

FURTHER IMPROVEMENTS IN LC-HRMS FOR THE ANALYSIS OF PESTICIDE RESIDUES IN FOOD

Amadeo R. Fernandez Alba^a

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The use of high-resolution mass spectrometry (HRMS) for the simultaneous target and non-target analysis of pesticide residues in food control is a subject that has been studied over the last decade. However, proving its efficacy compared to the more established triple quadrupole mass spectrometers (QQQ-MS2) is challenging. Various HRMS platforms based on Time of Flight or Orbitrap analyzers have been evaluated, seemingly showing this approach not to be as effective as QQQ-MS2 for quantitative analysis, especially in routine food testing laboratories. The two main reasons are (i) the lower sensitivity especially in the case of the fragment ions produced and (ii) the lack of familiarity and an understanding of the most appropriate combination of HRMS acquisition modes to use. In fact, the number of different acquisition modes can appear as a puzzle to inexperienced users. This work is therefore focused on obtaining experimental data to gain a better understanding of the extended acquisition capabilities of a new Q-Orbitrap platform. Experimental data were obtained for 244 pesticides and their degradation products in commodities of varying matrix complexity (tomato, onion, avocado, and orange) using various combinations of acquisition modes. The best results for targeted analysis were obtained with a combination of full scan (FS), all-ions fragmentation (AIF) and target MS2 (tMS2) modes, and for non-target analysis using full scan (FS) and data-dependent MS2 (ddMS2) modes. All these acquisition modes (FS, AIF, tMS2, and ddMS2) could be applied simultaneously with cycle times ≤ 1 s. The tMS2 especially, proved to be a very powerful approach to increase sensitivity for MS2 fragments and identification rates. Overall, the results for the various pesticide-commodity combinations were fully satisfactory in terms of limit of quantitation (LOQ) repeatability and identification when considered against the SANTE EU Guideline criteria. In addition, the screening capabilities were evaluated for a non-target survey with the use of spectral libraries, the presence of non-target compounds was detected, thus proving the efficacy of the proposed approach. Another issue often overlooked is the optimization of use of spectral libraries, but in our experiments the compounds present in these libraries were not blindly sought in the screening analyses. To minimize the potential for false positives detects in our study, the extractability of the compounds present in the libraries, was also taken into account. The extractability of compounds using a QuEChERS acetonitrile procedure was estimated based on the physicochemical properties of target compounds. By removing compounds that will not be extracted, reduces the occurrences of false detects, reducing the time required for data processing and thus improving the efficiency of the overall screening workflow.

Keywords: High resolution mass spectrometry, Q-Orbitrap, acquisition modes, screening and targeted analysis

PRACTICAL APPROACHES TO IMPROVING EFFICIENCY OF GC-MS/MS AND LC-MS/MS PESTICIDE RESIDUE ANALYSIS

K. Mastovska

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Gas chromatography and liquid chromatography combined with triple quadrupole tandem mass spectrometry (GC-MS/MS and LC-MS/MS) have become standard analytical techniques employed in current pesticide residue analysis. Modern GC-MS/MS and LC-MS/MS instruments offer high speed, sensitivity and selectivity, which can be utilized to improve various method performance characteristics and also help deal with challenging matrices. For instance, increased detection sensitivity can be used to improve analyte limits of quantitation (LOQ) or to decrease the sample introduction (injection volume) into the analytical system while maintaining the LOQ levels. The latter option is very attractive in routine analysis, where matrix can detrimentally affect chromatographic separation, ionization efficiency, method ruggedness, routine maintenance costs and instrument downtime. However, it is not always just the expensive, new instrumentation that can improve method performance and efficiency. Sometimes, even small details and relatively inexpensive tools can have a significant impact on routine method performance, enable better utilization of the instruments or prolong the life of the analytical columns. This presentation will provide an overview of practical approaches (including tips & tricks) that can improve GC-MS/MS and LC-MS/MS pesticide residue analysis without breaking the bank.

Keywords: GC-MS/MS, LC-MS/MS, Optimization, Method performance

GREEN SOLVENTS IN EXTRACTION OF MULTI-PESTICIDE RESIDUES IN FOOD

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Pesticides and their metabolites can be found in residual levels in food products. For their identification and quantification a wide range of extraction and cleanup techniques, together with many instrumental approaches, have been developed and employed. In last years great effort have been made to reduce the use of toxic solvents in order to achieve environmental-friendly analytical approaches. More recently, deep eutectic solvents (DES), a new generation of green solvents, have been used in pesticide extraction. In addition to its greenness, one of the advantages of DES is that it is possible to tailor their physico-chemical properties, which can be easily changed by varying the molar ratio of hydrogen bond donors and hydrogen bond acceptors in their structures. To date, several hydrophilic and hydrophobic solvents have yet been prepared at laboratory-scale and used as extractor solvents in microextraction techniques such as dispersive liquid-liquid microextraction. Indeed, by replacing conventional solvents with DES the main merits of microextraction techniques such as simplicity of operation, low cost, and environmental safety are enhanced¹.

The presentation will focus on the main features related to the application of DES in micro extraction of multi-pesticides in food.

Keywords: Natural deep eutectic solvents, Dispersive liquid-liquid extraction, mass spectrometry, hyphenated techniques

References: 1. Cunha, S.C. and Fernandes, J.O., Extraction techniques with deep eutectic solvents, *Trends Analytical Chemistry* 105 (2018) Pages:225-239.

Acknowledgments: The research leading to these results received financial support from FEDER (Programa Operacional Competitividade e Internacionalização - COMPETE 2020), from PIDDAC through FCT/MCTES project POCI-01-0145-FEDER-028708. Sara C. Cunha also acknowledges FCT for the IF/01616/2015 contract.

PESTICIDE EXPOSURE ASSESSMENT OF THE GENERAL POPULATION THROUGH HUMAN BIOMONITORING

H. Mol^a, Rosalie Nijssen, Ruud van Dam, Paul Zomer, Suryati Sunarto, Hester van den Top, Jonatan Dias, Arjen Lommen

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In the exposure of the general population to pesticides, food is a dominant source. Exposure- and risk-assessment of pesticides is typically based on residue data from food monitoring and food consumption data. The enormous variety in diets and residues therein make it challenging to estimate to what (mixtures of) pesticides the (individual) consumer is exposed. Another challenge is that in most cases residue data are only available for the raw agricultural commodities, and effects of processing (industrial or home-cooking) are difficult to address due to limited availability of processing factors. Beside food, exposure to pesticides may also occur through the environment (air/inhalation, dermal uptake), especially when residents live close to agricultural fields.

In human biomonitoring (HBM), exposure to pesticides is measured by analysis of biomarkers in body fluids (e.g. urine, blood) and other specimens (e.g. hair). It can bring added value for chemical risk assessment because it can reduce the assumptions needed regarding consumption rates, residue occurrence and processing effects, and it integrates exposures from the diet and potential additional sources (house-hold use, environmental).

In this presentation first the challenges in the chemical analysis of pesticide biomarkers in urine are outlined, covering both target methods and suspect screening approaches. For the latter, a workflow for non-target measurement, datamining, and identification is presented.

The methods are applied to analysis of 24h urine samples obtained in a pilot study where both urine and duplicate diet (i.e. food/drink as consumed, taking processing into account) samples were collected from 35 persons. A qualitative comparison between biomarkers in urine and the parent pesticides in the diet was made. Pesticides (/biomarkers thereof) found included boscalid, chlorpropham, tebuconazole, pyrimethanil, neonicotinoids, pirimiphos-methyl, chlorpyrifos/-methyl, and pyrethroids. The analyses also provided information to what extent the consumed diet, besides the parent compound, contained metabolites or degradation products of the pesticides which in some cases may contribute to the urinary biomarkers found in HBM. From the results it is clear that HBM is a very useful tool, complimentary to food analysis. However, more work is needed to establish quantitative relationships with external exposure and linkage to health-based guidance values.

The attention and application of HBM for pesticide exposure assessment in the EU has substantially increased in recent years, through several EU-funded projects [1,2]. Information will be provided on the activities done in these projects.

Keywords: Human biomonitoring, pesticide biomarkers, suspect screening.

References:

1. HBM4EU <https://www.hbm4eu.eu/the-substances/pesticides/>
2. SPRINT <https://sprint-h2020.eu/>

DETERMINATION OF MULTI-CLASS CONTAMINANTS USING MODERN CHROMATOGRAPHIC TECHNIQUES IN LIVESTOCK PRODUCTS, MILK AND DAIRY

L. Pareja¹, R. Souza¹, F. Puigvert¹, A. Muela¹, E. Carbajal², Tomás, López², M.V. Cesio^{3,4}, H. Heinzen^{1,3}

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Uruguay is one of the four main meat producers in Latin America. To increase productivity, the use of veterinary drugs is a widespread practice. Furthermore, the feed used for cattle raising can also be contaminated by pesticides of agricultural origin. Due to their high stability and lipophilic character, these products are very persistent and tend to bioaccumulate and biomagnificate along the food chain, being harmful to human health and the environment. For this reason, strict regulations have been adopted to limit their use and concentration in human and animal goods. In this sense, the development of analytical methods for the simultaneous determination of these compounds in a cheaply and easily way is crucial. One of the recent trends is the development of multi-class methodologies for the analysis of organic contaminants. These methods usually provide exceptional laboratory efficiency, with good results for many analytes, even in complex matrices.

In order to better understand the distribution of these compounds among the different organs of the animals (muscle, liver, kidney, fat and milk), several methodologies were developed and validated for the determination of pesticides and veterinary drugs¹⁻³. These methodologies have been applied to commercial samples in order to contribute protect consumers and assure fair trading practices of Uruguayan products.

Keywords: livestock products, GC/LC-MS/MS, multi-class methods

References: 1. European Commission DG-SANTE, (2017). Method validation and quality control procedures for pesticide residue analysis in food and feed. Document No. SANTE/11813/2017. 2. R. Souza, L. Pareja, M.V. Cesio, H. Heinzen, (2016). *Chromatographia*, 79 (17-18), 1101-1112. 3. R. Souza, P. Fernández, A. Muela, M.V. Cesio, H. Heinzen, L. Pareja, (2021). *Food Analytical Methods*, 14, 1-12.

A HIGH-THROUGHPUT METHOD FOR ANALYSIS OF PESTICIDE RESIDUES IN HEMP AND HEMP PRODUCTS

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Hemp has been undergoing a resurgence in interest and production within the food, medical and other communities due to its high content of cannabinoids, protein, fiber and other ingredients. For legal possession and use throughout the USA, hemp and hemp products must have delta-9-tetrahydrocannabinol (THC) concentration < 0.3%. As with most agricultural crops, pesticides may be applied when farming hemp and must therefore be monitored in food, feed, and medicinal products.

The aim of this work was to evaluate and validate the recently developed “quick, easy, cheap, effective, rugged, safe, efficient, and robust” (QuEChERSER) sample preparation mega-method to determine pesticide residues in hemp plants, flowers, powders, oils, and pellets. High-throughput analysis of final extracts for 106 targeted pesticides and metabolites from North American monitoring lists entailed: 1) ultrahigh-performance liquid chromatography - tandem mass spectrometry (UHPLC-MS/MS) with column back-flushing, and 2) instrument-top sample preparation + low-pressure gas chromatography (ITSP+LPGC-MS/MS). In QuEChERSER, a 2 g sample is extracted with 10 mL 4/1 (v/v) acetonitrile/water by mechanical shaking for 10 min, followed by 3 min centrifugation. For LC, 200 µL of extract is taken and solvent exchanged into initial mobile phase followed by a 5 min ultra-centrifugation step prior to the 10 min analysis. For GC-amenable pesticides, the remaining initial extract is partitioned with 4/1 (w/w) anh. MgSO₄/NaCl, and 1 mL is taken for automated ITSP cleanup in parallel with 10 min LPGC analysis. In the former case, the UHPLC column is back-flushed with 1/1 (v/v) methanol/acetonitrile for 3 min between each injection to keep the system clean and avoid ghost peaks.

Multi-level, multi-day validation results show that 70-120% recoveries with RSDs < 20% were achieved for more than 80% of the pesticides in hemp protein powder, oil, pellets, and fresh plant. Without dilution, dried hemp plant and flower were too complex and only showed good results for a limited number of analytes. Limits of quantification (LOQs) < 10 ng/g were achieved for nearly all pesticides, yielding 2.8% false negatives among >13,000 analyte results in the spiked samples.

In this presentation, each step of the protocol will be emphasized to describe the advantages of QuEChERSER for high-throughput analysis that meets the challenging needs for several complex hemp matrices.

Keywords: QuEChERSER; chromatography-tandem mass spectrometry (UHPLC-MS/MS; LPGC-MS/MS); pesticide residue analysis; hemp and hemp products.

PESTICIDES APPLIED TO DIFFERENT CROPS AND RISK ASSESSMENT FOR WEAT AREAS

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Pesticides are one of the main sources of pollution to aquatic ecosystems, even though legislation has been implemented to prevent overuse of pesticides. These compounds are continuously sprayed over large areas of cultivation, and only 1 % of the product reach the target crop. Mediterranean wetlands are the most sensitive ecosystems and are at great risk of losing their ecological value. Excessive cultivation and mass production have reduced their surface area because of agriculture, industry and urbanization. The Albufera de Valencia Natural Park is an example of a Mediterranean wetland, in which rice field, orchards and orange crops are the main agricultural activities.

The aim of this study was to establish concentrations and occurrence of different classes of pesticides, including parent compounds and degradation products to relate them spatial distribution of the main crops. Furthermore, risk assessment to the aquatic organisms and human health was implemented. Aquatic organisms were evaluated through the risk quotients (RQs). On the other hand, human health risk was estimated through the exposure to pesticide residues and through wastewater based epidemiology (WBE). The latter is based on the determination of human metabolites excreted by urine, such as 3-phenoxybenzoic acid a biomarker of 20 synthetic pyrethroids in wastewaters of different Wastewater Treatments Plants (WWTPs) of Valencia and Sueca (Spain) (cities that surround the Park).

Different pesticides and metabolites are detected in influent wastewater. The most frequent biomarkers were 3-PBA and trans DCCA (biomarker of cypermethrin, cyfluthrin and permethrin) with an occurrence of 71% and 63% and with a relevant intake estimated from 125.7 to 200.3 mg/ day/ inhabitants. Moreover, the results evidenced the presence of many selected pesticides in surface water. The most abundant ones are herbicides and fungicides, as the prochloraz.

In this study was applied for the first time the WBE approach to value the pesticide exposure of Valencia population. Furthermore, the detection of pesticides in the Natural Park pointed out that is important to create new barriers to avoid the discharges of contaminants to these sensitive.

Keywords: Wetlands, Pesticide Residues, Occurrence and distribution, Risk assessment

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INFRARED SPECTROSCOPY FOR A BETTER UNDERSTANDING OF SORPTION AND FATE OF PESTICIDES IN SOILS

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Sorption determines the fate of pesticides in the terrestrial and aquatic environments. Sorption controls the distribution of pesticides between solid, liquid and air phases and thus their off-site transport and ecosystem impacts. There is a lack of data on sorption and pesticides fate in tropical and subtropical environments such as in South America, Asia and Africa. There is a need for rapid and cost-effective approaches and tools for generating pesticide sorption data on a large number of soils so as to better understand the fate and behavior of pesticides in the environment.

Infrared spectroscopy is a technique that has long been recognized as having practical applications in agricultural and other industries. For example, it has been used to successfully predict total carbon, and other soil properties in several countries^[1]. Its successful application to predict sorption behavior of pesticides have been demonstrated through several studies^[1-3]. Currently, sorption coefficient (K_d) of pesticides is measured from the soil/sediment organic carbon (SOC) content alone, i.e. the “Koc approach”. Infrared spectroscopy with chemometrics e.g. partial least-squares (PLS) offers a technique for directly estimating sorption coefficients of pesticides in soils by incorporating SOC content, its chemistry and other properties influencing sorption of pesticides.

We combined mid-infrared (MIR) spectroscopy with PLS analysis to test the performance of this approach against the conventional (K_{OC}) approach”^[2]. We measured the K_d values of diuron herbicide in 101 soils from Australia and compared with those predicted by MIR-PLS model. A wide range of K_d values (0-70; mean 6.5 L/kg) and K_{OC} values (0-3500, mean 370) among soils showed that soil organic carbon alone controlled only 44% of the variation in K_d values. In contrast, the *MIR-PLS* regression demonstrated a significant improvement compared to the K_{OC} model. The study showed that the MIR- PLS method can provide a more accurate estimate of pesticide sorption than the K_{OC} model. Similarly, Farenhorst and collaborators demonstrated the effectiveness of near infrared spectroscopy (NIR) as a tool for estimating K_d values for pesticides and other organic compounds^[1,3]. For several pesticides (e.g. atrazine, 2,4-D, Diuron and Linuron herbicides) the MIR and NIR spectroscopy have been successful in estimating sorption in soils^[1-3]. Being a relatively high-throughput, IR spectroscopy can be very helpful in generating local data on sorption of pesticides, rather than relying on international databases.

INTENSIVE AND EXTENSIVE AGRICULTURE AS SOURCES OF PESTICIDES IN ARGENTINEAN PAMPEAN ECOSYSTEMS.

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In Argentina there are different regions dedicated to agro-production. The wide area occupied by the extensive agriculture of soy, corn, wheat, sorghum and sunflower are more than 37 million hectares. These scenarios have motivated different studies on the dynamics and fate of pesticides applied to this territorial extension, with a special focus on the Pampas region. Since 2005, insecticides such as cypermethrin, chlorpyrifos and endosulphans have been detected in surface waters and bottom sediments. In 2013 have begun studies on glyphosate and its metabolite AMPA in soybean crops, evidencing its pseudopersistence in soils with concentrations above 30 mg/kg. Studies of this herbicide in rainwater, in the región, have quantified up to 80 µg/L with a significant relationship between isohyets and rainfall concentrations. Based on these results, allowed to establish that the contribution from wet deposition, in accordance with the estimates for the EU, represents up to 8% of the total market per year in the country. This mechanism, added to surface runoff, makes its frequent detection in bottom sediments from rivers and streams of the Pampas, presenting a scenario of pseudopersistence in surface waters, after 5 years of monitoring on watersheds with agricultural impact. The second most relevant compound by occurrence and concentration, in these extensive systems, was atrazine with a frequencies of detection higher than 90% and concentrations above 2 µg/L in rivers such as the Guleguay with an average flow of 210 m³/s. In a complementary way, since 2015, studies are conducted in a superficial waterbody located in the Cordón Horticola Platense (CHP), that extend in Gran La Plata, Buenos Aires. This zone has been selected in order to compare the pesticide profiles of a intensive system (horticulture) in comparisson to an extensive one. In the CHP, over 5 years of sampling, not only a greater variety of compounds have been identified with respect to extensive systems both in water and sediments, but also with concentrations up to 500 times higher in sediments. Generic insecticides such as pyrethroids, neonicotinoids and chlorpyrifos emerge as dominant compounds in the mass profiles, to which are added fungicides both the azole and the strobilurin family. Unexpectedly, glyphosate and AMPA in horticulture were not only frequent, but also was observed in high concentrations. In territorial work and interaction with farmers, their use could be associated with chemical fallow and greenhouse management. These different research results lead to formulate proposals as a) consider to glyphosate+AMPA as tracers of agricultural pollution, b) promote the regulation/prohibition of atrazine due to its mobility towards surface waters, c) generate new studies on other soil and crops managements as agroecology and d) boost the reduction of the use of pesticides in agriculture both extensive and intensive.

Keywords: Atrazine, Glyphosate, Horticulture, Extensive agriculture.

DIRECT, SENSITIVE AND BROAD SCOPE MULTIRESIDUE ANALYSIS IN WATER VIA SPE-HRMS

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As part of the strategy against pollution of water enclosed in international regulations, the Environmental Quality Standard¹ (EQS) involves the identification of priority substances and the monitoring of different classes of contaminants, such as pesticides. The EPA methods historically consist of analytical methods for selected small groups of different classes from the Contaminant Candidate Lists (525.2) later extended to semivolatiles (525.3) that make use of Solid Phase Extraction (SPE) followed by gas chromatography coupled to mass spectrometry (GC-MS). Lately, drinking water methods EPA 525.3, 538, 540 and 559 diversified the type of organic contaminants introducing liquid chromatography (LC-MS) that adopt SPE too, nonetheless, the scope and ease of use remain limited to off-line approaches. A notable amount of manual work, laborious dry/elution sorbent and solvent change steps are required; therefore, the procedure often takes hours to get by instrumental analysis. We here revisited the EPA method 5432, but a sequential large volume injection of 0.22 µm pre-filtered water samples is injected using autosampler-only User Defined Procedures (UDP) and just one selection valve. A total volume of 500 µL is placed onto a preconditioned online-SPE cartridge where analytes are retained prior being backflushed once the organic gradient reaches the cartridge. The whole process takes near 6 min, performed in a slow fashion to avoid pressure spikes. Depending on the Orbitrap resolution setting, the MS has the potential to move the separation from retention time towards m/z axis. Variable Data Independent Acquisition (vDIA) or Parallel Reaction Monitoring (PRM) in combination with Full Scan let the instrument collect both quantitative MS1 and qualitative MS2 high resolution data. No column separation was used to allow the direct "SPE-HRMS" run end in less than 3 min, boosting throughput with high precision and accuracy. In addition, among the benefits of the method, the speed and broad scope of MS1 acquisition, abort the classical need of extraction solvents and large volume sample size handling often required. The current study followed the parameters needed for Initial Demonstration of Capability (IDC) and the Quality Assurance considerations according to Standard Methods for Water and Wastewater³. Acceptable compound linearity (> 0.995) was achieved over the concentration range from 0.025 µg/L up to 1.000 µg/L, excellent repeatability (< 5%) and accuracy (70-130%) was achieved for Laboratory Fortified blanks (LFB) at 0.250 µg/L and Laboratory Fortified Sample Matrix (LFSM) at 0.100 µg/L and near-zero calculated carryover to ensure avoiding cross-contamination during continuous SPE cartridge refill. Detection limits were near 10 ng/L, though, some of them still reach sensitivity down to 1 ng/L comparable to results in EPA 543. Larger injection volumes might aid sensitivity but ion-suppression and saturation of the packed sorbent could be affected.

Keywords: Pesticides, online-SPE, water, orbitrap.

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MEDICINAL HERBS: ADVANCES IN BRAZILIAN LEGISLATION AND DEVELOPMENT OF A MULTIRESIDUE AND MULTICLASS METHOD FOR PESTICIDES AND MYCOTOXINS ANALYSIS

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Since the 1990s, the use of Integrative and Complementary Practices (ICPs) has increased it in global proportions. One of the main reasons for its growth and increased visibility occurred mainly with encouragement from the World Health Organization (WHO). Through Ordinance N° 971/2006 the Brazilian Unified Health System (SUS), incorporated and implemented ICPs, including medicinal herbs, in the perspective of disease prevention, health promotion and recovery. Medicinal herbs have been recognized as a very valuable and an accessible resource for health care and are collected directly from nature. However, commercial cultivation has gained increasing momentum in view of the awareness and demand of these plants for therapeutic purpose, thus, the need determination of pesticide residues and mycotoxins. Just from 2014 on, through RDC n° 26, the minimum requirements for the registration, renewal and post-registration petitions of medicinal herbs were established in Brazil. However, the term was extended several times, through RDC N° 77/2016, 93/2016, 105/2016, 196/2017 and 235/2018, currently in force. These extensions resulted from the lack of laboratories having validated analytical methods. Pesticide residues in herbal products can accumulate due to agricultural practices such as spraying, soil treatment, cultivation in contaminated soil and use of contaminated water sources. Due to the long and discontinuous drying process, most of the time, the development and proliferation of fungi in medicinal plants might occur, and consequent mycotoxin contamination. The aim of this work was to develop, optimize and validate an analytical method for simultaneous multiresidue pesticide and mycotoxin determination. For this, 4 medicinal herbs were selected: Lemon balm (*Melissa officinalis* L.); Mallow (*Malva sylvestris* L.); Boldo (*Peumus boldus* Molina) and Guaco (*Mikania glomerata* Spreng.). Initial optimization experiments were performed with a scope of 167 selected pesticides from different classes and 13 mycotoxins, all analyzed by Agilent LC-AJS-MS/MS-ULTIVO. All preliminary studies were based on acetonitrile extraction followed or not by a dSPE clean-up step variation of MgSO₄, PSA and GCB. The final method has been validated in accordance with SANTE/12682/2019 guidelines performance criteria for selectivity, linearity, detection and quantification limits, precision and accuracy (from recovery studies). Recovery studies were performed at 10 µg kg⁻¹ for pesticides, 2 µg kg⁻¹ for group 1 mycotoxins and 100 µg kg⁻¹ for group 2 mycotoxins as the lowest able to validation level for LC-MS/MS. Finally, based on the results obtained, challenges, limitations and innovation on analytical instrumentation will be discussed.

Keywords: medicinal herbs, LC-MS/MS, sample preparation, Brazilian legislation

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FOODEX2 AS A TOOL TO FACILITATE EXPOSURE ASSESSMENTS TO PESTICIDES RESIDUES MONITORING DATA

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The ability to capture all the useful details of food groups in exposure assessments by EFSA is a crucial requirement for its risk assessment process. A system for unique and universal identification and characterisation of food and feed items is essential to provide a common link to all the diverse food and feed databases. As a result, a standardised food classification and description system called FoodEx2 has been developed, aimed at covering the need to describe food in data collections across different food safety domains among which also pesticides residues monitoring data. FoodEx2 consists of descriptions of a large number of individual food items aggregated into food groups and broader food categories in a hierarchical parent-child relationship structure. The description of individual foods can be complemented by additional information using facets. After its first release in 2011, FoodEx2 was reviewed and revised to match the needs expressed by the different users¹. The terminology was significantly expanded, particularly in raw primary commodities (RPC) and natural sources. These were further mapped to the matrix code present in the Annex I of Regulation (EC) No 396/2005² on maximum residue levels of pesticides in or on food and feed of plant and animal origin. The Codex Alimentarius classification of food and feed³ is also incorporated to all relevant RPC and their derivatives in FoodEx2. Both classification systems are present as implicit attributes and therefore, a user can browse the system based exclusively on them.

The use of FoodEx2 as a standard terminology is particularly important for linking pesticides residues data to European food consumption information and enhances the consistency and reliability of exposure assessments. Since 2019, pesticides residues monitoring data are submitted to EFSA coded according to FoodEx2. This has allowed more precise coding of processed and composite food that before were merely coded as 'not in list' as no direct mapping of these type of commodities with Annex I of Regulation (EC) No 396/2005 existed. It will also further facilitate the mapping of processed products reported within the consumption surveys widening the exposure assessment done under monitoring programs in Europe and presented via the annual report published by EFSA⁴ as well as under cumulative dietary risk characterisations of pesticides^{5,6}. Finally, FoodEx2 will be implemented in the new version of the Pesticide Residue Intake Model (PRIMo revision 4) to help estimate human deterministic acute and chronic dietary exposure (pre- and post-market) to pesticide residues.

FoodEx2 is already used by EU Member States when exchanging data with EFSA but it also boasts an international reach with the Food and Agriculture Organization and the World Health Organization using FoodEx2 to facilitate the collection of food consumption and food composition data on a global level. EFSA advocates and actively supports the harmonization of pesticides residues monitoring data worldwide and is engaged in improving and promoting best practice regarding the use of FoodEx2 towards achieving this goal. In this context an application is now being developed and will allow the easier use of the FoodEx2 by food business operators or inspectors when official inspections are carried out.

Keywords: FoodEx2, data standardisation, food consumption data, pesticides residues monitoring data.

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PESTICIDE RESIDUE CONTROL IN THE EUROPEAN UNION

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The massive increase in agricultural productivity in the twentieth century led to the development of pesticides to control pests and diseases that negatively affected the crop production. Nowadays, the use of pesticides is extended all over the world, where approximately 2.5 million Tons are applied every year to increase the production volume, as well as to extend the food shelf life or improve its appearance.

The consequences of pesticide use are of great importance to the consumer. Thus, it is essential to establish adequate control mechanisms for pesticide residues in food. In the European Union (EU), the European Commission is responsible for establishing those control mechanisms with the aim to ensure food safety, which includes compliance with Maximum Residue Levels (MRLs). Member State authorities are responsible for control and enforcement of the MRLs. To ensure that this is done in an adequate and uniform way, the European Union has four instruments:

- The EU multiannual control programme. This sets out the main pesticide-crop combinations to monitor and the minimum numbers of samples to take for each Member State. Member States have to report the results to EFSA, which publishes them in an annual report.
- The Rapid Alert System for Food and Feed (RASFF). This system circulates information on risks found and measures are taken to protect the consumer.
- The “Health and Food Audits and Analysis” office of DG Health and Food Safety (DG-SANTE). It carries out inspections to the Member States and to the main exporters to the EU to assess and audit their control activities.
- The European Union Reference Laboratories (EURL) coordinate, train staff, develop methods of analysis and organise proficiency tests to evaluate the skills of the different national control laboratories.

One of the main activities of the EURLs is quality assurance, through the coordination of the EU Guidelines on Quality Control Procedures (SANTE/12682/2019)¹ and the organisation of European Proficiency Tests (EUPT). Within this context, the EURL for pesticide residues in fruits and vegetables (EURL-FV) annually organises EUPTs on behalf of the European Commission to evaluate the competency of the EU National Reference Laboratories (NRLs) and EU Official Laboratories (OfLs) for analysing pesticide residues in fruits and vegetables.

Keywords: pesticide residues, Maximum Residue Levels, quality control, EU reference laboratory.

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APPLICATIONS OF THE US-EPA COMPTOX CHEMICALS DASHBOARD TO SOURCE PESTICIDES DATA

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The US-EPA CompTox Chemicals Dashboard¹ (<https://comptox.epa.gov/dashboard>) is a freely available web-based resource providing access to almost 900,000 chemicals and data of interest to environmental science. This dataset of chemicals has been assembled over a period of almost two decades as a result of the DSSTox project². These data include curated experimental³ and predicted property data^{4,5}, *in vivo* hazard data and *in vitro* bioactivity data generated as part of the ToxCast and Tox21 programs^{6,7}. Taking advantage of almost two decades of data curation the data include pesticide rich data content as represented by a specific number of lists (<https://comptox.epa.gov/dashboard/chemical-lists/?search=pesticide>). Where available, pesticides are mapped against their metabolites and transformation products. Advanced search capabilities support mass- and formula-based searches to support mass spectrometry targeted and non-targeted analysis approaches⁸, including batch searches.

This presentation will provide an overview of the Dashboard, the available data streams, and how it can be used for the purpose of various mass spectrometry based analysis approaches, metadata candidate ranking and reporting of data. *This abstract does not necessarily represent the views or policies of the U.S. Environmental Protection Agency.*

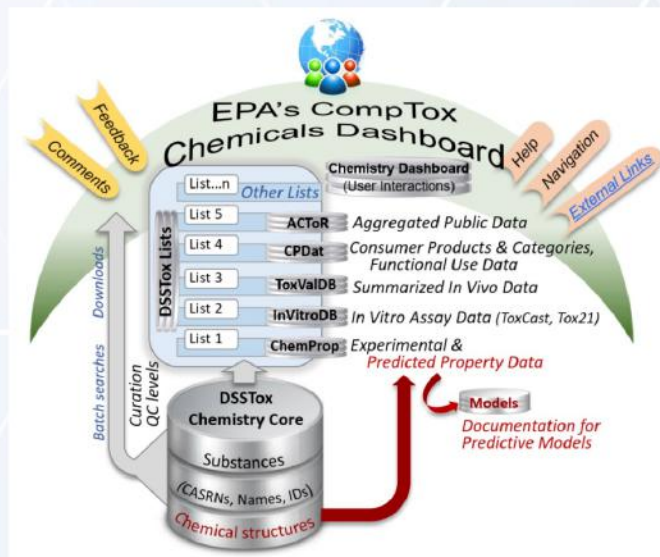
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Keywords: Website, Database, Chemistry, Toxicity

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PROBABILISTIC TECHNIQUES APPLIED TO DIETARY RISK ASSESSMENT FOR PESTICIDE RESIDUES

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The high demand for food and the new agricultural production models have generated an increasing use of pesticides with the consequent risk to the environment and the health of consumers. Residual concentrations of pesticides in food and the processes to reduce them have attracted special interest for public health, science and the general public. In this context, risk assessment studies have become a vital tool to determine whether there is a potential risk to the consumers or not. Probabilistic techniques in particular have gained wide acceptance because they have several advantages over conventional deterministic methods.

In our study we have put in practice a probabilistic dietary risk assessment methodology using the @Risk software for both chronic and acute exposure to pesticide residues. The chronic model was created with two inputs: one variable (food consumption) and one constant (pesticide residue concentration in food). The main output of the model was the probability that the exposure to a pesticide exceeded the ADI.¹ The acute exposure model was created with two variables input: food consumption and pesticide residue concentration. The outputs of this model were the NESTI (mg/kg bw/day) and the percentage of probability that the exposure to a pesticide-food combination exceeds 100% of ARfD.²

The two proposed models, chronic and acute, allowed a satisfactory evaluation of dietary exposure to pesticide residues for 4 age groups (6–23-month-old children, 2–5-year-old children, pregnant women and 10–49-year-old women) of the Argentinean population. The long-term exposure probabilistic evaluation model was applied to 39 compounds that possessed a quantifiable probability of exceeding 100% of the ADI ranging 4.6–100%, depending on the age group and the pesticide evaluated. Regarding the short-term evaluation model, totals of 443 and 128 pesticide-food combinations were evaluated in the 2–5-year-old children group and 10–49-year-old women groups, respectively. There was a tendency to decrease the value of the exposure expressed in terms of %ARfD in both groups when applying the stochastic method.

This presentation pays special attention to highlight the technical difficulties that arise when probabilistic techniques are applied, especially when there is not much experience in this field of research. It is focused on providing data and practical advice for those who are starting to work with this type of methods.

Keywords: Risk assessment, dietary exposure, pesticide residues, probabilistic techniques.

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MONITORING PROGRAM FOR PESTICIDE RESIDUE ANALYSIS IN FRUITS AND VEGETABLES IN PANAMA 2015-2019

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As part of the food safety system maintained by the Republic of Panama, a National Program for the Control and Monitoring of pesticide residues in fruits and vegetables has been implemented since 2007. Through this program, a selective monitoring of pesticide residues present in local crops and imported ones is carried out looking for the compliance with the maximum limits for pesticide residues (MRLs) in food set by Codex commission, the Environmental Protection Agency (EPA) or the European Community (CE), and they have been adopted in Panamá through regulation, in order to ensure the compliance with Good Agricultural Practices (GAP) during production, and thus achieving an adequate level of consumer protection.

The samples evaluated are firstly those intended for domestic consumption. They are collected close to the point of production in the distribution system, from packers and distributors, where they are held for sale. Also, the imported samples are collected when they are introduced into the commerce of Panama.

The determination of pesticide residues in the monitoring program is performed in two ways. On one hand, a screening of organophosphates and carbamates through an anticholinesterase ELISA assay is employed. The ELISA assay allowed the analysis of 12,719 samples during 2015-2019. A multiresidue QuEChERS validated protocol followed by gas chromatography and liquid chromatography coupled with tandem mass spectrometry (GC-MS/MS and LC-ESI-MS/MS) was used to analyze 1,134 samples, corresponding to 103 different crops in the same period. No residues were detected in 43.1% of the analyzed samples and 40.4% of them contained residues that did not exceed the MRL. Exceedances of MRL were detected in 16.5% of the samples. The most frequently detected pesticides by crop were: chlorpyrifos in strawberry and celery, tebuconazole in strawberry and celery, metalaxyl in chili pepper, carbendazim in strawberry and onion, pyrimethanil in strawberry, azoxystrobin in strawberry and chili pepper, fipronil in chili pepper, imidacloprid in tomato, flutriafol in strawberry, bifenthrin in chili pepper and strawberry, and boscalid in strawberry. The ratio of violative samples analyzed during the study period per year was: in 2015 14.9% of the samples exceeded the MRL, in 2016 19.9%, in 2017 21.7%, in 2018 20.0% and in 2019 10.6 respectively. The pesticide residues most frequently found above the MRL were: fipronil, chlorpyrifos, propiconazole, chlorfenapyr, among others less occurring ones. It is worth to mention that 28.3% of the total samples analyzed using the LC or GC- MS/MS contained two or more pesticide residues, of which 18.7% had two or more pesticide residues that violate the MRLs in crops such as celery, lettuce, strawberry, chili pepper and tomato.

Keywords: monitoring, MRLs, pesticide residues.

DIETARY RISK ASSESSMENT CONDUCTED BY JMPR TO SUPPORT THE MRL SETTING BY THE CODEX ALIMENTARIUS

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Human exposure to pesticide residues presents in food is a worldwide concern, and the assessment of the health risks from this exposure is an essential part of pesticide registration process in many countries and critical for the establishment of international food standards by the *Codex Alimentarius*. At international level, the assessments are conducted by the FAO/WHO Joint Meeting on Pesticide Residues (JMPR), which is the scientific body that supports the decisions made by the *Codex Alimentarius*, including setting maximum residue limit (MRL)¹.

The dietary risk assessment process consists of four steps: hazard identification, hazard characterization, exposure assessment and risk characterization. In the first two steps, the Acceptable Daily Intake (ADI) and the Acute Reference dose (ARfD) are established. Within the JMPR, the chronic exposure is estimated using the Supervised Trial Median Residue values (STMR), obtained normally from the data provided by the manufacturer, and the GEMs/Food Cluster Diets consumption data. Furthermore, the long-term exposure is estimated for each crop/pesticide using either the STMR or Highest Residue values derived from supervised trials, and the 97.5 percentile of consumption provided by various countries. In the fourth step of the process, the question whether the exposure can lead to a health concern is answered. Risk may exist when the chronic and/or long-term exposures exceeds the toxicological parameters².

In this presentation, the procedure of conducting dietary risk assessment for compounds evaluated by the JMPR are explained in detail, together with examples of how the results of this process affect the decisions made by the *Codex Alimentarius*.

Keywords: Dietary exposure, JMPR, Codex Alimentarius

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May 18-20

Short Oral Presentations

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Implementation

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IMPROVING ANALYTICAL PERFORMANCE FOR SIMULTANEOUS DETERMINATION OF PESTICIDES AND MYCOTOXINS IN OLIVES

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Sebastián Elgueta

IMPROVING ANALYTICAL PERFORMANCE FOR SIMULTANEOUS DETERMINATION OF PESTICIDES AND MYCOTOXINS OLIVES - PART 1: PESTICIDES

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The olive tree (*Olea europaea* L.) is native to the Mediterranean. It grows in temperate climates and may be cultivated in arid and infertile areas¹. Olive fruits and oil are rich in nutrients and phenolic compounds that present antitumor and anti-inflammatory properties². As other crops, olives are subjected to pests and diseases caused by insects, fungi and weeds which may reduce the production¹. To control such pests is necessary to apply pesticides which can leave residues on the drupes³. Determination of pesticide residues in fatty matrices requires a simple and practical extraction approach covering a large scope of compounds. In this study different versions of QuEChERS approach were evaluated aiming to improve analytical performance. An extensive study was conducted evaluating extraction with or without water addition to the samples (slurry), different sample amounts, extraction with acetonitrile containing acetic or formic acid, the use or non-use of buffering (acetate or citrate) and a liquid nitrogen freezing out clean-up combined with EMR lipid cartridges. After method optimization, a validation study was undertaken based on SANTE document, using an Agilent 1260 Infinity II Prime LC-TQ-MS/MS Ultivo. For extraction, 10 g of ground olives were extracted with 10 mL of acetonitrile (1% acetic acid) followed by addition of 3 g MgSO₄ and 1.7 g NaAc. An aliquot of the upper layer was transferred to a tube and placed for 90 s in liquid nitrogen. An volume of 2.4 mL of extract was applied to EMR- lipid cartridge and then, a 2-fold dilution with the LC mobile phase was done before analysis. Linearity of analytical curves was assessed at seven levels, from 1 to 75 µg/L, considering not only the determination coefficient, but also back-calculated concentrations. Recovery studies were performed by spiking blank olives with 165 pesticides at 10, 20, 50 and 70 µg/kg, with 7 replicates each level. As a result, 87% of the pesticides were successfully validated, 2% were not detected and 13% did not fulfill SANTE validation requirements (recoveries within the range of 70-120% and RSD% ≤ 20%). Limits of quantification were of 10, 20, 50 and 70 µg/kg for 79%, 2%, 4% and 2% of the pesticides, respectively. The linear range was from 5 to 75 µg/L for 80% of the studied pesticides. For most pesticides, the back-calculated concentrations deviations were not lower than ±20% at 1 µg/L. Matrix effect (ME) was negative for 92% of the pesticides and it was not significant (< ±20%) only for 27% of the pesticides. Then, matrix-matched calibration curves have to be used for reliable quantification. Despite of most pesticides presented ME > ±20%, 10 g of sample was chosen instead of 5 g, in order to achieve the required detectability. Four samples of organic olives were analysed and one was positive for trifloxistrobin a concentration below the LOQ. The

Determination method will be implemented in routine analysis for monitoring purposes.

Keywords: *Olea europaea* L., Residues, QuEChERS, LC-MS/MS.

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DETERMINATION OF GLYPHOSATE, AMPA AND GLUFOSINATE IN HONEY. COMPARATIVE TESTS ON THE SAMPLE PREPARATION STAGE.

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Beekeeping is an activity of great economic and eco-systemic importance, and Argentina is a major country in the world in this activity. Regarding the cleaning and safety of honey, residues and chemical contaminants' unwanted presence is of great concern, both by residues originated in the treatments applied to the hive and by the use of agrochemicals in agriculture that potentially contaminate the beekeeping chain. To meet today's quality and safety requirements is necessary to realize more pesticide control analysis. Argentina, The United States and Brazil use 80% of glyphosate's world total. In our country since 1996 has been applied to various transgenic crops headed by soy, with a significant annual load (200 thousand tons).

Therefore, the main objective was to develop an analytical methodology to determine glyphosate, AMPA and glufosinate in honey and related matrices such as nectar. Based on the pre-column derivatization strategy with FMOC-Cl and analysis by UHPLC-MS/MS. Different alternatives were evaluated and adapted to the objective. For methodology optimization: extraction solvents, volume and concentration of the derivatizing reagent, volume and concentration of the borate buffer, different reagents to achieve the optimum pH (pH 9), reaction time and cleaning alternatives of the extracts also were evaluated (L-L partition and SPE).

Recovery tests at two concentration levels (10 and 100 $\mu\text{g kg}^{-1}$) in triplicate were performed to evaluate the methodology. First, honey samples weighed in 50 mL centrifuge tubes were placed in a thermostated bath at 40-50°C for 5 min to achieve fluidity. They were then spiked with the standard mixture (glyphosate, AMPA and glufosinate) and vortexed to homogenize. After that, the extraction, derivatization and cleaning stage were performed for each of the evaluated alternatives. The final methodology involves an extraction step with water and mechanical agitation for 30 min followed by the derivatization reaction and finally L-L partition with dichloromethane as a clean-up stage¹. Satisfactory results have been obtained, showing that this method is consistent and reliable, with RSDs < 20% and recoveries between 70-105% at 5, 10, 25 and 50 $\mu\text{g kg}^{-1}$.

Also, together with the optimization of the sample preparation, to achieve a better response of the analytes as a whole, the instrumental conditions were optimized based on experiments' statistical designs to increase detection sensitivity to obtain low detection and quantification limits. In this way, it was possible to achieve an acceptable analytical method for determining glyphosate, AMPA and glufosinate that was applied to analyze raw and commercial honey samples.

Palabras claves: Glyphosate, honey, chromatography-spectrometry.

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WHAT HAPPENED WITH PESTICIDES RESIDUES IN MINIMALLY PROCESSED FOODS? THE CASE OF STRAWBERRIES

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Ready-to-eat (RTE) fruit and vegetables have become popular among consumers¹. RTE fresh fruit and vegetables are valued for their fresh-like characteristics and high nutritional value, and are obtained by minimal processes such as washing, cutting and disinfection. To improve quality and increase shelf-life, RTE products are usually packaged under modified atmosphere and stored under refrigeration. RTE fruit and vegetables should be also safe foods, no matter the minimal processing steps before consumption, avoiding chemical or biological contamination. Chemical contamination can be due to pesticide application during produce cropping and postharvest and their occurrence could be risky for consumers' health.

In this study, the effects of some common minimal processes were evaluated on fresh strawberries. Strawberries were taken as a model of the dynamics of pesticide residues in RTE products, as they have been steadily in the top-ten position of fruits with the greatest number of residues in the USDA

Surveys². Studied processes were calix removal, washing, disinfection with peracetic acid and sodium hypochlorite and modified atmosphere packaging. Pesticide residue levels were evaluated after each process and throughout 9 d storage in passive modified atmosphere at 5 °C.

A QuEChERS CEN 15662 protocol was validated for 27 pesticides using an Agilent 1200 LC coupled to a 4000 QTRAP (AB SCIEX). The linear range was from 5 to 100 µg kg⁻¹, checked for five levels. The back calculated concentrations (BCC) were <20%. For 78% of pesticides analyzed the LOQs was 5 µg kg⁻¹ and 10 µg kg⁻¹ for the other 22%. Residues of azoxystrobin, carbendazim, difenoconazol, propamocarb and spinosad (sum of A and D1) were found in concentration ranges of 0.005 to 2.2 mg kg⁻¹. Only carbendazim and propamocarb exceeded the established MRL. Strawberry calix concentrated the greatest number of pesticides. Pesticide level dropped 67 to 80% after its removal. Washing the intact fruit before calix removal, washed 12 to 40% of residues whereas peracetic acid disinfection cleaned up to 80% of pesticides. Sodium hypochlorite took out up to 84% pesticides. No significant differences in pesticide dissipation in the modified atmosphere experiments were detected. Calix removal followed by a hypochlorite disinfection was the most efficient step for pesticide removal. Fruits washed without calix removal showed higher pesticide levels than those washed without it, evidencing fruit cross contamination if washed when the calix is present. Washing and disinfection represent useful minimal processes that do not alter food quality and contribute to its safety, reducing the pesticide residues concentration in all cases.

Key words: pesticide residues; strawberry; minimal processing food; processing factor.

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ASSESSMENT OF SERUM LEVELS OF ORGANOCHLORINE PESTICIDES AND THEIR METABOLITES IN THE GENERAL POPULATION OF ARGENTINA (2005 – 2019)

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Persistent organic contaminants (POCs) are chemically stable, fat soluble, bio-accumulative compounds and can be transported long distances. The extensive use of organochlorine pesticides (OCPs) has become a public health issue. Possible adverse health effect, such as endocrine disruption, immunological, neurological, reproductive and behavioral disorders are associated with chronic exposure to low concentrations. The International Agency for Research on Cancer (IARC) has classified them as carcinogens included in groups I, II A or IIB.

Argentina banned their use and production by the 1990s and ratified the Stockholm Convention Treaty (2001), which eliminates or restricts the production and use of POCs. Despite suspected adverse human health effects due to POCs exposure in Argentina, available information is scarce.

Thus, in order to carry out an epidemiological evaluation of the presence and prevalence of OCPs and some of their metabolites in the general population of Argentina, blood samples (681) derived to CENATOXA, were analyzed (period: 2005 to 2019). Age-gender distribution were: 1 and 85 years old (53% adults and 57% children), 46% women and 54% men. The environmental exposure was the predominant etiology (89%). The samples extraction was performed according to Dale et al¹ and they were analyzed by GC-uECD, with dual injection. Organochlorine pesticides investigated were: aldrin, α -chlordane, γ -chlordane, dieldrin, endrin, α -endosulphan, β -endosulphan, HCB, α -HCH, β -HCH, γ -HCH, δ -HCH, heptachlor, heptachlorepoxyde, mirex, o,p'-DDD, o,p'-DDE, o,p'-DDT, p,p'-DDD, p,p'-DDE, and p,p'-DDT.

Highest frequency and concentrations of group's were: DDT (53%) (0.88 ± 2.85 ng/mL), HCH (53%) (0.48 ± 0.77 ng/mL), aldrin (31%) (0.24 ± 0.33 ng/mL) and heptachlor (21%) (0.18 ± 0.32 ng/mL). Profile group means per year showed a prevalence of DDT and HCH. DDT concentration increased over time due to the main contribution of its active p,p'-DDE metabolite. The HCH group showed relatively constant values with an increase in β -HCH metabolite and decrease in the rest of the isomers.

The profile and quantification of OCPs in the CENATOXA during the evaluated years shows a clear decrease: The mean concentrations (low levels) of all the pesticides show a tendency to decrease, indicating scarce recent exposures, which is correlated with a period of around three decades since its prohibition. The prevalence of the persistent and bioaccumulative metabolites β -HCH and pp'-DDE proves an intensive use of the pesticides HCH and DDT in previous years.

In addition, the levels of OCPs are comparable to those which were reported by other countries. In conclusion, the human biological monitoring of OCPs exposure in Argentina should be continued and expanded.

Keywords: Environmental contamination, organochlorine pesticides, general population, Argentina

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ENVIRONMENTAL BIOMONITORING: THE ROLE OF PESTICIDE RESIDUES ANALYSIS

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The study of pesticide impact in agroecosystems moves towards the search and identification of pesticide occurrence not only in common environmental abiotic compartments, but also in non-target organisms, looking for understanding the effects of pesticide diffuse contamination with a holistic approach. Pesticide residues analysis in biota is of vital importance for the assessment of environmental biomonitors. Aiming to evaluate honey bees and aquatic macroinvertebrates as environmental biomonitors, beehives, odonate nymphs, *Corbicula* spp. and *Aegla* spp. were sampled in six opportunities in four selected agroecosystems of Uruguay. Multiresidue pesticide analysis methodologies had to be fit for this specific purpose. The scope of the methods was extended to include the relevant LC and GC amenable pesticides used in the studied agroecosystems.

The QuEChERS citrate buffered approach was used in every case for sample preparation, except for beeswax where a LLE with acetonitrile at 80 °C was employed. Analysis were performed by LC-(QqQ)-MS/MS and GC-(QqQ)-MS/MS. Acceptable recoveries (70-120 %) and RSDs \leq 20 % were obtained for 80 to 100 compounds, depending on the matrix. Limits of quantitation ranged from 0.0001 mg kg⁻¹ to 0.05 mg kg⁻¹.

A total of 287 samples were analyzed, resulting in 46 different compounds detected including 9 herbicides, 13 fungicides, 18 insecticides and 6 metabolites. Concentrations ranged from 0.0001 mg kg⁻¹ to 0.5 mg kg⁻¹. In the case of beehive matrices (honey bees, beeswax, honey and beebread), most of the pesticide residues were found in beeswax and beebread. For aquatic macroinvertebrates, the positive findings were detected mostly in *Corbicula* spp. and odonate nymphs. Frequency of occurrence of each detected pesticide was calculated for beehive and aquatic macroinvertebrates samples, resulting that 20 % was the maximum in all cases.

The information obtained from the environmental compartments for pesticide residues was different for the beehive and the aquatic macroinvertebrates, proving their complementarity. Simultaneous pesticide residues determination in biota from different environmental compartments, yields a wider panorama of the overall pesticide presence in the place under study. The results showed the importance of performing a global assessment of pesticide residues in agroecosystems through the integration of data from different compartments.

Keywords: environmental biomonitoring, pesticide residues, honey bees, aquatic macroinvertebrates
Please indicate how do you want to present your work: Oral communication

PLACENTA CONCENTRATIONS OF PERSISTENT ORGANIC POLLUTANTS IN PANAMANIAN WOMEN: THE PA-MAMI COHORT.

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Persistent organic pollutants (POPs) are a group of compounds that include organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). They have the ability to interfere with the hormonal system, exhibiting (anti-)estrogenic activity. These compounds can cross the placental barrier, causing adverse effects on the children.

The Aim of this study is to determine the concentrations of POPs, as well as the estrogenic activity in a cohort of women from the Azuero peninsula, Panama (PA-MAMI cohort).

A total of 39 placenta samples from women have been analyzed. A total of 5 OCPs [including 4-4'-Dichlorodipenyldichloroethylene (4-4'-DDE), lindane [γ -HCH], hexachlorobenzene (HCB), beta-hexachlorohexane (β -HCH) and mirex] and 3 PCB congeners (PCB-138, PCB-153 and PCB-180) were quantified. The estrogenic activity of the extract was analysed by the E-SCREEN test in a subsample of 20 placentas.

All placental samples were positive for ≥ 3 of the analysed POPs, while 28 out 39 (71.8%) of the samples analysed had at least 6 POPs. The frequency of quantification among OCPs was highly variable: 100% (39/39) of 4-4'-DDE, 82.1% (32/39) of lindane, 79.5% (31/39) of HCB 10.3% (4/39) of mirex and β -HCH the only unquantified compound (0/0). PCBs were quantified in 76.9% (30/39) of PCB 153, 69.2% (27/39) of PCB 138, 38.5% (15/39) of PCB 180. The OCPs concentrations obtained were: 4-4'-DDE showed the highest median concentration (P25-P75) [280 (180-580) pg/g placenta], followed by lindane [380 (200-480) pg/g placenta], HCB [90 (60-120) pg/g placenta] and mirex [$<$ LOD ($<$ LOD- $<$ LOD) pg/g placenta]. Concerning PCBs, PCB-153 showed the highest median concentration [16 (12-26) pg/g placenta], followed by PCB-138 and PCB-180 and [15 (2-24) pg/g placenta and $<$ LOD ($<$ LOD- $<$ LOD) pg/g placenta, respectively].

Regarding to the xenoestrogenicity measured in the placenta samples, it has been observed that 80.0% (16/20) of the analyzed placentas presented xenoestrogenicity. The mean activity was 1.6 ± 1.1 E₂Eq/g of placenta, whereas levels greater than 2.0 E₂Eq/g of placenta were detected in 5 samples. These findings would indicate that the combined effect of endocrine disrupting substances would exert an estrogenic effect in the majority of cases.

The present work provides, to our knowledge, the first evidence of a widespread presence of endocrine disrupting chemicals in placentas from Panama. Given the concerns on the consequences of prenatal exposure to these compounds has been suggested for the children health, preventive measures to eliminate or minimize the risk of POP exposure during pregnancy are warranted.

Keywords: Placenta, Estrogenicity, Organochlorine Pesticides, Women.

EVALUATION OF A BIOBED PERFORMANCE DURING THE SIMULATED APPLICATION OF PESTICIDES USED IN SOYBEAN CROPS AND THE SUBSEQUENT SCALING TO FIELD

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The environmental contamination caused by the wastewater generated due to pesticides application in the fields is well known. In the recent years different options have been studied for its treatment. As a solution, in Uruguay the Good Agricultural Practices Guidelines suggest the use of biobeds in the horticultural production. However, for extensive production there is not a recommended solution to the farmers because of the lack of information about the degradation of the usually applied pesticides in biobeds. Therefore, the study of the degradation of the pesticides applied in soybean crops using biobeds in environmental conditions was proposed. The pesticides' application schedule for this crop was followed and a bioreactor was installed and controlled in a soybean farm. For the first experiment, seven containers with 15 and 10kg of biomixture were installed under a greenhouse. One of them was a blank and the rest were three replicates of two different geometries. The biomixture was prepared with bran, peat and soil in 2:1:1%v. The pesticides' selection and their application schedule were discussed with an agricultural engineer; a concentration of 50 mg/kg was set for the application of the pesticides in the biobed to standardize the experiment. After the evaluation of the performance of small-scale bioreactors, a biobed was installed in a soybean production field. The biomixture was prepared with the same composition and proportions of the first experiment, and for the biobeds' construction three 1000-liter tanks were used. Additionally, a tank was buried under the ground to collect the leached waste that was further recirculated to the biobed. A sampling schedule was planned for each of the experiments.

To follow the decrease in the concentration of the pesticides in the samples, an analytical methodology was validated using HPLC-MS/MS and GC-MS/MS.

In the small-scale trial, the degradation of 2,4-D, dicamba, sulfentrazone and saflufenacil, was more than 80% after a one-year experiment. In the real scale biobed, some of the results obtained were: 90% of degradation for metolachlor and more than 70% for flumioxazin after 6 months.

As a conclusion, biobeds are a useful tool in soybean production fields, seeking to provide a solution on how to treat the wastewaters that are generated throughout the production cycle. A close link has also been achieved with producers by involving them in the installation, use and control of the biobed; and different disclosure instances have been held with other farmers, showing the experience of the producer who used the biobed.

Keywords: biodegradation, rainfed pesticides, analytical assessment.

BIOINDICATORS FOR MONITORING THE PESTICIDES DEGRADATION IN BIOBEDS

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Biological beds are efficient, low-cost and straightforward systems developed for the good management of pesticides on-farms. To prevent pollution during filling and cleaning equipment and accidental spillages, these systems are used to retain and degrade pesticides by the action of microorganisms. The design consists of a waterproofed hole in the ground filled with a biologically active matrix (biomixture). In these systems, the degradation of pesticides is evaluated using complex analytical techniques. However, it is necessary to introduce bioassays in order to obtain more information on the environmental matrix. In this sense, earthworms, such as *Eisenia fetida*, are used as sentinel organisms to evaluate risks of polluted soil or substrates. And seeds of terrestrial plants, such as *Lactuca sativa*, are used to assess phytotoxicity.

In this work, the sensitivity and efficacy of the proposed bioindicators^{1,2} were evaluated to monitor a biobed composed of wheat stubble, river waste and soil (50:25:25% in volume), in relation to the monitoring of pesticides degradation by chromatography-mass spectrometry (UHPLC-MS/MS). The pesticides used were atrazine, prometryn, clethodim, haloxyfop and dicamba. Also, the enzymatic activity (hydrolysis of fluorescein diacetate, FDA and phenoloxidase) was evaluated. Samples were taken on the initial day (after pesticide application) and days 10, 15, 30, 60 and 90.

The results showed a high percentage of degradation of all pesticides for day 90 (>99% for atrazine, prometryn, clethodim, dicamba and >90% for haloxyfop), while the test with seeds shows a recovery trend with to the initial day (the germination index values were from zero to 46%). Regarding the avoidance test, 98% of the earthworms choose the control biomixture (without pesticide application), that is, the bioassay showed the high sensitivity of this species at very low concentrations of pesticides and/or metabolites present. On the other hand, an increase in the enzymatic activity was registered by phenoloxidases after the addition of pesticides, while the activity by FDA was practically not altered.

This work shows the need for integrated monitoring taking into account the pesticides analyses and the application of bioassays. The avoidance test's high sensitivity suggests incorporating an alternative test that evaluates effects on earthworms when they are directly exposed to polluted biomixtures. The different levels of injuries could be quantified through a photographic record.

Keywords: biobeds, monitoring, *Eisenia fetida*, *Lactuca sativa*

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HIGHLY HAZARDOUS PESTICIDES: COMPLIANCE OF MAXIMUM RESIDUE LEVELS, NATIONAL POISON SURVEILLANCE AND HUMAN RISK ASSESSMENT IN CHILE.

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In the last years, the national food surveillance of Chile (NFS) has reported serious evidences of pesticide residues in fresh vegetables (RIAL, 2019). The excessive applications, the incorrect use of preharvest interval (PHI), and unauthorized pesticides are the main reasons for Maximum Residue Levels (MRL) transgressions (Elgueta et al., 2017). The NFS coordinated by the Agricultural and Livestock Service (SAG), has reported a high number of transgressions of MRL due to pesticide residues 12-25% from the total of samples evaluated. The main notifications are reported mainly in leafy vegetables, peppers and tomatoes. On another hand, the National Poison Surveillance (REVEP) coordinated by the Ministry of Health (MINSAL) has reported serious notifications of intoxications of farm workers due to the exposure of toxic pesticides. In both national surveillance systems, the main molecules reported are methamidophos, chlorpyrifos, methomyl, and I-cyhalothrin (REVEP, 2019; RIAL, 2019).

The Highly Hazardous Pesticides (HHPs) can cause adverse effects to human health and the environment (FAO/WHO, 2016). The current Chilean regulation is not considering and recognizing the presence of HHPs in food, soil or water bodies. There is a concern about the potential effects of pesticide residues on the Chilean population (Elgueta et al., 2017). The aim of this work was classified pesticides commercialized in Chile as HHPs following the eight criteria of Guidelines on HHPs by the Food and Agriculture Organization (FAO) and the World Health Organization (FAO/WHO, 2016), the REVEP report, the RIAL report, the Dirty Dozen list of Pesticide Action Network (PAN), the Chilean scientific evidences on health risk assessment and not approved pesticides in the EU, US or Japan.

From the results obtained several pesticides can be considered HPPs in Chile: ethoprophos, oxamyl, methamidophos, methomyl, omethoate, I-cyhalothrin, myclobutanil, 2-4 D, acetamiprid, difenoconazole, dimethoate, metribuzin, profenofos, propiconazole, pyridaben, chlorpyrifos, tebuconazole, and triadimefon, imidacloprid, atrazine, dimethomorph, cyprodinil, dicloran, iprodione, kresoxim-methyl, buprofezin, linuron and penconazole. Some of these pesticides have reported evidences of health chronic risks to the Chilean population (Elgueta et al., 2019; Elgueta et al., 2020).

Based on the evidences, the ecotoxicological and dietary risk assessment should be included in the Chilean regulations and pesticide registration to improve the enforcement of HHPs in the country. It's necessary the implementation of national surveillance systems to evaluate the impacts of HHPs in humans, non-target organisms, soil and water bodies.

In conclusion, based on official data reported, scientific evidences and health risk assessment some HHPs such as methomyl, chlorpyrifos, ethoprophos, oxamyl, I-cyhalothrin, atrazine, imidacloprid should be prohibited in the Chilean market.

Keywords: Highly Hazardous Pesticides (HHPs), Maximum Residues Levels.

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9TH
LAPRW
PANAMÁ
2023
FOOD AND
ENVIRONMENT

The logo features the text '9TH LAPRW PANAMÁ 2023 FOOD AND ENVIRONMENT'. The '9TH' is in green. The 'L' is green with a leaf on its left side. The 'A' is brown with a coffee bean inside. The 'P' is red with a white outline of a map of Central America. The 'R' is orange with a pineapple inside. The 'W' is blue. To the right of the 'W', the text 'PANAMÁ 2023' is in white on a blue background, with a white butterfly icon. Below this, 'FOOD AND ENVIRONMENT' is written in blue.

May 18-20

Vendor Presentations

Workshop
Implementation

BRUKER

VENDOR SESSION 1

VALIDATION OF A MUCH FASTER CLEARANCE METHOD FOR PESTICIDES IN FOOD EXTRACT USING A COMBINED TARGET AND NON-TARGET APPROACH USING BRUKER IMPACT II QTOF

Noud van der Borg

AGILENT

VENDOR SESSION 2

NEW DEVELOPMENTS FOR MULTIRESIDUE PESTICIDE ANALYSIS USING HIGH RESOLUTION MASS SPECTROMETRY LC-QTOF

Victor Mondragón

INNOVATEK/RESTEK

VENDOR SESSION 3

LPGC - THE FAST WAY TO SPEED UP YOUR MULTIRESIDUE PESTICIDE ANALYSIS FOR FOODS!

Jana Hepner

SCIEX

VENDOR SESSION 4

WHAT CAN SENSITIVITY GIVE YOU OTHER THAN LOWER LOQS?

Guadalupe Miranda

EUROFINS

VENDOR SESSION 5

ANALYTICAL CHALLENGES IN THE ANALYSIS OF PESTICIDE RESIDUES IN FOOD

Mariela S. Viera

INNOVATEK/THERMO

VENDOR SESSION 6

WHAT WILL BE ON YOUR PLATE TOMORROW? BE READY FOR FUTURE REQUIREMENTS WITH TODAY'S MS TECHNOLOGY

Citlalli Aguilar

WATERS

VENDOR SESSION 7

DETERMINATION OF PESTICIDE AND MYCOTOXIN RESIDUES IN DRIED CANNABIS FLOWER: LC-MS/MS AND GC-MS/MS METHODOLOGY TO MEET THE RECOMMENDED AOAC REGULATORY REQUIREMENTS

Oscar Cortés-Ledezma

BAYER

VENDOR SESSION 8

WHAT CAN WE DO WITH A CHEMISTRY DEGREE?

Laura McConnell, Renan Karpfenstein and Renata Volpi

SHIMADZU

VENDOR SESSION 9

LC-MS/MS A POWERFUL TECHNIQUE FOR RESIDUAL PESTICIDE ANALYSIS IN DIFFERENT MATRICES

Cristina Matos

BRUKER

VALIDATION OF A MUCH FASTER CLEARANCE METHOD FOR PESTICIDES IN FOOD EXTRACT USING A COMBINED TARGETED AND NON-TARGET APPROACH USING BRUKER IMPACT II QTOF.

What would be the impact of a four times faster analysis method for the quantification of low-level pesticides according to guidelines in different matrices? A much faster method would be beneficial for the speed of clearance of samples or would open a possibility to have an increased number of samples per instrument and would lower total sample cost. This validation looks at the possible drawback of this much faster method and defines if this method could be used in a validated environment according the European Sante guidelines. Within this new setup an investigation was done if speeding up this method would have any implication on the reviewing time within the analytical software or would increase false positives of negatives. For the non-targeted work flow the number of unknowns for the standard and fast method which we can identify and process by using MetaboScape software is investigated and LC-HRMS and GC-APCI-HRMS workflows are compared.

AGILENT

NEW DEVELOPMENTS FOR MULTIRESIDUE PESTICIDE ANALYSIS USING HIGH RESOLUTION MASS SPECTROMETRY LC-QTO

Pesticide testing laboratories routinely need to analyze samples for large lists of analytes with high confidence and high throughput. Conventionally, a targeted acquisition approach, using a triple quadrupole mass spectrometer, is used to quantitate a list of target analytes. However, government plans are causing significant growth in the number of pesticides to monitor. Thus, the cost associated with standards and their preparation (usually in multiple matrices) sometimes becomes a limiting factor.

For this reason, there is an increasing demand for alternate cost-effective methodology to allow efficient expansion of the testing capabilities beyond the target compound list of routine quantitation. Some compounds occur frequently enough in samples, that quantitating during the initial screening is cost-effective. However, for other compounds, it is practical to consider not building a calibration curve but rather quantitate after screening, depending on what is found initially in the sample.

High-resolution quadrupole time of flight (Q-TOF) mass spectrometry is an attractive alternative to triple quadrupole systems because the Q-TOF platform has the capability of measuring accurate mass and isotope pattern for both molecular ions and fragments, enabling high confidence in compound identification. Q-TOF systems are also able to collect data at a fast rate, making it possible to collect quality data from both molecular ions and fragments while still maintaining sufficient data points across a chromatographic peak. This is key for those compounds that merit simultaneous quantitation but also for suspects, which will be more easily identified if a true representation of a chromatographic peak can be generated. With recent technological breakthroughs, the quantitation suitability of Q-TOF systems has significantly improved owing to enhanced sensitivity, selectivity, and dynamic range. Q-TOF is growing into a fit-for-purpose platform for laboratories that are interested in simultaneously performing quantitation for priority targets and suspect screening for a broader list of pesticides.

INNOVATEK/RESTEK

LPGC - THE FAST WAY TO SPEED UP YOUR MULTIRESIDUE PESTICIDE ANALYSIS FOR FOODS!

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Food testing labs need fast turn-around times to analyze samples submitted for multiresidue pesticide analysis and deliver accurate results. Now, they can take advantage of their mass spectrometer's vacuum to give their gas chromatography workflow a significant speed boost. Installing a new factory-coupled column set allows the vacuum in the MS detector to lower the pressure inside the analytical GC column, which results in run times three, or more times faster than a conventional GC-MS column configuration. The technique is called low pressure gas chromatography (LPGC). Given the challenges with making difficult column connections this technique has lacked adoption in the past. The authors present data showing a typical GC-MS/MS multiresidue pesticide workflow for various food commodities using a conventional 30 meter column compared with the faster analysis using this innovative pre-connected column set to demonstrate the ease and effectiveness of implementing this technique. A comparison will be made between the two identifying the benefits and challenges of this and other alternative fast GC approaches.

Keywords: LPGC, GC, pesticides, food.

SCIEX

WHAT CAN SENSITIVITY GIVE YOU OTHER THAN LOWER LOQS?

The extensive use of pesticides in agriculture has led to the demand for comprehensive and sensitive analytical techniques to achieve lower limits of quantification. To ensure consumer safety many countries have set maximum residue limits (MRL), which are the highest level of pesticide residues legally tolerated in food.

Generally, the European Union is known to have one of the more restrictive MRLs established for pesticides in food and animal feed. For example, a general default MRL of 0.01 parts per million (ppm) applies where a pesticide is not specifically mentioned. This is why food testing laboratories need very sensitive and robust instrumentation, which allows them to quantify pesticide compounds down to their MRL accurately.

With every new mass spectrometry technology, the first question is always: "How much lower can we go?" However, sensitivity is about more than chasing ever-lower limits of quantitation (LOQ). Sensitivity, at its core, offers flexibility. Sensitivity can improve detection confidence, tighten precision, and simplify workflows. This webinar demonstrates the various advantages of next-level sensitivity using the SCIEX Triple Quad™ 7500 LC-MS/MS System – QTRAP® Ready with multiple contaminant testing case studies. Topics discussed will include ion statistics, ionization efficiency and selectivity, all with the intent of driving simplified laboratory workflows.

EUROFINS

ANALYTICAL CHALLENGES IN THE ANALYSIS OF PESTICIDE RESIDUES IN FOOD

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Pesticides are a very important role in the development of the modern agriculture, increasing food productivity. The application of pesticides can occur during production and storage, controlling of fungi, insects and weeds that can decrease the quality of the food and causing economic losses. Therefore, the application of pesticides is essential to preserve the quality and prolong the shelf life of food.

However, the improper application of pesticides may leave residues in food, which has led different governments and international agencies to set maximum residue limits (MRLs) for food. A maximum residue level is the highest level of a pesticide residue that is legally tolerated in or on food or feed when pesticides are applied correctly (Good Agricultural Practice)¹.

There are different regulatory agencies at the levels of pesticide residues in food and feed such as European Commission (EU- European Union)¹, Food and Drug Administration (FDA- United States)², Codex Alimentarius International Food Standards (FAO- Food and Agriculture Organization of the United Nations)³; National Health Surveillance Agency (Anvisa- Brazil)⁴. These agencies are responsible for organize monitoring programs and generate data for the toxicological evaluation of maximum residue limits. Moreover to presenting results of the analysis of the food consumed by the population.

Chromatography with mass detectors is the main technique for the analysis of pesticides in food. The combination of these two techniques has the advantage of separating the components by chromatographic analysis and high selectivity with structural information from mass spectrometry that allows their identification and confirmation in concentrations of the order of ppb.

In South America, Eurofins has two specialized centers for the analysis of pesticides in food in Brazil and Chile. These laboratories a combination of liquid and gas chromatography techniques coupled with mass spectrometry detectors for analysis of pesticides. The scope of Eurofins' analysis covers the main pesticides currently used in agriculture as well as banned pesticides, which are no longer used. The scope of both laboratories applies to different types of foods such as fruits, cereals, oilseeds and others.

Thus, the determination of pesticide residues in food is important due to the risk that these compounds may pose to human health, in addition to their persistence in the environment and tendency to bioaccumulation. Public and private laboratories have been working on the development of efficient and reliable analytical methods, capable of identifying and quantifying pesticides in complex samples, guaranteeing food security for the population.

Keywords: Pesticide, chromatography, mass spectrometry.

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INNOVATEK/THERMO

WHAT WILL BE ON YOUR PLATE TOMORROW? BE READY FOR FUTURE REQUIREMENTS WITH TODAY'S MS TECHNOLOGY

Citlalli Aguilar, Ph.D

Mass Spectrometry Product Specialist, Thermo Fisher Scientific

How do you ensure that the mass spectrometer you purchase now will be able to handle your analytical needs today, tomorrow and beyond? Learn how you can quantitate large numbers of pesticides at today's MRL requirements while gaining the ability to easily add new ones without labour-intensive method and assay development. High-resolution, accurate mass MS technology offers confident untargeted and targeted analysis and also allows for screening for unknown or unexpected pesticides. Plus, by capturing accurate mass data for each sample, you can retrospectively analyse each sample for additional analytes of interest without the need to rerun your sample. With this, you can comply with today's requirements and be confident that your MS technology will be able to tackle whatever is on your plate tomorrow.

WATERS

DETERMINATION OF PESTICIDE AND MYCOTOXIN RESIDUES IN DRIED CANNABIS FLOWER: LC-MS/MS AND GC-MS/MS METHODOLOGY TO MEET THE RECOMMENDED AOAC REGULATORY REQUIREMENTS.

Oscar Cortés-Ledezma,¹ Kim Tran,¹ Kari Organtini,¹ Marian Twohig,¹ and Christopher Hudalla;²

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Although cannabis products are legal for medicinal or adult use in many US states, Canada in some countries in Latin America, there are currently no harmonized guidelines for pesticide and mycotoxin residue tolerances. Consequently, each state or nation with legalized cannabis has its own list of such contaminants with legal residue tolerance limits that may be quite different in each region. AOAC International has published Standard Method Performance Requirements (SPMRs) to describe the minimum recommended performance characteristics to be used to evaluate methods for determination of pesticides in cannabis. AOAC International has used the lowest tolerance level as the target action level for any proposed method with a recommended LOQ at 50% of the action level. The methodology in this presentation is suitable to determine all pesticides and mycotoxins currently regulated by any of the US states or Canada at the AOAC-recommended LOQ.

Although most of the target pesticides and mycotoxins are amenable to LC-MS/MS analysis, many compounds have much lower detection limits using GC-MS/MS methods. Consequently, to obtain the low detection limits required, both types of chromatography were employed for this study. APGC (atmospheric pressure chemical ionization for GC-MS) was chosen for the GC amenable compounds due to its greater specificity and selectivity compared with EI (electron ionization)-based mass spectrometry. Another significant benefit to this approach is that APGC-MS/MS can be performed on the same mass-spectrometer as LC-MS/MS.

BAYER

WHAT CAN YOU DO WITH A CHEMISTRY DEGREE?

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Chemistry is a fundamental area of science, and knowledge of chemistry is extremely valuable, providing avenues to pursue numerous career pathways. Bayer is a Life Science company with a more than 150-year history with core competencies in the areas of health care and agriculture, and a purpose, “Science for a better life”. This Round Table Discussion will introduce some of the many agriculture industry career pathways that one can pursue with a chemistry degree. Three Bayer scientists will give a short description of their career paths and their work at Bayer. A moderated question and answer and discussion with audience members is planned.

Keywords: crop protection, regulatory, risk assessment, chemistry.

SHIMADZU

LC-MS/MS A POWERFUL TECHNIQUE FOR RESIDUAL PESTICIDE ANALYSIS IN DIFFERENT MATRICES

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Pesticides have been used for decades as substances intended for preventing, destroying, repelling or mitigate any pest. These compounds are widely used in food production and other products used for human consumption among other uses. Every country has their own pesticides products, so it is known that there is a wide variety of compounds used for this purpose and every country have their own regulatory agency with different permitted concentration levels (MRLs) depending on their harmful properties to humans. In order to monitor these compounds, over the years, more efficient methods have been used for the analysis of pesticides in different matrices. One of the most common and efficient techniques for analyzing these residues is LC-MS/MS, since it offers sensitivity, selectivity and efficiency to obtain reliable and accurate results. Most of the laboratories that analyzes pesticides residues uses GC-MS/MS as a complementary technique to the LC-MS/MS, because certain compounds do not ionize well by ESI-LC-MS/MS. On this conference we will explore the utility of APCI-LCMS method for the quantitation of pesticides frequently analyzed by GC-MS/MS on cannabis products. Also, we are going to explore the use of LC-MS/MS for analyzing pesticide residues in food as fruits.



EPRW 2022

14th EUROPEAN PESTICIDE RESIDUE WORKSHOP

PESTICIDES IN FOOD AND DRINK

SAVE THE DATE

19-23 September 2022 BOLOGNA, Italy

Dear Colleagues and Friends,

You are warmly invited to the 14th European Pesticide Residue Workshop in person!

On behalf of the Scientific and Organizing Committee, I have the honor to announce the next EPRW which returns to Italy after 20 years.

We are looking forward to meeting all of you again from the 19th to the 23rd of September 2022 at Palazzo dei Congressi, in Bologna, Italy.

Do not miss Europe's leading meeting for the latest concepts and developments in the field of pesticide residues in food and drink. The EPRW is an excellent opportunity to exchange information and experience among colleagues and connect experts from all over the world, coming from governmental and private food control laboratories, public authorities, regulatory bodies, universities and research institutes, food producers and distributors, agrochemical manufacturers and other interested parties. We expect proficous interactions between the experts and all important vendors of analytical equipment and consumables that will present their latest equipment for pesticide residue analysis in a large exhibition area.

The EPRW is hosted in Bologna, a UNESCO city with the largest medieval city area in the world, ancient porticoes and towers, home to one of the oldest universities, founded in 1088. Bologna is a charming but also a testing destination for the quality and variety of food. Last but not the least, Bologna is easily connected to international airports and offers a variety of accommodation.

We are looking forward to welcoming all of you in Bologna, Palazzo dei Congressi, 19-23 September 2022!

Patrizia Pelosi
EPRW 2022 Chair

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Web site in progress: eprw2022.com

May 18-20

Poster Presentations

Workshop
June 1-3

Development and Application of Analytical Methods

A-01

DETERMINATION OF PESTICIDES AND MYCOTOXINS IN FEED. APPLICABILITY OF AN ANALYTICAL METHOD IN ROUTINE ANALYSIS.

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In routine analysis it is often necessary to introduce minor changes in protocols or extend the applicability of previously validated methods to similar matrices. The SANTE guidelines contemplate on-going validation as a quality control process to verify analytical performance through a reduced number of experiments¹.

In this work, a validated QuEChERS method for the determination of pesticides and mycotoxins in corn and alfalfa was used for the analysis of a large number of different types of feed samples (cereals, pastures, silages). Briefly, 2 g of sample were hydrated with 10 ml H₂O (2% CH₂O₂), followed by extraction and partition with 10 ml acetonitrile, MgSO₄/NaCl (4:1). An aliquot of the extract was then cleaned-up using d-SPE with MgSO₄, C18 and PSA, prior to analysis by UHPLC-MS/MS².

A modification of the clean-up step had to be introduced due to the large number of samples to be processed and availability of sorbent salts at the time of analysis. Thus, for cereal-based samples only MgSO₄/C18 was used while MgSO₄/PSA was used for pasture-based samples.

Following the concepts of the on-going validation, the mean recovery (Rec%) was evaluated at the same concentration level from validation (100 µg/kg). Precision was evaluated as repeatability and intermediate precision, repeating the test 2 and 3 consecutive days for corn and alfalfa, respectively. The recovery results obtained after the modifications were compared with those from the initial validation through statistical t-tests. Finally, an additional quality control test was done by applying the methodology to a European Union Proficiency Test (EUPT CF18-2014) in wheat flour.

As a result, 80% of the studied compounds (117 pesticides and 2 mycotoxins) showed recoveries in the 60-140% range accepted for routine analysis by the SANTE guide, with RSDs <20% in both matrices.

From the statistical tests, the Rec% of more than 85% of the studied compounds were not affected by the changes introduced. Moreover, for compounds such as acephate, chlorpyrifos methyl, clethodim, fenthion and metribuzin in corn, and methomyl, metribuzin, thiabendazole, profenofos, spinosad D and terbuphos in alfalfa their Rec% improved with respect to the initial validation. Finally, the results from the EUPT test were compared to the declared concentration through a z-score, verifying the aptitude of the method for the determination of azoxystrobin, epoxiconazole, linuron, pyraclostrobin and carbendazim.

Keywords: Feed, Pesticide, On-going validation

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A-02

PESTICIDE RESIDUES IN ONION VARIETIES MARKETED IN URUGUAY

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Onion is one of the most consumed vegetables all over the world, and Uruguay is not the exception. As a part of a global study of the pesticide intake of the Uruguayan population, we present the results of the evaluation of pesticide residues content in three onion varieties marketed in Montevideo. Samples of spring onion (*Allium fistulosum*), white and red onion (*Allium cepa*) were analyzed for 57 pesticide residues through gas chromatography coupled to tandem mass spectrometry. The compounds studied included the pesticides approved to be applied to onion plus the banned organochlorines. As onion is a bulb, the food contamination by non-approved and no longer used organochlorines cannot be dismissed because they are very persistent compounds that are still found in soils of old farms, where horticultural activities have been carried out for decades.

The residues were extracted from the samples using a validated AOAC 2007.01 variant of QuEChERS with a slight adaptation. All the compounds showed recoveries between (70-120%) with relative standard deviation below 20%.

The method was linear in the range 0.01-0.25 mg kg⁻¹ with a strong matrix effects for all the analytes. Upon validation, the LOQs were 0.01 mg/kg for most of the compounds. Residuals and the Back Calculated Concentration (BCC) were below 20%.

The analyzed samples contained chlorpyrifos and azoxystrobin, and one of them also contained procymidone, all of them below the *Codex Alimentarius* MRLs. No organochlorines were detected in the samples. Surprisingly the declared “organic” sample contained low levels of chlorpyrifos.

Keywords: Pesticide residue; onion, Uruguay, MRM.

A-03

VALIDATION OF GC-MS/MS MULTI-METHOD FOR THE DETERMINATION OF PESTICIDE RESIDUES IN FRUITS AND VEGETABLES.

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GC-MS/MS MRM (Multiple Reaction Monitoring) analysis play a key role in the targeted analysis encompass pesticide registered for use and those whose use has been banned, with particular emphasis on substances of high toxicity.

The research aimed to develop and validate a multi-residue method for determination of pesticide residues in fruits and vegetables using the Agilent Intuvo 9000GC system combined with a triple quadrupole mass spectrometer equipped with an EI ionization source (Agilent, Triple Quad 7010B). The chromatographic separation was done using an Agilent HP-5MS column (15m x 0.25mm x 0.25 μ m). The quantitative analysis was based on the multiple reaction monitoring (MRM) technique.

The method validation procedure was performed for 240 pesticides according to SANTE/12682/2019 guidance document [1]. Strawberries and tomatoes were chosen as representative matrices. Recovery tests were carried out using blank samples fortified with pesticide mixture at 0.001, 0.002 and 0.005 mg/kg levels. QuEChERS method was used to isolate the analytes and remove the impurities.

The recovery of the majority of tested compounds ranged from 70-120% and was characterized by a precision of less than 20%. The limit of quantification (LOQ) was set at the lowest validation level for which accuracy and precision parameters fulfilled the requirements of SANTE document. The applied method enabled the determination of most of the tested compounds at the level of 0.001 mg/kg in both matrices.

Validation studies indicate the suitability of the method to simultaneous determination more than two hundred compounds from various chemical classes including their metabolites in one analytical run at very low limits of quantifications.

Keywords: pesticide residues, fruits, vegetables, GC-MS/MS.

References: 1. Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed. SANTE/12682/2019.

A-04

RESIDUAL EFFECT AND DISSIPATION OF SELECTED INSECTICIDES APPLIED TO SOYBEAN CROPS FOR THE CONTROL OF DEFOLIATING CATERPILLARS

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Soybean crops are one of the most affected by insects, especially stink bugs and defoliator caterpillars such as *Rachiplusia nu* and *Anticarsia gemmatalis*. Insecticide application is usual as pests exceed the action threshold in almost all crop cycles. This work's aim to study the residual effect of selected insecticides currently used in soybean crops and determine their dissipation curves in leaves and soil, to establish a relationship between the residual concentration and the mortality of a colony of larvae fed with the field-treated leaves. The field experiment was carried out on a soybean crop by randomized plot design with three treatments, chlorpyrifos (900 cc/ha), triflumuron (90 cc/ha), and control (without application) with four replicates. Leaves and soil samples were collected at different times and taken to the laboratory.

Field control efficacy was estimated by larvae population density at the time of sampling. The residual efficacy was performed feeding 4th instar *A. gemmatalis* larvae with leaves collected from each plot at 8- and 13-days post-application. At the same time, an analytical methodology based on the QUEChERS template using LC-QqQ-MS/MS was developed and validated to determine 11 insecticides in leaves and soil, at 0.1; 0.5 y 1.0 mg/kg according the EU guidelines¹

The final method begun with the extraction of the pre-soaked sample with water, followed by the addition of MeCN, MgSO₄ and NaCl. The leaves and soil extracts were hand shaken for 5 and 3 min, respectively. In addition, the soil was ultrasonicated for 5 min. The leaf extract was purified by d-SPE with C-18, MgSO₄ and Al₂O₃ while MgSO₄ and Al₂O₃ were used for soil. After the clean-up, the extracts were centrifuged and filtered for LC-QqQ-MS/MS analysis.

For leaves, 10 out of the 11 pesticides presented good results between 69 and 104% with RSD ≤12% for the three levels tested. In soil, 9 out of the 11 pesticides showed recoveries in the range 66% to 115% with RSD of 3-7%.

All the insecticides presented quantification limits of 0.1 mg/kg, except for carbaryl in leaves (0.5 mg/kg), bifenthrin and lambda cyalothrin in soil (0.5 mg/kg). The matrix-matched calibration curves presented good linearity in the range 0.01 to 0.5 mg/kg for leaf matrix and from 0.01 to 1 mg/kg in soil (back calculated concentration residuals < 20%). All the insecticides presented medium and high signal suppression for leaf and soil extract, respectively.

The bioassays showed that triflumuron caused a mortality of 90% up to 13 days post-application, whereas despite having an initial control efficacy of over 95% in the field chlorpyrifos reached 55% mortality at 8 days post- application. The concentration levels found in the samples are in accordance with the bioassays, as the triflumuron dissipation curve shows a slightly slower drop than chlorpyrifos, that showed a marked decrease over time. The experimental half-lives determined for both compounds were 24-48 hours depending on the matrix.

Keywords: soybean crops, insecticides residues, dissipation curves, QuEChERS **References:** 1. European Commission DG-SANTE, (2019). Method validation and quality control procedures for pesticide residue analysis in food and feed. Document No. SANTE/11813/2017.

A-05

EFFECTS OF CLEANING PROCEDURES ON THE CONCENTRATION OF PESTICIDE RESIDUES ON CRISP FRESH-CUT LETTUCE (CV. VERA).

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Consumption of ready-to-eat vegetables has increased due to new trends in diet and lifestyle, thus having an impact on both commercial and domestic environments. It is widely known that different production systems may lead to pesticide residues in food. Therefore, the need for analyzing the effects caused by different cleaning strategies regarding the amount of pesticide residues is of great interest.

To achieve this goal, we analyzed crisp lettuces (cv. Vera) that were grown under controlled conditions. Lettuces were separated into two groups, a control was set where no pesticides were applied, and a second group was fumigated with six pesticides used on the Mercosur region. After harvest, both groups of lettuces were chopped into stripes and mixed to form homogenous batches. The second group went through two cleaning procedures. Power ultrasound technology was evaluated at different frequencies (25, 37, 45, 80 kHz) at fixed times (10 and 15 min). This novel method was compared with three domestic methods: tap water, chlorinated water 100 ppm, peracetic acid 80 ppm and acetic acid 4%, where the lettuce was soaked in each solution for 10 min.

Samples before and after each treatment, as well as the control (blank sample) and commercially obtained samples were taken for pesticides analysis, maintaining them in freezer until analysis. Additionally, wash water used in cleaning methods was tested for pesticides too, using the method described by L. Pareja et al ¹.

In order to quantitate the amount of pesticide reduction, a modified QuEChERS acetate version was validated according to the SANTE guidelines ². The methodology involved the extraction of the pre-pulverized lettuce (through cryogenic milling) with acetonitrile acidified with acetic acid, the mixture was shaken manually, then salting out salts were added, and the mixture was shaken again for three minutes. After centrifugation, the extract was filtered through a 0.45 µm syringe filter for LC-QqQ-MS/MS analysis looking for 17 pesticides normally used in lettuce. With this method the quantitation limits proved to be adequate for monitoring the compliance with the Maximum Residue Levels (MRLS) established by *Codex Alimentarius*³; 10 µg/kg for two pesticides and 50 µg/kg for the remainder.

The main results obtained were that 7 out of 22 commercial samples presented quantifiable pesticides residues, though they were below the MRLS³. The highest levels were for propamocarb in two samples at 2.5 and 4.2 mg/kg, while the MRL is 100 mg/kg. Other pesticides found were acetamiprid, boscalid, carbendazim, iprodione, pyraclostrobin, pyrimethanil and spinosad.

All in all, a method for pesticide analysis was validated for lettuce, all the cleaning procedures managed to reduce pesticide residues in similar amounts, though chlorpyrifos turned out to be the most resistant. Water samples were all under the detection level.

Keywords: Pesticides, lettuce, QuEChERS, decontamination process.

References: ¹L. Pareja, M.J. Martínez-Bueno, V. Cesio, H. Heinzen, A.R. Fernández Alba. Trace analysis of pesticides in paddy field water by direct injection using liquid chromatography–quadrupole-linear ion trap-mass spectrometry., *J. Chromatogr. A*, 1218 (2011) 4790–4798.

²European Commission DG-SANTE, Document No. SANTE 11813/2017. Analytical quality control and method validation procedures for pesticide residues analysis in food and feed

³Codex Alimentarius Commission, *Codex Pesticides Residues in Food Online Database* updated up to and including its 36th Session (July 2013).

A-06

VALIDATION OF A MULTI-RESIDUE LC-MS/MS METHOD FOR THE DETERMINATION OF PESTICIDE RESIDUES IN CEREALS AND FEEDING STUFF

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Investigation of plant protection products residues in food of plant origin and feeding stuffs is crucial in ensuring food safety. Modern multi-residue methods based on liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) can be used for simultaneous determination of hundreds of pesticides from different chemical classes as well as their metabolites in many matrices at very low limits of detection to evaluate the fulfilment of requirements regarding maximum residue levels of pesticides (MRLs).

The aim of the study was the development and validation of a multi-residue method for pesticide residues determination in cereals and feeding stuff using an Eksigent® ekspert™ ultraLC 100-XL system interfaced with a mass spectrometer equipped with an electrospray ionization source operated in the positive and negative mode (AB Sciex, Qtrap 6500). Chromatographic separation of analytes was performed using a Kinetex C18 (100 x 2.1mm x 2,6µm) column and water/methanol gradient. Multiple reaction monitoring (MRM) mode was used for detection and quantification of analytes.

The method validation was carried out according to the SANTE/12682/2019 guidance document [1] using 2 representative matrices. The recovery tests were performed by spiking blank samples of wheat and soybeans with a solution of about 430 pesticides at 0.001, 0.002 and 0.005 mg/kg levels. QuEChERS extraction was used to isolate the analytes and remove the impurities. The aliquot of extract was 10-time diluted with the LC mobile phase prior to the instrumental determination. The limit of quantification (LOQ) was set at the minimum concentration level, which was quantified with acceptable and required accuracy and precision.

Recoveries of the majority of compounds tested were in the 70–120% range and were characterised by precision lower than 20%. The high sensitivity of the method allowed the successful determination of the majority of compounds at the level of 0.001 mg/kg.

The validation results indicate usefulness of the developed method in routine analysis of pesticide residues in cereals and feeding stuff at very low levels.

Keywords: pesticide residues, cereals, feeding stuff, LC-MS/MS.

References: 1. Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed. SANTE/12682/2019.

A-07

DISSIPATION DYNAMICS OF METAMITRON AND DIFLUFENICAN APPLIED IN CHEMICAL PROTECTION OF LUPIN SPECIES.

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Dissipation kinetics of pesticide residues is an important tool to confirm safe and proper use of candidate pesticides having potential to be applied on selected minor crops to control pests, weeds and diseases affecting the production of these crops. In this work, we focused on study of dissipation rates of met amitron and diflufenican herbicides after application to lupines. These studies were a combination of field trials, in which the pesticides were applied in the ways we proposed to use them on lupines (on-soil or foliar spraying), followed by laboratory analysis for the presence of pesticide residues.

Three species of lupine were included in the studies, white lupin (*Lupinus albus*), yellow lupin (*Lupinus luteus*) and narrow-leaved lupin (*Lupinus angustifolius*). Samples obtained from field experiments were collected and well homogenized in laboratory. For isolation pesticide residues from green plant material, we applied a miniaturized extraction with acetonitrile, liquid-liquid partition by salting out and a cleanup step by dispersive-solid phase extraction (QuEChERS method). ChloroFiltr® sorbent was employed in place of graphitized carbon black to selectively remove chlorophyll from green plant extracts [1]. Freezing out additional step and different d-SPE cleanup sorbents were used for extraction procedure of high-protein content dryseeds of lupine. Final analysis were performed using ultra performance liquid chromatography coupled to tandem quadruple mass spectrometry (UPLC-MS/MS).

The dissipation of selected herbicides approximately fitted to a first-order kinetic model, with half-life values ranging from 2.86 to 4.88 days for met amitron and from 4.10 to 9.62 days for diflufenican, depending on the lupine species. In case of on-soil application, pesticide residues in lupines plants were below 0.01 mg/kg approximately 27 days after treatment, for both herbicides. The observed dissipation patterns of the applied herbicides were different owing to different chemical structures, applied doses, species of lupine, growing and harvest time but the final residues in the samples collected in the last sampling time were always below the limit of quantification indicating that the proposed plant protection products could be used on the studied crops without the risk of leaving residues.

Keywords: herbicides, minor crops, dissipation study, lupines.

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A-08

DETECTION OF CHLORPYRIFOS FROM CLAY-BIOMIMETIC NANOCOMPOSITE ELECTRODE

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The present work deals to developing an impedimetric biosensor for the detection of chlorpyrifos using the nanocomposite formed by montmorillonite (SWy-1) clay modified with a molecule that mimics the active site of the enzyme acetylcholinesterase (SWy-1-M). Chlorpyrifos is an organophosphate insecticide widely used in the control of domestic pests and in agriculture in different cultures. However, its use should be cautious, as it can lead to serious damage to human health, since small amounts can quickly inhibit the activity of the cholinesterase enzyme, and block the transmission of nerve impulses, causing seizures, fainting and even death [1]. In this sense, effective, low-cost and quick response methods are needed to detect this substance in environmental and food samples. Biosensors are an alternative to these situations, since they are simple to build and operate, sensitive and portable devices, facilitating work and ensuring results as accurate as traditional methods [2]. In the experimental actions the nanocomposite was synthesized by mechanical stirring, obtaining a stable suspension, which was used for the modification of a platinum electrode. The structural characterization was obtained from high resolution thermal analysis (DSC) and SEM images techniques, indicating the effective modification of the clay by the biomimetic molecule, as well as the effective interaction of the composite with the pesticide. The electrochemical study of the formed biosensor was carried out by electrochemical impedance spectroscopy and cyclic voltammetry. The measurements were carried out in KCl 0,1 mol L⁻¹, pH 7, containing the redox species Fe(CN)₆^{3-/4-}. The electrode surface coverage (θ) was $\theta = 0,65$ and $0,42$ SWy-1 and SWy-1-M, respectively. The interpretation of the results of the electrochemical impedance spectroscopy was based on the charge transfer reaction involving the Fe(CN)₆^{3-/4-} species at high frequencies, followed by diffusion through the monolayer at low frequencies. The heterogeneity of the modifying films on the electrode surface limited the transport of the active species through the montmorillonite layer, since the SWy-1 particles, when deposited, formed non-regular overlapping plates, observed by SEM images. The DSC results revealed a disorganization in the structure of the organophilic clay with the insertion of the pesticide, from the variation of the energies of interaction of the structural waters of the system. The sensors built showed chlorpyrifos linearity in the concentration range from $(1 \times 10^{-8} \leq C_{\text{chlorpyrifos}} \leq 1 \times 10^{-7})$ mol L⁻¹, with $R = 0,9999$ for SWy-1-M, and $\text{LOD} = 1,41 \times 10^{-10}$ mol L⁻¹. The practical usefulness of the sensor was tested on tomato samples, obtaining a recovery percentage between 97 and 102%, together with the low standard deviation, indicating the robustness of the sensor.

Keywords: montmorillonite, biomimetic, chlorpyrifos.

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2. SGOBBI, L. F.; MACHADO, S. A. S.. Functionalized polyacrylamide as an acetylcholinesterase-inspired biomimetic device for electrochemical sensing of organophosphorus pesticides. *Biosensors and Bioelectronics*, (2018). Pages: 290–297.

A-09

FULL VALIDATION AND ISO/IEC 17025 ACCREDITATION OF A MULTIRESIDUE METHOD TO DETERMINE PESTICIDE RESIDUES IN OAT

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Accreditation provides recognition by official bodies for a laboratory's technical competence in performing for samples requiring ISO/IEC 17025 conformance services. One of the requirements for accreditation is method validation in order to prove laboratory ability to perform certain analyses. Oat is considered a matrix with high starch and/or protein, low water and fat content. Therefore, the goal of this study was to develop and validate an analytical method for determination of 186 pesticide residues in oat and to evaluate method performance through a proficiency test, as a prerequisite for laboratory application to be accredited. For this, QuEChERS extraction method was validated followed by UPLC-TQ-MS/MS analysis. The validation study was performed based on INMETRO/CGCRE 008 document (Brazilian Legislation). Recovery studies were performed by spiking blank oat at 10, 20 and 50 $\mu\text{g kg}^{-1}$, performed by two analysts, seven replicates for each concentration level plus blank sample. The results showed that 82% of pesticides studied (186 compounds) presented recoveries within the acceptable range of 70-120% for all evaluated concentrations. For 74% of pesticides, LOQ was the lowest spiked level (10 $\mu\text{g kg}^{-1}$). The validated method obtained satisfactory performance for those studied analytes in terms of detectability, selectivity, accuracy, precision and linearity, except for 34 pesticides (~18%). For this reason, the method scope was reduced for 152 pesticides. Thus, the validated method showed to be appropriate to determine pesticide residues in high starch and/or protein, low water and fat content matrices, once it was attested by a proficiency test and the results for all reported pesticides were in conformity. Hence, the laboratory will request the accreditation by official body (INMETRO) in Brazil.

Keywords: Feed, Pesticide, On-going validation.

References: 1. SANTE/12682/2019-https://ec.europa.eu/food/sites/food/files/plant/docs/pesticides_mrl_guidelines_wrkdoc_2019-12682.pdf.

2N. Michlig et al. "Validation of a sample preparation method for the analysis of pesticide residues in maize and alfalfa". Latin American Pesticide Residue Workshop (2017). PA45.

A-10

QUECHERS-BASED METHOD FOR NEONICOTINOID INSECTICIDES DETERMINATION IN HONEY FROM THE ARGENTINE LIVESTOCK-AGRICULTURAL AREA

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Due to the great versatility of neonicotinoid applications for the systemic protection of crops against pests and the great target specificity towards invertebrates, this kind of insecticide is widely used nowadays. Several studies have shown that neonicotinoids translocate to the nectar and pollen of treated plants, which represents a potential risk to pollinators, and could also end up in honey produced by bees. Thus, a QuEChERS-based methodology was optimized to evaluate the content of neonicotinoid residue in honey samples. Also, the palynological, physicochemical and chromatic properties of 20 % of the samples were measured. In agreement with the requirements of the Argentine legislation, palynological tests showed that each honey sample was unifloral, with a predominance of clover honey^[1]. Interestingly, one of them was composed of 50 % soybean pollen (*Glycine max* L.). The palynological results exhibit the characteristics of the studied area, with low species diversity.

Regarding the analytical residue procedure, a two-step experimental design method was carried out to determine the optimal extraction and cleanup conditions for eight neonicotinoids (acetamiprid, clothianidin, dinotefuran, flonicamid, imidacloprid, nitenpyram, thiacloprid and thiamethoxam). Firstly, a two-level fractional design was carried out considering seven independent variables: temperature, pH and time for the sample soaking stage, the concentration of magnesium sulfate and sodium chloride to improve the extraction of the analytes, as well as the amount of C18 and PSA sorbents, were also investigated. After the screening stage, a Box-Behnken design was performed composed of the three significant variables: soaking time and pH, and the amount of PSA. The factorial design methodology combined with the surface response analysis allowed to optimize the process for the efficient extraction of neonicotinoid compounds from honey. The extracts were evaluated on a UHPLC-MS/MS system and quantified with the internal standard method. Afterwards, the proposed method was validated following the SANTE 12682/2019 guidance document, reaching satisfactory results: recoveries between 79-120 % (RSD \leq 20 %) for the three spiked levels 0.25, 1 and 5 $\mu\text{g kg}^{-1}$, the LOQs of 0.25 $\mu\text{g kg}^{-1}$ to acetamiprid and thiacloprid and 1 $\mu\text{g kg}^{-1}$ for the remaining neonicotinoids. The method was applied to the analysis of 131 honey samples collected from a livestock-agricultural area during the last three honey harvest seasons. Imidacloprid was the most frequently found neonicotinoid, detected in 8 % of the honey samples. Residues of imidacloprid + thiamethoxam were determined in one sample and another sample presented acetamiprid residues. Although neonicotinoid concentrations were low ($<1 \mu\text{g kg}^{-1}$), suggesting no human risks, they may pose a risk to honeybees through chronic exposure.

Keywords: neonicotinoids, honey, QuEChERS, surface response.

References: 1. Resolution SAGPyA N° 274/95, Typification by botanical origin. *Argentine legislation* (1995).

A-11

EVALUATION OF THE DISTRIBUTION AND PERSISTENCE OF FORMIC ACID AND OXALIC ACID IN HONEY BEES AND BEEHIVE PRODUCTS BY ION CROMATOGRAPHY COUPLED TO Q-ORBITRAP.

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Loss of honey bee (*Apis mellifera*) colonies has become a major threat to the agricultural production and apicultural industry. The ectoparasitic mite *Varroa destructor* is the most damaging pest of honeybee. Synthetic acaricides are the most common treatments employed to fight *V.destructor*. However, there is an increasing concern about their use because of its accumulation in some hive products and the resistance developed by mite populations¹. Natural products such as formic acid (FA) and oxalic acid (OA), are receiving greater attention as a possible alternative control strategy². The present work evaluates the presence, persistence and distribution of FA and OA before, during and after the application of the treatments in field conditions. Furthermore, the impact of these treatments on adult bees and the development of bee brood at different stages was also studied. The analysis of these organic acids is a very difficult task, as they are highly polar compounds with low molecular weight. We present an efficient and simple method based on ion chromatography coupled to a quadrupole Orbitrap accurate high-resolution mass spectrometry for the analysis of FA and OA in adult honey bees, bee brood samples (prepupae, pupae and larvae) as well as honey, beeswax, and beebread. Beebread samples presented the highest concentration level of FA and OA, reaching values of 770 and 490 mg/kg, respectively, during treatment application. They showed 88% of FA dissipation three months after treatment, in contrast with the dissipation of OA, which was of only 11% in this matrix. Matrices with the lowest percentage of FA dissipation were honey, prepupae and adult bees (around 8-10%). All matrices showed OA dissipation lower than 38%.

Keywords: IC-Q-ORBITRAP, natural acaricides, honey-wax-pollen-bee-brood system.

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A-12

METHOD DEVELOPMENT AND VALIDATION TO DETERMINE PESTICIDE RESIDUES IN CHICKPEAS AND LENTILS.

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Recent years have seen an increasing number of people who consume legumes as a good source of protein, carbohydrates, and fiber. Of course, these crops are susceptible to pest infestation, and improper pest control practices during production and storage may lead to excessive pesticide residues in the final product, thus jeopardizing food safety. As part of an investigation of pesticide residues and their levels in legumes, this work aimed to develop improved sample preparation methods in two of the most-consumed legumes (lentils and chickpeas) in South America. The analytes were selected according to agricultural practices for the cultivation of legumes in general.

Since the matrices have different composition, the final method must yield acceptable results for a wide range of legumes. Method development experiments to modify the AOAC 2007.01 QuEChERS approach led to optimal conditions. Firstly, 5 g sample were hydrated with distilled water, and after 30 min, extraction was performed with acetonitrile containing 1% acetic acid. To optimize phase separation, different amounts of NaCl were added followed by anh. MgSO₄ and sodium acetate (NaOAc). The organic phase was then cleaned up with PSA and anh. MgSO₄. The resulting extracts were analyzed by GC-MS/MS. Method validation was conducted for 102 analytes. Average recoveries at the spiking levels (10, 20, 50 and 100 ng/g) ranged from 70-123% with RSDs less than 20%. The linear range was 5-200 ng/g. For lentils, limits of quantification (LOQs) were < 10 ng/g for 38% of the analytes and 10-20 ng/g for the 62% remainder. In the case of chickpeas, 64% of the analytes had LOQ < 10 ng/g with all LOQs < 20 ng/g. Matrix effects we calculated according to the current SANTE guidelines.¹

Samples from various brands were analyzed to test method performance, and no residues were found above the LOQs. These multi-contamination methods are useful to ensure the safety of these foods and will be applied for gather data for dietary risk analysis of the Uruguayan population.

Keywords: pesticide residue analysis, lentils, chickpeas.

Reference: 1. SANTE/12682/2019.

A-13

AUTOMATED PREPARATION OF CALIBRATION STANDARDS ACCORDING TO SANTE REQUIREMENTS

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Overview

The preparation of working standards for calibration in analytical laboratories is a recurring, labour-intensive task. Manual liquid handling steps are often error prone and subject to individual variation. Requirements for preparation and documentation are regulated for pesticide analysis in the SANTE document 12682/2019¹. This presentation describes the automated preparation of standard mixes from individual or mixed standard reference materials using an industry standard x,y,z-robotic system.

Problem Statement

For the preparation of calibration standards the SANTE analytical quality control and method validation document sets five major requirements:

- Reference substances and stock solutions should be stored in a cool place, preferably in a freezer, away from light and moisture.
- Standards should be remixed after equilibration to room temperature. If septa are punctured they should be replaced as soon as possible.
- Standard vials should be permanently labelled.
- The documentation should ensure full traceability of all steps.

Solution

The presented workstation is based on a modular x,y,z-robotic system operated by the CHRONOS software. Reference materials as well as the prepared working standards and calibration dilutions are stored dark in a Peltier-cooled drawer, which is permanently flushed with dry inert gas. Traceability is ensured through the use of 2D-barcodes on all vials. Vial barcodes are checked and registered before every liquid handling step. Racks for temporary room temperature equilibration and a vortex mixer for different vial sizes are provided. Punching of septa is avoided by using a decapper/recapping station. A balance enables precise gravimetric monitoring of potential solvent evaporation.

Conclusion

Multi-compound stock solutions from reference materials as well as the dilutions for daily calibrations can be prepared automatically and unattended. The automated workflow provides highly reproducible and accurate standard preparations and dilutions. It leads to a significant time saving. The dilution workstation fulfils the SANTE criteria according to 12682/2019. The described CHRONECT Multimix dilution setup and workflow can also be applied to other analyte groups beyond pesticides.

Keywords: Preparation of mixed standards, dilution, automation

References: 1. Directorate-General for Health and Food Safety. (2019). Method Validation Procedures for Pesticide Residues Analysis in Food and Feed. In: Sante/12682/2019.

A-14

FULLY AUTOMATED QUECHERS WORKFLOW FOR ORGANOPHOSPHATE PESTICIDES IN ORANGE JUICE

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This presentation describes for the first time a fully automated QuEChERS extraction and clean-up workflow for homogeneous matrices like fruit juices, in this case, demonstrated for orange juice, using an industry standard robotic x,y,z-sampling system for online or offline GC-MS and LC-MS pesticide analysis.

The fully automated QuEChERS extraction and extract clean-up for GC-MS and LC-MS is realized by using an industry standard robotic x,y,z-system for analyzing organophosphate pesticides in orange juices. The automated workflow includes the extraction with acetonitrile, salting out, and is using μ SPE cartridges for matrix clean-up prior to injection into a GC-MS/MS system. The method validation techniques such as pre-spike and post-spike were fully integrated into the automated workflow as well.

QuEChERS is the well-established quick, easy, cheap effective, rugged and safe pesticide extraction procedure, developed by M. Anastassiades and S.J. Lehotay in 2003. Since then, this technique has become a widely used sample preparation approach in pesticides residue analyses. According to the QuEChERS website, about 45 minutes are needed to manually prepare eight samples in the laboratory. In the traditional QuEChERS method, acetonitrile as extraction solvent is added, followed by adding buffer salts. The manual clean-up of the extracts after centrifugation is achieved via dispersive solid phase extraction before injecting the cleaned extract into GC-MS or LC-MS for analyses.

With the complete automated method validation, calibration the achieved linearities of the organophosphate pesticides in orange juice matrix range from 1 ng/mL to 100 ng/mL. The calibration precision achieved was better than 0.995 for all compounds. By spiking 10 ng/mL of pesticides into the orange juice samples, recoveries were obtained in the of range 70% to 115%, while the precision from pre-spike (n=7) and post-spikes (n=6) under the same concentration was less than 10% RSD. The calculated method detection limits (MDLs) of the monitored pesticides were in the range of 1.8 ng/mL to 4.1 ng/mL which were well below the regulated maximum residue limits (MRLs) of 10 ng/g.

Keywords: online QuEChERS analysis, micro-SPE, clean-up, automation.

A-15

DITHIOCARBAMATE DETERMINATION IN YERBA MATE (ILEX PARAGUARIENSIS) PRODUCED IN BRAZIL BY GC-MS.

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Ilex paraguariensis, known as yerba mate, originating of South America is an important commercial product in Latin America. Yerba Mate has become popular worldwide over the years due to many pharmacological properties as great antioxidant capacity, anti-inflammatory, antiproliferative, antimutagenic and antiobesity properties, besides this might contribute to preventing the development of cancer and cardiovascular diseases. In Brazil, there are no authorized pesticides for the cultivation of yerba mate. However chemical control for most pests is carried out according to recommendations for other crops. Among pesticides popularly used are fungicides such as captan and dithiocarbamate. The aim of this work was to optimize and validate an analytical method for determine dithiocarbamates from several commercial yerba mate produced in different municipalities of Rio Grande do Sul state, in Brazilian southern region. For this, an amount of 10 ± 0.2 g of yerba mate was weighed into a 250 mL glass screw-capped bottle and 25 g of ultrapure water was added (ratio 1:2.5). Thereafter, 15 mL of isooctane and 90 mL of tin (II) chloride in hydrochloric acid-solution were added. The bottles were closed immediately and heated for 1 h in a water shaking bath at 80 °C, under continuous mechanical shaking. Afterwards, those bottles were cooled down to room temperature in a cold-water bath. From the organic layer of each bottle, an aliquot of 1.5 mL was transferred into a tube for the cleanup step. The tubes were shaken and centrifuged at 3000 rpm for 3 min. Then, 1 mL of the organic layer (CS₂ and isooctane) was transferred into an autosampler vial and analyzed by GC-MS. The separation was performed on ZB-5MS fused silica capillary column (30 m × 0.25 mm ID × 0.25 μm). A sample volume of 1 μL was injected in split mode (1:10) with an injector temperature of 250 °C. The temperature ramp started at 40 °C for 1.8 min, rising to 240 °C at 50 °C min⁻¹, and held for 2 min. Helium was used as carrier gas at a constant flow rate of 1 mL min⁻¹. The transferline was heated to 200 °C and the source to 230 °C. Mass spectrometry mode was SIM (Selected Ion Monitoring) (76 and 78 m/z). In the validation study, the following parameters were assessed: detection limit (LOD), quantification limit (LOQ), accuracy, precision (RSD_r and RSD_{wr}) and matrix effect. Method LOD and LOQ were, respectively, 0.1 and 0.3 mg CS₂ kg⁻¹. The calibration curves were linear with correlation coefficients $r^2 > 0.99$. The deviation of the back-calculated concentrations of the calibration standards solutions from the true concentrations is in the range of ± 20%. Recoveries values were in the range of 71.3 to 118.2%, RSD ≤ 20%. The observed matrix effect was very low (-5.1), indicating that cleanup was efficient to remove interferences from the extract. The validated method was applied to 20 samples of yerba mate grown in the main producing cities in Rio Grande do Sul state. Dithiocarbamate residues was not found in any sample. This study for dithiocarbamates determination has a great importance, in order to guarantee that this processed product is safe for consumers.

Keywords: Dithiocarbamate; YERBA MATE (*Ilex paraguariensis*); GC-MS.

Acknowledgements: CAPES, CNPq, MAPA, MCTI and UFSM.

A-16

METABOLITE OF DITHIOCARBAMATE: METHOD DEVELOPMENT, VALIDATION AND SURVEY OF ETHYLENETHIOUREA IN POLISHED RICE.

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Dithiocarbamates (DTC) have been used for over 60 years. The toxicological importance of those fungicides in food is related to their metabolization to ethylenethiourea (ETU), known to altering thyroid function and has been suspected of causing certain toxicities. Rio Grande do Sul state is responsible for approximately 25% of total DTC sold in Brazil, and 98% is represented by mancozeb (is the third best-selling pesticide). Due to fast degradation in presence of moisture and/or oxygen, photolysis and low water solubility, DTC are among the most difficult organic contaminants to be determined. Given rice importance, the goals of the present study were to optimize and to validate an analytical method for ETU determination, and apply the validated method to determine ETU in 36 polished rice samples.

ETU sample analyses were based on a modified QuEChERS extraction. Firstly, 10 g of slurry rice:water (1:1) were prepared. After 10 mL of alkaline acetonitrile (1% NH₃.H₂O) were added and the tubes were placed into a mechanical shaker for 3 min at maximum speed. Thereafter, 1 g of NaCl and 4 g of MgSO₄ were added into the tube and energetically shaken for 30 s followed by 4 min centrifugation at 4000 rpm. To the cleanup step, 2 mL of the upper layer was transferred to a tube containing 50 mg of PSA + 150 mg of MgSO₄ and then vortex for 20 s. The same centrifugation step was conducted once more and 500 µL of the upper layer was diluted (1:1) with acetonitrile:water (85%) into an autosampler vial and analyzed by LC-MS/MS. Analyses were conducted using an OBELISC N (5 µm, 100A, 150 mm x 2.1 mm) HILIC column at a constant temperature of 35 °C. Mobile phases were water 5 mM ammonium formate (A) and acetonitrile 0.1% formic acid (B). The mobile phase was used in isocratic elution of 15% A at a constant flow rate of 0.35 mL min⁻¹. The injection volume was 5 µL, and run time was 5 min.

The linearity of the analytical curves, dynamic linear range, limits of detection (LOD) and quantification (LOQ), matrix effect (%), selectivity, precision (repeatability and intermediate precision) and trueness (recovery %) were evaluated. Linear dynamic range of ETU was from 1 to 250 ng mL⁻¹, which corresponds to a range of 4 to 1000 µg kg⁻¹. It was observed a matrix effect of -93% due to ionization suppression in the ESI source by the co-eluting matrix components. As consequence, ETU was quantified by matrix-matched calibration to compensate any losses in analytical signal. The recoveries were in the range of 78 to 91% and RSD_≤18.5%. The lowest concentration level that fulfilled all SANTE document requirements was 5 µg kg⁻¹, considered the method LOQ. The method met the SANTE validation criteria and presented reliable results for analysis of real samples. In none of the analyzed samples, ETU was detected. Since, rice is an extremely consumed food in Brazil and DTC are massively used, analysis of not only CS₂ but also ETU should be performed in order to guarantee food safety.

Keywords: Dithiocarbamate; Ethylenethiourea; LC-MS/MS.

A-17

APPLICATION OF GC-Q-EXACTIVE ORBITRAP TO THE ANALYSIS OF PARTS-PER-TRILLION OF PESTICIDE RESIDUES IN APPLE AND APPLE JUICES.

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The application of High-Resolution Mass Spectrometry (HRMS) to the analysis of pesticide residues in fruits and vegetables is gaining popularity. HRMS coupled to Gas Chromatography (GC) is being successfully applied due of its potentiality for target and non-targeted approaches¹. GC-Q-Exactive ORBITRAP is already competing with traditional triple quadrupole detectors for the multiresidue analysis in foodstuff because of its improved sensitivity and high selectivity. Fruits and juices are often consumed by children, a group of population very sensitive to the presence of pesticide residues in foodstuffs so methods of control with high sensitivity are demanded.

This study has developed a new analytical method based on the use of GC-Q-Exactive ORBITRAP for determining 262 pesticides residues in apple and apple juice samples being the first application of the above-mentioned instrumentation to the analysis of fruit juices. For that, a modified QuEChERS extraction method has been satisfactorily applied to both types of matrices. The mass spectrometer operated in full scan mode which will also allow for retrospective analysis. For confirmation of the compounds, NIST spectral library and exact mass were used maximizing the reliability of the qualitative and quantitative analysis and minimizing the risk of false positive and negative.

The proposed method was validated in both matrices according to SANTE document². Calibration curves were evaluated by triplicate between 0.5 and 100 µg/l for juices and 1 and 250 µg/kg for apple. Limit of quantification (LOQ) was 0.5 µg/l (apple juice) and 1 µg/kg (apple) for most of the compounds. Recovery was mostly between 70-120% and precision ≤20%. The proposed method was applied to the analysis of 82 fruits and 15 juices finding positive results in 24 of them. Most of the target compounds were below the Maximum Residue Limit (MRL) stated by the European Union except chlorpyrifos ethyl, chlorpyrifos methyl, ethoxyquin and metalaxyl in fruit samples and dieldrin, phthalimide, cis 1,2,3,6-tetra-hydrophthalimide and pyrimethanil in juice samples.

This method has demonstrated its sensitivity and reliability of the results obtained with GC-Q-Exactive ORBITRAP for the analysis of very low concentrations of pesticide residues in fruits and juices. In addition, the proposed methodology will allow for carrying out further investigations aimed at the identification of metabolites and/or transformation products through post-target and non-target analysis.

Keywords: GC-Q-Exactive ORBITRAP, multiresidue, pesticides, juice.

References: 1. Vargas-Pérez, M, Domínguez, I, Egea González, F J, Garrido Frenich, A. Application of full scan gas chromatography high resolution mass spectrometry data to quantify targeted-pesticide residues and to screen for additional substances of concern in fresh-food commodities, *Journal of Chromatography A* 1622 (2020) 461118.

2. European Commission, Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed. SANTE/11813/2017, (2017) 2–44.

A-18

MULTIRESIDUE METHOD FOR SIMULTANEOUS DETERMINATION OF TRIAZOLE COMPOUNDS AND THEIR METABOLITES IN FRUITS AND VEGETABLES BY ULTRA PERFORMANCE LIQUID CHROMATOGRAPHY-TANDEM MASS SPECTROMETRY.

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The triazole compounds are becoming the most important type of fungicides due to their exceptional antifungal activity, relatively low resistance risk and their long-term stability in soil and water. These compounds might be degraded to common metabolites, known as triazole derivative metabolites (TDMs): 1,2,4-triazole and 1,2,4-triazol 1-yl-acetic. However, these compounds might also come from other specific degradation routes.¹

Two extraction methods, depending on the matrix used, based on SLE and QuEChERS procedure have been developed for the determination of 21 triazole compounds and 5 metabolites, including TDMs as 1,2,4-triazole and 1,2,4-triazol 1-yl-acetic, in courgette, orange, grape and strawberry. The analysis was carried out by ultra high-performance liquid chromatography (UHPLC) coupled to mass spectrometry, using Q-Orbitrap as analyser, in just 10.5 min. The proposed method was validated according to SANTE 12682/2019 guidelines, achieving recoveries between 70 and 124%, and repetitive results (relative standard deviation, RSD) $\leq 20\%$. Limits of quantification (LOQ) were $\leq 10 \mu\text{g kg}^{-1}$ for most of the monitored compounds. This method can be used for the routine analysis of pesticides.

The developed and validated method was successfully applied to the analysis of 13 samples. More than 70% of these samples contained residues of triazole compounds. The fungicide most frequently found was myclobutanil, with concentrations ranging from 0.01 to 0.15 mg kg^{-1} , achieving the highest concentration (0.15 mg kg^{-1}) in a strawberry sample. Moreover, this compound exceeded the MRLs established by EU at 0.01 mg kg^{-1} and 0.15 mg kg^{-1} in grape and strawberry samples, respectively. Nevertheless, the majority of triazole compound levels were found at concentrations below the MRLs.

Furthermore, a suspect screening analysis was carried out to search possible pesticides present in the samples, and some of them were detected at concentrations higher than MRLs. For example, cyprodinil, whose MRL is 0.02 mg kg^{-1} in grape, was detected at 0.29 mg kg^{-1} in this matrix.

Keywords: Triazole, UHPLC-Q-Orbitrap-MS, QuEChERS, SLE.

References: 1.J. Li, Y. Wang, W. Li, P. Xu, B. Guo, J. Li, H. Wang, Tissue distribution and metabolism of triadimefon and triadimenol enantiomers in Chinese lizards (*Eremias argus*), *Ecotoxicol. Environ. Saf.* 142 (2017) 284–292. <https://doi.org/10.1016/j.ecoenv.2017.04.035>.

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A-19

INDIVIDUAL AND MULTIRESIDUAL DETERMINATION OF HERBICIDES IN BIOBEDS USING AN AGILENT 1260 INFINITY II PRIME LC ULTIVO TQ

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The agricultural growth production in Brazil and all over the world is possible due to several factors, including the use of pesticides applied to avoid losses in production. Due to the increased demand for food and, as a consequence, the use of pesticides, there is a rising concern about the proper disposal of pesticides waste. Therewith, from 1990 on biological beds started to be constructed, in order to reduce contamination due to accidental spills during the preparation of the spray solution as well as during sprayers washing process. The objective of the study was to develop and validate two methods for pesticides determination, a multiresidual composed of 6 herbicides and an individual one for the imidazolinones class herbicides in the biomixture that makes up the biobeds responsible for their degradation. For multiresidual method extraction, 5 g of biomixture were taken, 10 mL of MilliQ water and 10 mL of acetonitrile 1% acetic acid were added and vortexing for 30 sec followed by the addition of 4 g MgSO₄ and 1 g of NaAc. After stirring for 1 min centrifugation at 4000 rpm for 3 min was applied. Subsequently 2 mL of the extract was filtered through a 0.2 µm PTFE syringe filter. For imidazolinone herbicides extraction, 5 g of biomixture were taken followed by the addition of 10 mL of 0.5 mol L⁻¹ NaOH solution, 10 mL of acetonitrile, 4 g of MgSO₄ and 3 g NaCl, vortex for 1 min after each addition. Adjustment to pH 3 was done by adding concentrated HCl and formic acid / ammonium formate buffer. Centrifugation at 4000 rpm for 10 min. An amount of 2 mL of the extract was transferred to a tube containing 250 mg of MgSO₄ and 200 mg of C18. After centrifugation an aliquot was evaporated, resuspended and filtrated. Chromatographic analysis was performed by an Agilent 1260 Infinity II Prime LC Ultivo TQ. As a preliminary step, recovery studies (n=3) were carried out by adding those pesticides under study to blank biobed sample. In order to be validated both methods should meet the requirements for recovery (between 70 and 120% and the RSD ≤ 20%). Thus, the method referring to the imidazolinone group, presented satisfactory results for all concentration levels 20, 50 and 100 µg kg⁻¹ resulting in LOD of 2.5 µg kg⁻¹ and LOQ of 20 µg kg⁻¹. For the multiresidual method all spiked levels 20, 50, 100 and 150 µg kg⁻¹ met requirements of recovery study, and LOD and LOQ values were set as 2 and 20 µg kg⁻¹, respectively. The linear range of the multiresidue method, for all compounds, is 25 - 500 µg kg⁻¹. Although biomixture is a very complex matrix composed of soil, straw and peat, which is why there may be the extraction of many interferences, satisfactory results were obtained for all compounds when applying that developed and validated extraction methods. In this way, it is possible to monitor the effectiveness of herbicides degradation into biobeds systems.

Keywords: biobeds, herbicides, imidazolinones, LC-MS/MS.

Acknowledgements: AGILENT, EMBRAPA, CAPES, CNPq, MAPA, MCTI and UFSM.

A-20

A RAPID, SIMPLE, AND EFFICIENT AUTOMATED METHOD FOR THE EXTRACTION OF PESTICIDES FROM DIFFICULT FOOD MATRICES

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In the modern world, consumers increasingly want to know what is in their food and that the substances they are putting in their body are safe. This, along with stringent regulatory requirements, is leading the call for improved extraction of food contaminants such as pesticides. The QuEChERS method has been shown to be practical for pesticide analysis on a number of different sample types. While the QuEChERS method is relatively quick compared to other methods, it is also a manual and tedious process. Herein, a rapid, simple and efficient automated method for the extraction of difficult food matrices that improves the pesticide extraction process is being reviewed. The extraction of avocados and cranberries is performed via extraction on the EDGE and compared to the QuEChERS method. The EDGE method utilizes the same solvent and clean up sorbents as the QuEChERS method, making it a simple transition for labs currently running QuEChERS.

The EDGE extraction allows for extraction, cleanup, and filtration in less than ten minutes. Filtration sub 0.3 μm is possible on the EDGE allowing for direct injection of the extract for UPLC analysis. In this study extraction of avocado and cranberries was the focus, however; the EDGE extraction method is applicable to many different types of difficult matrices such as tea and spices. No matter the matrix on the EDGE the same rapid, simple and efficient automated method is sufficient leading to good pesticide recovery data. The extraction and determination of multiple pesticide residues from these difficult matrices will be described showing improved recoveries and workflow in comparison to QuEChERS.

Keywords: Extraction, Automation, QuEChERS.

A-21

MULTIRESIDUE ANALYSIS METHOD FOR QUANTIFICATION OF PESTICIDES IN FRUITS, VEGETABLES, CEREALS AND BLACK TEA USING UPLC-MS/MS.

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Pesticide residue analysis is a critical part of any monitoring program to check MRL compliance in raw food commodities but also for residues in ingredients and finished foodstuffs. These analyses still present many challenges to testing laboratories, from sample processing, extraction and choices of cleanup and determination steps, through to data analysis, review, interpretation and reporting of results.

In this poster, we evaluate the performance of a large scope LC-MS/MS multiresidue method for the analysis of a number of samples, representative of the varieties types of commodity; high-water content (spinach), high acid and high-water content (strawberry), high oil and very low water content (soybean), high protein and low water and fat content (wheat) and difficult or unique commodities (black tea). Samples were extracted using QuEChERS CEN methodology, diluted and analyzed by LC-MS/MS. A targeted, time-windowed MRM method, containing 552 pesticides and relevant metabolites, was created from the Quanpedia database.

The performance of the LC-MS/MS method was assessed using the relevant guidelines from SANTE/12682/2019 focusing on pesticides in the current coordinated multiannual control programme of the EU. Blank extracts were spiked with a mixture of representative 256 pesticides at 0.005, 0.01 and 0.05 mg/kg. The method was found to yield excellent retention and peak shape for all analytes, even for early elutors using a post injector mixing kit. Despite the complexity of the various matrices, the LOD for the majority of the 256 compounds tested was 0.005 mg/kg; >90% for spinach, strawberry and soybean, 83% for tea and 79% for wheat.

A-22

THYMOL RESIDUES EVALUATION IN ADULT HONEY BEES, BROOD AND INSIDE THE BEEHIVE BY HIGH RESOLUTION MASS SPECTROMETRY

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Honey bee is an essential plant pollinator playing an indispensable role in agricultural production. Nowadays, the focus is on research about the decrease of honey bee population, attributed to various causes, being the parasitic mite *Varroa destructor* a major threat to the honey bee. Thymol has been considered as an organic varroacide with less toxicity than synthetic chemicals as amitraz, coumaphos or tau-fluvalinate. The present study evaluates the presence, persistence and distribution of thymol during five-month sampling period; before, during and after the application of thymol treatment in field conditions. Moreover, its impact on the development of bee brood was also studied at different development stages which consist on larvae, prepupae, pupae and adult honeybee. Samples of beebread (processed pollen), honey, beeswax, adult bee, pupae, prepupae and larvae were analysed by gas chromatography coupled to time of flight mass spectrometry (GC-QTOF-MS) for an accurate identification. Adult bees where the samples with the highest concentration level of thymol during treatment application (Thymovar® strips, 30 gr of thymol per hive) by the beekeeper, however they showed 69% of thymol dissipation three month after treatment. Regarding the bee brood, concentrations of thymol decreased significantly (89-97% of disappearance) in a period of three months, though about 42 µg/kg of thymol persisted in larvae. Thymol was found to accumulate in honey and beeswax at level of 882 µg/kg and 1305 µg/kg, respectively, in the studied period. These data suggest that thymol treatment, using waxes not treated with thymol in previous years, represents no risk for adult and developing bees, since the residues levels found in this study, during and after the treatment, are far from the LC50 reported for bee and larvae. Moreover, the status of the bee colonies, considering the population of adult and brood bees, and the reserves of beebread and honey, followed a similar evolution in the group of treated colonies and in the group of control colonies, so it was not detected a negative effect due to the treatment. However, the main issue of using thymol as varroacide is the residues in honey, which can affect its organoleptic quality. In the present study, it has been shown that thymol accumulates in honey in field conditions. The concentration of thymol found during and after the treatment are above the tolerance value of 800 µg/kg, and very close to the taste threshold of 1100 µg/kg during the treatment application. These values indicate that the taste of the honey may be changed.

Keywords: GC-TOF-MS, thymol residues, natural acaricides, honey-wax-pollen-bee-brood system.

A-23

BROWN RICE: VALIDATION AND PESTICIDE SURVEY

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Nowadays, the growing concern about a healthier diet has made brown rice a preference against polished rice, in some households, because of its higher amount of fiber, vitamins and minerals, which are mainly found in its outer layer, known as bran. Both crops and rice grains can be affected by pests and fungal diseases; which can cause economic losses, making pesticide application necessary for their control. Pesticides represent a problem for food consumers, due to their accumulation in them. For these reasons, the objectives are to validate an analytical methodology for trace levels determination of deltamethrin, kresoxim methyl, cyproconazole, epoxiconazole and azoxystrobin in brown rice; and to determine its presence in 20 commercial samples. The extractive method used was QuEChERS; analytes were determined by gas chromatography with a μ ECD detector; and confirmed by mass spectrometry. Matrix-matched calibration was performed due to the existence of a matrix effect. The calibration curve was linear in the range of 0.005 to 1.5 ppm. The linearity of the method presented a correlation coefficient R^2 greater than 0.9996, for all pesticides. Precision was evaluated at 3 concentration levels, with a relative standard deviation (RSD) lower than 10% for $n = 9$. Recovery was studied at 3 concentrations in triplicate, with results between 80% and 102%, in all cases. The detection and quantification limits were 0.28 and 0.88 $\mu\text{g} / \text{kg}$, 0.25 and 0.77 $\mu\text{g} / \text{kg}$, 0.28 and 0.90 $\mu\text{g} / \text{kg}$, 0.25 and 0.75 $\mu\text{g} / \text{kg}$, 0.29 and 0.92 $\mu\text{g} / \text{kg}$, for deltamethrin, kresoxim methyl, cyproconazole, epoxiconazole, and azoxystrobin, respectively. The expanded uncertainty was lower than 20%. After validation, 20 brown rice samples, purchased from different stores, were analyzed. The results indicated that the studied pesticides were detected in all the analyzed samples. The maximum concentrations were 31.70 $\mu\text{g} / \text{kg}$, 34.01 $\mu\text{g} / \text{kg}$, 21.58 $\mu\text{g} / \text{kg}$, 163.65 $\mu\text{g} / \text{kg}$ and 33.91 $\mu\text{g} / \text{kg}$, for deltamethrin, kresoxim methyl, cyproconazole, epoxiconazole and azoxystrobin, respectively. The Maximum Residue Limits (MRLs) established by the European Union were exceeded for epoxiconazole and kresoxim methyl in 1 and 12 samples, respectively; while 19 samples exceeded the MRL established by SENASA for epoxiconazole. In conclusion, the validated analytical methodology is selective and sensitive, with adequate precision, accuracy and uncertainty, with detection and quantification limits lower than the MRLs established by national and international legislations, allowing the determination of deltamethrin, kresoxim methyl, cyproconazole, epoxiconazole and azoxystrobin in brown rice.

Keywords: Brown rice – Pesticides – Survey – Validation.

A-24

VALIDATION OF MULTI RESIDUE METHOD OF PESTICIDES IN PASSION FRUIT (PEDULIS) USING LC-MS/MS AND GC-MS/MS AND ANALYSIS OF FRUITS AND COMMERCIAL PRODUCTS

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Brazil is the world's largest producer and consumer of passion fruit, mainly *Passiflora edulis*, popularly known as yellow or sour passion fruit. Juice is the main industrial product, but the use of peel as a functional food has been explored. This study aimed to validate multiresidue methods for the determination of 80 pesticides in passion fruit peel and pulp by LC-MS/MS and GC-MS/MS and to analyze samples of passion fruit and industrial products. A total of 55 samples of passion fruit were obtained from producers in the states of Bahia, Rio de Janeiro, Goiás and the Federal District, and 30 samples of frozen pulp and 12 samples of passion fruit flour were purchased from the Federal District. The method was satisfactorily validated on both devices, with recoveries between 70% and 120% and the relative standard deviations (RSD) <20% for most compounds, with LOQ of 0.005 or 0.01 mg kg⁻¹. Approximately 27% of the 80 monitored analytes were detected, and of these 70% have no authorized use in Brazil for the cultivation of passion fruit. At least one analyte was detected in 60% of the bark samples analyzed, mainly imidacloprid, carbendazim and methamidophos, at maximum concentrations of 0.05, 0.07 and 0.1 mg kg⁻¹. Approximately 25% of the fruit pulp samples were positive for at least one pesticide. Of the pesticides detected with authorized use in passion fruit, none exceeded the MRL established for the crop. About 63% of commercial frozen pulp samples were positive, indicating possible contamination in the industrial process. Four samples of passion fruit flour contained pesticide residues, mainly methamidophos. The peel dehydration process increased initial residue levels by up to 15 times (imidacloprid). The estimated chronic and acute exposures did not indicate concern for Brazilian consumers' health, being higher for methamidophos (0.01% of IDA) and carbendazim (0.14% of ARfD) due to juice consumption and 1.3% of IDA and ARfD of methamidophos by consumption of flour. However, the illegal use of pesticides in the passion fruit cultivation indicates that farmers are not following good agricultural practices, probably because they do not have good technical assistance in the field.

Keywords: LC-MS/MS, GC-MS/MS, passion fruit, juice, passion fruit flour.

A-25

PESTICIDES RESIDUES REDUCTION FROM FISH DURING HOUSEHOLD COOKING

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Pesticide residues are distributed in the environment and become pollutants for biotic and abiotic systems, threatening their stability and representing a public health hazard^{1,2,3}. Fish are exposed to contaminants through direct contact with water or sediment, and by other already contaminated organisms' intake. The objectives of this work were an analytical methodology validation for the simultaneous organochlorine pesticides determination in fish muscle, and the study of the cooking effect on their initial content. The analytes extraction was carried out by QuEChERS (Quick Easy Cheap Effective Rugged Safe) methodology, and they were determined by gas chromatography with a micro electron capture detector (GC- μ ECD). The results were confirmed by a gas chromatograph coupled with a mass spectrometer (GC-MS). The methodology validation was carried out following the SANTE Guide recommendations⁴. The matrix added calibration curve was linear in the range of 0.001 to 0.5 mg/l, with regression coefficients R^2 greater than 0.99. Precision was evaluated at three levels, 0.001; 0.05 and 0.5 mg/l, with a relative standard deviation (RSD) lower than 10 % (n=5). Recovery was studied at the same concentrations (n=3), with values between 88 and 110%. The expanded uncertainty estimation was performed, being less than 20% in all cases. Then, the household cooking effect on the initial pesticides concentration in fish was evaluated. The study was performed with an electric oven, in triplicate. A thermocouple was used in order to verify that the temperature at the thermal center of the samples were 71 °C. After cooking the fish samples, the concentration of each compound was determined. The thermal destruction percentage during the cooking process was 55.5; 50.4; 44.0; 37.6; 32.6; 52.2; 44.1 and 63.7% for transchlordane, endrin, endosulfan, dieldrin, heptachlor epoxy A; cis-chlordane; lindane and heptachlor epoxide B, respectively. No reduction was observed for aldrin and DDD. The statistical analysis of the results indicated that the method is linear, and has high sensitivity, accuracy and precision, being useful for the determination of organochlorine compounds in fish muscle. It can be concluded that cooking at 71 °C in the thermal center ensures the partial elimination of the analytes studied, with the exception of aldrin and DDD. It is considered relevant to continue the research in order to evaluate the effect that other cooking conditions will have, allowing optimization of the results.

Keywords: Organochlorine pesticides; Fish; Household cooking process; GC-MS.

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PESTICIDES RESIDUES DETERMINATION IN COMMON BEAN USING QUECHERS APPROACH AND GC-MS/MS ANALYSIS

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Common bean (*Phaseolus vulgaris* L.) is an important legume worldwide. It is a staple food in Latin America (especially in Brazil) and Africa accounting for approximately 50% and 25% of the world's consumption in volume, respectively. Common bean is rich in high-quality protein, carbohydrates, fiber and micronutrients¹. Although common bean importance worldwide, studies on contamination of this commodity with pesticides are rarely reported in literature. So, the goals of this study were to optimize and validate a multiresidue method and apply it in monitoring of pesticides in common beans. Extraction was performed applying QuEChERS approach to ground samples. In the extraction approach optimization study, C18 alone and a combination of C18 with PSA were evaluated for clean-up of the common bean acetonitrile extracts. Direct injection of the final acetonitrile extracts into the GC-MS/MS system or injection only after a solvent exchange step for isooctane/toluene (9:1, v/v) were also evaluated. The best performance has been achieved using the combination of C18 and PSA for clean-up followed by the solvent exchange step before GC-MS/MS analysis. Method validation was done analyzing blank common bean samples spiked at 20, 30, 50 and 100 $\mu\text{g kg}^{-1}$ with 5 replicates at each level ($n=5$). Linearity and linear range were assessed by the analysis of standard solutions at concentrations of 5, 15, 25, 50, 75, 100 and 150 $\mu\text{g L}^{-1}$ prepared in blank matrix extract and in organic solvent. Considering the analytical curves in matrix extract, from the 142 compounds studied, 53.5% presented an $r^2 > 0.990$, 43.7% had an r^2 within the range of 0.960 to 0.989, and 2.8% compounds were not detected at any concentration. The method was successfully validated for 91 (64.1%) of the 142 compounds studied (139 pesticides and 3 degradation products). Some of these pesticides can occur in the samples by legal application to the crops and others by illegal application. LOQs were equal to 20, 30, 50 and 100 $\mu\text{g kg}^{-1}$ for 18 (12.7%), 17 (12.0%), 21 (14.8%) and 35 (24.6%) compounds, respectively. Fifteen (10.6%) compounds were not detected at any level and 36 (25.4%) did not fulfill requirements for quantitative method. Matrix effects were higher than 20% for 78.9% of the compounds, for this reason quantification had to be done with matrix-matched standards. Sixteen common bean samples of southern Brazil were analyzed. Two samples were positive, one for tebuconazole and a second for picoxystrobin, permethrin and cyproconazole. Cyproconazole is not allowed for the crop, consisting of a violation. Then as demonstrated the validated approach is suitable for pesticide residues determination in common bean. Results of the sample analysis showed that the control of pesticide residues in common bean is necessary to ensure food safety.

Keywords: *Phaseolus vulgaris* L.; pesticides; LC-MS/MS;

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A-27

PESTICIDE RESIDUE ANALYSIS IN DRIED SAMPLES BY QUECHERS AND LC-HRMS (ORBITRAP™)

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The determination of pesticide residue in dried samples is considered to be a complex task due to low water content, high starch and/or protein levels. The QuEChERS method has been widely used in pesticide residue analysis, although it was originally developed for samples with more than 75% moisture and non-fatty matrices^{1,2}. This work aimed to develop and implement an analytical method for pesticide residue determination in dried samples (e.g. wheat flour and oat) by QuEChERS extraction (AOAC method³ with modifications¹) and Ultra-High Liquid Chromatography coupled to Exactive Plus Orbitrap™ High Resolution Mass Spectrometry (UHPLC-HRMS) for screening and quantification.

Chromatographic separation was performed on a Dionex UltiMate 3000 UHPLC, with a Thermo Scientific Hypersil Gold aQ (50 x 2.1mm, 1.9µm) column at 40°C, 2µL sample injection, using eluents: aqueous and methanolic solutions, both with 5mM ammonium formate and 0.1% (v/v) formic acid in a gradient program, at a flow of 0.3mL.min⁻¹. The identification and quantification were done by HRMS with HESI. The data acquisition was achieved using positive and negative modes in Full MS and All Ion Fragmentation (AIF) with 35k and 17.5k resolution, respectively. The quantitative analysis identified targeted compounds by retention time (RT) obtained from extracted ion chromatograms using a 5ppm mass accuracy for the mono-isotopic mass and at least one isotopic peak. The method was suitable and highly sensitive for 58 compounds in wheat flour and 65 in oat, at levels ranging from 0.008 to 0.060mg kg⁻¹. The LOD and LOQ were 0.005 and 0.010mg kg⁻¹, respectively and blank samples showed no interference in the studied compounds (matrix effect). The recovery test results (N = 5) at three different levels were 53-135% for wheat flour and 76-104% for oat with RSD lower than 20% for both matrices. These results comply with criteria established by the European Community⁴.

The methodology contributes to data acquisition in pesticide residue monitoring programs and ensuring food safety for public health. It is a simple, quick and inexpensive extraction technique that uses less solvent and is quite efficient in pesticide residues analysis. The UHPLC-HRMS has been proved a good screening and quantification tool. It allows evaluating compounds based on mass accuracy, fragmentation and comparison of RT with reference materials or prediction even when they are not available. The Full Scan and AIF acquisition modes enable a simultaneous determination of a large number of substances from different classes and low concentration levels in foodstuff, including non-target screening workflows. Thus, this study showed an analytical method with reliability, high selectivity and efficiency in only 12 minutes. The UHPLC coupled with Orbitrap™ HRMS has not been described in the literature for pesticide residue analysis in dried samples.

Keywords: Pesticide residue, wheat flour, oat, Orbitrap

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A-28

HOMOGENEITY AND SHORT-TERM STABILITY ASSESSMENT OF A CANDIDATE REFERENCE MATERIAL OF PESTICIDE RESIDUES IN FREEZE-DRIED AVOCADO (PERSEA AMERICANA VAR. HASS) USING QUECHERS BASED METHOD AND LC-MS/MS

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In general, with the purpose to ensure sustainability and increase the productivity of crops that have high commercialization potential, such as avocado, both in local and international markets, an adequate phytosanitary management and the extensive use of pesticides are necessary. However, these can represent a risk to human health and the environment, and in this sense their monitoring is critical to ensure compliance with the requirements in terms of maximum pesticide residues. In this sense, chemical analysis laboratories should have available tools for the validation of their methods, as well as for the assurance and quality control of the results. As an alternative, there is the use of Reference Materials (RM), which must be sufficiently homogeneous and stable, to be considered suitable for their intended use in a measurement process. However, the offer of these in different combinations of matrices and analytes is limited. Consequently, the objective of this work was to evaluate the homogeneity and stability of a candidate for pesticide reference material in freeze-dried avocado using a previously validated measurement method.

Considering the above, a candidate reference material of pesticides in avocado was prepared based according to ISO 17034 standard. To obtain de RM, the avocados were homogenized and spiked with 22 analytes of different chemical groups, after that the later the material was freeze-dried, sieved and packaged; 50 units were produced with a net content of 25 g. Homogeneity was assessed using a completely randomized block design. On the other hand, the stability was evaluated by means of an isochronous study at 4 °C for 45 days, with -80 °C as the reference temperature. To carry out these evaluations, a method based on QuEChERS extraction and instrumental measurement by LC-MS/MS with gravimetric preparation was validated, in the parameters of selectivity, linearity, repeatability and bias as recovery at two concentration levels.

Regarding the attributes of the validated measurement method, these were shown to be fit for the intended purpose. With respect to the evaluation of homogeneity, uncertainties due to this between 0.2 % and 3.3 % were obtained for the majority of the evaluated compounds, except for thiamethoxam whose uncertainty was 6.3 %. Further, only propamocarb and abamectin showed a significant trend ($p < 0.05$) for packaging. On the other hand, in the stability study, with some exceptions, there were no significant regressions for the kinetics of order 0, 1 and 2 ($p < 0.05$), with uncertainties for stability of 1.0%-9.0%. In conclusion, the candidate for reference material presented uncertainties lower than the previously established target uncertainty, so it can potentially be used as a tool in quality assurance of test results or in interlaboratory comparison exercises.

Keywords: Reference material, pesticide residue analysis, homogeneity study, stability study.

A-29

VALIDATION OF AN ANALYTICAL METHOD FOR THE DETERMINATION OF PESTICIDES IN CANNABIS

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The recent regulation and legalization of medicinal cannabis in Colombia create challenges and new opportunities. Testing laboratories need a reliable way to ensure quality, validate safety, and mitigate potential risks from toxic materials present in cannabis and its derived products. The levels of pesticides present in cannabis samples are considered low and non-threatening for human consumption, it is necessary to have adequate analytical instrumentation to quantify these compounds and comply with normative and regulatory requirements¹. Gas chromatography and mass spectrometer are chosen for the analysis of pesticides in cannabis. The validation of analytical methods allows demonstrating that it is adequate for its intended use^{2, 3}

This is why AOXLAB developed and validated a method for the quantification of pesticides in cannabis was carried out in a gas chromatograph coupled to Shimadzu® GCMS-TQ8050NX mass spectrometry with AOC 6000 autosampler. Helium UAP was used as entrainment gas at a flow of 1 mL/min and an SH-Rxi column. -5ms (30 m × 0.25 mm × 0.25 µm). The gradient oven temperature was 70 °C for 2 minutes, 19 °C / min to 170 °C, then 3 °C / min to 210 °C, followed by 8 °C / min to 300 °C. Injection port, ion source, and interface temperatures: 250 °C, 230 °C, 250 °C, respectively. Splitless injection mode. Injection volume: 1.0 µL. The mass selective detector was operated in the electron ionization mode, with an ionization potential of 70 eV. Data acquisition was performed by MRM, surveying two characteristic transitions of each compound. The relative retention time, the analysis of the database, and the retention rates were the identification criteria⁴. Sample preparation: 2 g sample is extracted with 10 mL water/acetonitrile: acetic acid 1% (1/1 v/v) by mechanical shaking for 30 min, followed by 30 min centrifugation. MgSO₄/ NaCl (4/1 p/p) are added, followed by 6 min centrifugation. 1 mL of the extract obtained is taken into sorbent mixture and used for GCMS analysis. The validation of the method included: selectivity, linearity, precision, accuracy, linear range of quantification and limits of detection and quantification. Due to the nature of the samples, the extraction of the components was carried out with acetonitrile and QuEChERS salts, followed by cleanup.

The analysis of 191 pesticides was carried out by comparing the chromatograms obtained from the samples and the signals of the standards and the data of areas and retention times were extracted, coefficients of variation were <5%. The results of detection limits estimated by the signal-to-noise ratio complied with the precision and specificity parameters. In this study, cannabis samples were analyzed for 4 different matrices, plant material, cannabis extracts, crystals, and oral solutions. Plant material samples from 5 different areas of Colombia were analyzed. It was found that they comply with current regulations under the guidelines of the European Pharmacopoeia.

The analytical method evaluated and validated in this work is a tool for the quality control of cannabis plant material, cannabis extracts, crystals of cannabidiol (CBD), and oral solutions with CBD content, for their subsequent use or export.

Keywords: pesticides, cannabis, gas chromatography, mass spectrometry.

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A-30

PROCESSED ORGANIC FOODS: ARE THEY FREE FROM PESTICIDE RESIDUE?

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Organic farming is being propagated worldwide due to growing concern for food safety and its direct bearing on human health. The purchase of organic products is linked to sustainable, conscious consumption and green consumption. The presence of pesticide residues in food has caused a great concern among the consumers and food processing treatments such as washing, peeling, canning or cooking lead to a significant reduction of pesticide residues. But what about the processed organic foods that are currently being offered in the supermarket, are they free from pesticide residue? In this background, we evaluated 45 samples of organic processed foods including breakfast cereal, sugar, wheat flour, cookie, pasta, olive oil, juice, coffee, chocolate, and chocolate powder, and spice, collected from June to December 2020 in markets in São Paulo city, Brazil. The QuEChERS sample preparation method was used to determine the presence, or not, of 235 pesticides using GC-MS/MS and LC-MS/MS for all matrices (except for oil olive which utilized S19 method). Five samples showed pirimiphos-methyl residue, one pasta sample, with 0.01 mg/kg, and four breakfast cereal samples with 0.03; 0.04; 0.10; and 0.15 mg/kg each one. The concentrations were below the MRL for wheat (5 mg/kg for stored products for pirimiphos-methyl) remembering that all of these products are made up by the organic content multi-ingredient and because of that, the care in choosing of the raw products for processed food must be meticulous. Pirimiphos-methyl is not included in Annex VII of the Instrução Normativa nº 17 (1) and therefore not allowed in organic farming. Even though of being properly grown and processed, organic foods can often not be entirely free of pesticides and other synthetic chemicals used in conventional farming. These contaminations could be due to cultivation on previously contaminated soil, percolation of chemicals through the soil, cross-contamination with wind drift, cross-contamination due to silos spraying, spray drift from neighboring conventional farms, contaminated groundwater or irrigation water, or even can occur during processing, storage, and transport. The presence of synthetic chemicals, however, does not necessarily preclude that the food can be described as organic, providing all requirements related to the production process have been satisfied. We highlight the need to monitor processed organic samples sold in supermarkets to increase consumer confidence, and the fact that Brazilian processing companies still face difficulties in finding organic primary ingredients, due to the fact that organic production is still carried out on a smaller scale, mainly by family production.

Keywords: GC-MS/MS; LC/MS/MS; QuEChERS

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A-31

A COMPARISON OF IC-MS/MS AND LC-MS/MS TECHNIQUES FOR THE MULTI-RESIDUE ANALYSIS OF POLAR PESTICIDES AND METABOLITES IN FOOD

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One of the most challenging groups of pesticides are the polar pesticides, such as glyphosate, perchlorate, chlorate, and the like, which often occur as residues in food, but are not always included in pesticide monitoring programs. Several analytical methods are detailed in the EURL-SRM-QuPPE method- "Quick Method(s) for the Analysis of Numerous Highly Polar Pesticides in Food Involving Extraction with Acidified Methanol and LC-MS/MS". Polar anionic pesticides are commonly retained and separated using a hydrophilic interaction liquid chromatography (HILIC) column that provides strong retention of polar pesticides that are unretained under conventional reversed phase conditions. Another common approach is to use porous graphitic carbon (PGC, or Hypercarb™), which has unique properties as a stationary phase to retain polar analytes. Finally, IC-MS/MS based workflows have been implemented recently in many labs to achieve excellent sensitivity and reliable determination of multi-residue polar anionic pesticides and metabolites at low µg/kg levels in a single run.

In this study, a modified Quick Polar Pesticide (QuPPE) extraction procedure using a cartridge solid phase clean-up is evaluated for applicability to a wide range of matrices, including leek, fruit-based baby food, turmeric powder, and ginseng. The prepared matrix extracted spikes (MES) are injected onto a) LC-MS/MS equipped with a HILIC column b) LC-MS/MS equipped with a porous graphite Hypercarb column, and c) IC-MS/MS system equipped with an anion exchange column and suppressed conductivity. Data will be compared across the three detection methods, and evaluated for compliance to SANTE guidelines and EU MRLs. Absolute recovery, precision, and retention time stability for spiked samples at 10 and 50 ng/g will be summarized with advantages and disadvantages summarized for each technique.

Key Words: Polar pesticides, IC-MS/MS, LC-MS/MS.

A-32

FAST ANALYSIS OF MULTI-CLASS PESTICIDES PANEL IN GARLIC AND CUMIN EXTRACTS USING A SINGLE RUN LC-HIGH RESOLUTION MASS SPECTROMETRY

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Increasing food safety concerns and the growing agricultural trade has resulted in stringent pesticide regulations globally. To comply with such regulatory standards, screening methods for multi-class of pesticides is becoming important. Using liquid chromatography coupled high resolution mass spectrometry offers highly sensitive, specific, and selective detection in complex matrices for analysis of multi-class pesticides in food samples (garlic and cumin).

An Accucore aQ column was utilized for the separation of all analytes within 15 minutes. Garlic and cumin were extracted with organic solvent using a simplified QuEChERS method and no dSPE clean up. A 1 μ L of sample was injected with a ultra-high pressure liquid chromatography (UHPLC) coupled to a compact high field Orbitrap mass spectrometer. A multi-residue method was developed for quantitation and screening of unknown contaminations in a 15-minute run. Precursor exact mass extracted at 5ppm plus accuracy of retention time to ± 0.1 min and fragmentation matching to show robustness of the method which are required for the EU SANTE Guidance 12682_2019. All pesticides analyzed show excellent Limits of Quantitation and Detection between 0.5 to 10ppb, while reproducibility (injection = 8 per level) showed excellent precision and linearity with $R^2 \geq 0.9800$. Pre-spiked (MES) samples showed good %Rec between 1ppb and 5ppb between 70-120% which is within the SANTE Guidance. Unknown samples of garlic and cumin were also screened for other possible contaminates. Furthermore, the method was developed using software with built-in workflows for streamlining method development and routine analysis.

A-33

MULTIPLE RESPONSE OPTIMIZATION OF A QUECHERS EXTRACTION AND HPLC ANALYSIS OF COCCIDIOSTATS COMPOUNDS IN CHICKEN LIVER

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Coccidiostats are veterinary compounds used for the treatment and prevention of coccidiosis, which threaten poultry farming. These compounds can persist in animal tissues after slaughter and therefore can enter the consumer's organism¹. In the present work, a multi-residue extraction method based on QuEChERS (quick, easy, cheap, effective, rugged and safe) and a high-performance liquid chromatography method with diode array and fluorescence detection were developed for the simultaneous determination of four coccidiostats, toltrazuril, decoquinate, ethopabate and robenidine, at ppb level in chicken liver.

The QuEChERS extraction was optimized using an experimental design approach that includes a screening step to obtain the critical variables, an optimization step using multiple response surface analysis and the calculation of a desirability parameter. In addition, the optimized method was compared with other three reported extractions: non-optimized QuEChERS (a), Solid-Liquid (S-L) (b) and Solid Phase extraction (SPE) (c) which have been used to extract coccidiostats from chicken tissues, according to literature. All procedures were ranked using the Eco-scale rating system to quantify their environmental impact, based on energy and hazardous solvents consumed and waste generated.

The optimized method was validated with fortified samples, reaching an average recovery of 80%. This average extraction yield was higher than those achieved by the other methods evaluated: 70, 30 and 70 % for non-optimized QuEChERS, S-L and SPE respectively. In addition, the Eco-Scale results show the optimized QuEChERS, with a value of 84 points, as an ecofriendly method compared to values <79 points for the remaining extraction methodologies. On the other hand, the chromatographic method provided limits of detection (LOD) between 21 and 46 µg/kg, which are lower than the maximum residue limit (MRL) required for these coccidiostats in chicken tissues.

Using the optimized QuEChERS extraction, analyte recovery was significantly improved compared to other previously published techniques. On the other hand, in comparison with different extraction techniques, higher Eco-scale values were obtained. The analytical figures of merit, and the fact that four coccidiostats can be extracted by a simple technique and analyzed simultaneously by HPLC, prove that this method is suitable to be used in the routine analysis of poultry liver samples.

Keywords: QuEChERS, coccidiostats, Design of experiments.

References: 1. Silva, J. et. al. Multiple response optimization of a QuEChERS extraction and HPLC analysis of diclazuril, nicarbazin and lasalocid in chicken liver, *Food Chemistry* 311 (2020) 126014.

A-34

DEVELOPING A ROBUST LC-MS/MS METHOD FOR THE DETERMINATION OF ANIONIC POLAR PESTICIDES IN A RANGE OF FOODSTUFFS WITHOUT DERIVATIZATION

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Interest in the determination of highly polar, anionic pesticides in foodstuffs has increased noticeably in the last 5 years, this is the result of concerns regarding the potential safety of glyphosate. As a consequence of this the demand for surveillance has increased. Due to the physiochemical properties of highly polar, anionic compounds such as glyphosate and ethephon, standard analytical methods using reversed phase chemistries such as C18 are not applicable, due to insufficient retention. Alternative approaches to allow for the direct analysis of highly polar, anionic pesticides in food commodities have been sought by many pesticide residue laboratories for years. A number of developments have been made recently, which can provide improvements in chromatographic retention and separation and avoid the need for a number of different single-residue methods using different chromatographic conditions and avoiding derivatization or ion-pairing.

This poster highlights a modern, alternative chromatographic approach, which provides excellent retention, separation and detection for a range of polar anionic pesticides, using the Torus DEA chemistry on a standard UPLC-MS/MS platform and discusses key steps taken to ensure robust and reliable LC-MS/MS methods were developed. [1] With a desire to maximize efficiencies and ability to extract multiple polar analytes using a single method, this approach looks at extending the analytical scope from the traditional glyphosate, glufosinate and AMPA target list. In developing these methods, consideration was given to the main renowned challenges:

1. **Retention:** Highly polar, low molecular weight compounds can create challenges for reversed phase C 18 columns. Good analytical practice calls for all analytes to elute after the column 's void volume.
2. **Separation:** Focussing on an extended scope of analytes, including metabolites, increases the importance for baseline chromatographic separation, to avoid false detections of incurred residues.
3. **Matrix complexity:** Applying generic analyte extraction methods, crude food extracts are typically generated, which can cause increased matrix load on the LC-MS/MS system, resulting in unwanted matrix effects.
4. **Detection:** Required limits of detection vary depending on food commodity, compound and defined residue definition (eg: compound specific or summed MRL), where reliable detection should be achievable routinely and within accepted guidelines for good analytical practices.

A-35

ADVANCES IN HILIC CHROMATOGRAPHY APPLIED TO THE DETERMINATION OF HIGHLY POLAR PESTICIDES IN FOOD AND FEED

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Hydrophilic interaction liquid chromatography (HILIC) is an alternative LC mode for separation of polar compounds. In the recent years, HILIC has been recognized as an important solution for the analysis of compounds not amenable to reverse phase chromatography. The highly anionic polar herbicide glyphosate and related compounds such as glufosinate, ethephon and fosetyl present some characteristics that makes their determination very difficult when reversed phase chromatography is applied due to the lack of retention of these compounds in this mode. HILIC appears in this context as a useful tool to solve those issues. In this work, the performance of several HILIC columns, namely Obelisc N (Sielc), APP (Waters), PolarX (Restek), HILIC-Z and Poroshell 120 CS-C18 (Agilent), were evaluated for the application on 14 highly polar anionic pesticides determination in several food and feed matrices. Obelisc N presented the best results in terms of scope, as it is able to analyze all the 14 target compounds for the most of the matrices. However, LOQs were unfavorable for the most challenging matrices such as animal origin (liver and kidney) and feed (dry parsley powder, dry garlic powder and soya cake/meal) for glyphosate and HEPA. The APP column presented good results regarding LOQs as it is able to determine most of the compounds down to 0.02 mg kg^{-1} . On the other hand, this column is not able to determine compounds such as bromide, chlorate, perchlorate and N-acetyl-glyphosate, in our conditions. HILIC-Z presented some selectivity and peak splitting issues, as well as lack of retention for the majority of the compounds. PolarX and Poroshell 120 CS-C18 were evaluated only for the feed, the most challenging matrices. PolarX presented good results, except for N-acetyl-glyphosate, which could not be eluted within acceptable time. For the other compounds, low LOQs (0.02 mg kg^{-1}) were achieved for most of the compounds, for all matrices. Poroshell 120 CS-C18 presented good retention for most of the compounds. However, high suppression was observed for compounds like HEPA, MPPA, N-acetyl-AMPA and phosphonic acid when these compounds are measured in matrix.

Monitoring

M-01

PASSIVE BIOMONITORING OF LA BRAVA LAGOON (ARGENTINA) USING THE FISH OLIGOSARCUS JENYNSII

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La Brava lagoon is a site protected by the Agency for Sustainable Development (OPDS) in Argentina. Despite of this status it is surrounded by extensive agriculture. The aim of this study was to evaluate the influence of agriculture by means of the effect of oxidative stress in *O. jenynsii*, a fish species representative of this ecosystem. Two samplings were carried out during one year; one in spring (2019), when the application of agrochemicals has just started, and another in summer (2020), during the maximum application of chemical compounds. Twenty fish and surface water samples (n=3) were taken in each sampling. The fish were measured and weighted, also, the liver of each organism was weighed, in order to obtain the condition index (K) and the hepatosomatic index (HIS). The activities of the enzymes Catalase (CAT) and Glutathione S transferase (GST) were measured, as well as the levels of Malondialdehyde (MDA) in liver, gill and brain, all spectrophotometrically. Water samples were analyzed by UPLC-MS/MS (Waters Xevo TQS-micro™) to quantify current use pesticides. The results showed that levels of Glyphosate and Chlorpyrifos remained constant in these two sampling periods. AMPA and Imidacloprid were only found in summer. Both, the K and HIS indices were lower in summer than in spring. An increase of 581% in CAT activity from liver and 597% from gills in summer with respect to spring time was observed. Likewise, GST increased in liver 159% and no significant changes in MDA levels were detected between both seasons. These results show the role of antioxidant enzymes in fish, since oxidative stress damage was not observed in terms of lipid peroxidation, may be due to the increase of the antioxidant enzyme activities. The results found for the liver and gills are consistent, since liver is the main detoxifying organ and gills are the organ with the highest exposure to agrochemicals¹. In this way, biomarkers of oxidative stress in target organs are able to show the effects of some of the most used pesticides in the region.

Keywords: biomonitoring, fish, agrochemicals, agriculture.

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M-02

THE OCCURRENCE OF MYCOTOXINS IN CEREAL GRAINS IN 2019.

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Mycotoxins are secondary metabolites of micro-fungi and occur in all farming systems. Mycotoxin contamination of cereal grains is a serious problem in agricultural production worldwide. There is a large variation in the year-to-year results regarding the detected mycotoxin levels, due to the impact of applied agrotechnic and geo-climatic conditions.

The aim of the study was to evaluate the content of mycotoxins in Polish cereals harvested in 2019. The research was carried out by Department of Pesticide Residue Research of Institute of Plant Protection – National Research Institute within the framework of the multi-annual program financed by Minister of Agriculture and Rural Development.

The research program included 7 species of cereals: barley, maize, cereal mix, oat, wheat, triticale and rye. Samples of cereal grains were collected from production sites by inspectors of Plant Health and Seed Inspection. In total, 162 samples of cereal grains were analysed for 14 mycotoxins: aflatoxin B1 and B2 (Alpha B1 and B2), aflatoxin G1 and G2 (Alpha G1 and G2), ochratoxin A (OTA), fumonisin B1 and B2 (FUM B1 and B2), HT-2 and T-2 toxin (HT-2 and T-2), deoxynivalenol (DON), 3-acetyl-deoxynivalenol (3-AcDON), 15-acetyl-deoxynivalenol (15-AcDON), nivalenol (NIV) and zearalenone (ZEA).

A multi-method based on acetonitrile/water extraction for isolation of mycotoxins and a twenty-times dilution of the extract with LC mobile phase prior to instrumental analysis to minimize matrix effects was applied to the determination of mycotoxins. The chromatographic determination of mycotoxins was performed using an Eksigent® ekspert™ ultraLC 100-XL system interfaced with a mass spectrometer equipped with an electrospray-ionization source operated in the positive and negative mode (AB Sciex, Qtrap 6500). Chromatographic separation was achieved using a Kinetex C18 (100 x 2.1mm x 2.6µm) column and water/methanol gradient. Multiple reaction monitoring (MRM) mode was used for detection and quantification of analytes.

Cereal grains were contaminated with 10 from 14 tested mycotoxins. 74.7% of the samples contained mycotoxins, wherein 49.4% of samples several of them. The most frequently found were OTA (40.7%), HT-2 (45.1%) and T-2 (30.2%), DON (24.1%) and its metabolites: 15-AcDON (16.7%) and 3-AcDON (1.9%). ZEA (8.0%), FUM B1 (3.7%) and FUM B2 (13.6%) and NIV (1.2%) also occurred. Mycotoxins were detected in all tested cereals, in barley (100.0%), maize and cereal mix (86.4%), oat (77.3%), wheat (86.7%), triticale and rye (63.6%). The contents of mycotoxins exceeded maximum levels [1,2] in 10 samples (6.2% of the total samples tested).

Keywords: mycotoxins, cereal grain, monitoring.

References: 1. Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs.

2. Commission Recommendation of 27 March 2013 on the presence of T-2 and HT-2 toxin in cereals and cereal products.

M-03

OFFICIAL TESTING OF PESTICIDE RESIDUES IN POLISH CROPS IN 2020

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Since 1996 Institute of Plant Protection-National Research Institute (IPP-NRI) have been performing official testing of pesticide residues in crop samples taken at the primary production stage for Main Inspectorate of Plant Health and Seed Inspection, within the supervision framework of the trade turnover and application of protection plant products. The purpose of the studies is to check whether plant protection products are used in compliance with Plant Protection Regulation requirements.

In 2020, the studies were conducted within the framework of the multi-annual programme “Protection of cultivated plants with the consideration of food safety, reduction of yield losses and threat to humans, livestock and the environment” financed by Minister of Agriculture and Rural Development. The research covered the determination of pesticide residues in 1.409 samples of 50 commodities randomly collected from domestic farms by inspectors of Plant Health and Seed Inspection. Overall, the residues of 564 compounds were sought. Methods fulfilling the requirements of the SANTE/12682/2019 [1] guidance document and accredited under ISO/IEC 17025:2017 [2], in particular the multi-residue methods based on gas and liquid chromatography coupled to tandem mass spectrometry (GC-MS/MS, LC-MS/MS) were applied in the studies.

Pesticide residues were found in 43.2% samples. In total, residues of 99 pesticides were detected in the tested products. Multiple residues were found in 24.8% of the samples. Pesticide residues were found in fruits (68.9%), vegetables (53.2%), pulses (11.1%), cereals (25.2%), spices (100.0%) and sugar plants (51.0%). They were most often detected ($\geq 50\%$) in samples of apples (80.3%), grapes (80.0%), strawberries (69.2%), cherries (68.9%), sweet cherries (67.7%), peaches (66.7%), plums (57.1%), parsnips roots (82.9%), celeriac (74.2%), dill (70.6%), cucumbers (69.0%), tomatoes (61.5%), green onions (61.5%), chinese cabbages (61.0%), parsley roots (56.8%), carrots (54.5%), and sugar beet roots (51.0%). The most commonly detected were residues of tebuconazole (10.6%), difenoconazole (7.3%), azoxystrobin (7.0%), boscalid (6.8%), captan (5.0%), acetamiprid (4.8%), fluopyram (4.7%), pyraclostrobin (4.3%), pirimiphos-methyl (4.0%), chlorpyrifos (2.8%), carbendazim (2.7%) and pendimethalin (2.6%).

Overall, 99.8 % of the analysed samples were compliant with the legal limits. Residues above the EU MRLs were found in 0.2% of the samples tested (cereals), while the residues of unauthorised plant protection products use in 7.8% of the samples, mostly in vegetables.

Keywords: pesticide residues, official testing, products of plant origin.

References: 1. Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed. SANTE/12682/2019.

2. General requirements for the competence of testing and calibration laboratories. EN ISO/IEC 17025:2017.

M-04

EFFECTS OF CLIMATE CHANGE ON THE MOBILITY OF ORGANOPHOSPHATES PESTICIDES IN SOILS OF THE ARROYO GRANDE COASTAL AQUIFER, BOLIVAR.

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This research project will model the effects of climate change on the transport of organophosphate pesticides in soils, the risk to the groundwater of the coastal aquifer of Arroyo Grande in the North of the Colombian Caribbean. This body of water is a source of fresh water used for agricultural activities and for the supply of drinking water, located north of the department of Bolívar and is an area of great projection for the development of tourism in which there are no policies for the sustainable use of this valuable resource¹. The project will be start with the characterization of the hydro-geochemical parameters of 4 well soils in operation and to close to places where organophosphate pesticides are used to combat crop pests, and other soil with possibilities to supply future demand in this area, which has a great urban projection.

The modeling will be adjusted from tests of undisturbed soil columns where the concentration of the organophosphate pesticides Chlorpyrifos © and Malathion © will be monitored after 7, 14, 30 and 60 days. The extraction of pesticides from the soil samples will be carried out by ultrasound assisted and quantified by Gas Chromatography coupled with Mass Cromatography². Then the transport of pesticides in the soil columns will be modeled with the MACRO 5.2, this software has shown good results to model and simulate the transport of pesticides in countries like Norway and the Netherlands³.

The model obtained will be used to simulate the direct effects generated by climate change such as the increase in temperature and the decrease in rainfall due to future scenarios will be simulated proposed by according to RCP 8.5 model⁴ and the indirect effects such as the increase in the use of pesticides and the use of new wells to supply the water demand in the region to evaluate the probability of risk of the Arroyo aquifer groundwater Big. This will try to contribute to the planning of policies that serve for the sustainable development of land use and this water resource of great socioeconomic potential for the department of Bolívar.

Keywords: pesticides, modelling, MACRO, groundwater.

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M-05

MONITORING OF PESTICIDE RESIDUES IN POLISH RIVER BASINS IN 2019

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National authorities are responsible for enforcement of pesticide legislation following Regulation 1107/2009 and Directive 2009/128/EC while establishing a framework for Community action to achieve the sustainable use of pesticides. Professional users are responsible for proper application of plant protection products, thus ensuring that treated crops and environment will be free of excessive pesticide residues. According to the provisions of Directive establishing a framework for Community action to achieve the sustainable use of pesticides the EU Member States are obliged to establish national action plans to reduce risks associated with the use of plant protection products. The measures adopted also include those related to the monitoring of pesticide residues in water intended for human consumption and the monitoring of surface waters, groundwater and bottom sediments.

In 2019, a total of 452 water samples originating from 76 sampling points of Polish river basins were collected for laboratory analysis. The samples were taken from May to October, at monthly intervals. 270 pesticides and their metabolites were selected for testing in surface water samples, mostly active substances of plant protection products registered for use in EU countries.

During the monitoring in 2019, 71 different pesticides were identified and quantified in surface water samples, usually at low concentration levels. Most popular group of pesticide activity determined in collected samples were herbicides (31 substances), then fungicides (26), insecticides (12) and two metabolites of pesticides were found. The highest overall frequency of detection was obtained for popular herbicides – metazachlor, nicosulfuron, terbuthylazine, bentazone and widely used fungicides – tebuconazole and azoxystrobin, substances currently used in intensive chemical plant protection. The highest residues of plant protection products were determined for herbicides nicosulfuron (7.377 µg/L) in the Mogielnica River in May and chlorotoluron (5.924 µg/L) in Orla River in August, then for insecticide tebufenozide in the Drweca River (2.364 µg/L) in July and another one herbicide, metazachlor in October in the Proсна River, at a concentration of 2.260 µg/L. The highest sums of all detected pesticide residues in a single water sample were recorded for the Wielkopolska Voivodeship e rivers: Mogielnica – 11.628 µg/L and Orla – 10.371 µg/L, both samples collected in August, and in a sample of Drweca River, Kuyavian-Pomeranian Voivodeship, in July 2019 – 6.011 µg/L. During the entire sampling season, in 213 water samples out of 452 collected (47.1%), no residues of plant protection products were detected.

In summary, environmental monitoring and control activities are an important element of the risk analysis related to the use of plant protection products, and ultimately contribute to the dissemination of knowledge about their safe use in plant production.

Keywords: surface water monitoring, river basins, pesticide determination.

M-06

SOY-BASED INFANT FORMULA: SURVEY OF GLYPHOSATE RESIDUES IN BRAZILIAN RETAIL BETWEEN 2011 AND 2020.

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Nowadays many alternatives to replace animal milk are available and plant-based food is an option. The soy-based formula (SBF) is usually used to feed children that have allergies or intolerance to lactose. Composed of a mixture of vegetable oils, maltodextrin, starch, and sucrose, the SBF is lactose-free and commonly fortified with amino acids and minerals¹. In Brazil, soy-based formulas could contain both soy extract, and isolated protein. Alternative of plant origin may be a potential source of contaminants. There is a concern about this type of food intended for children for example infant formula. This concern is mainly related to the fact that children are in the development phase and also because they present a greater food intake per kilogram of body weight².

Glyphosate (GLY) is the most widely used herbicide with a broad spectrum of action that controls the growth of weeds and acts as a desiccant in the harvest, and its residues are commonly found in grains, mainly in soybeans³. There is a possible association of GLY with the induction of human breast cancer, infertility, developmental toxicity, and endocrine-disrupting activity⁴⁻⁵.

In Brazil, there is no specific legislation on pesticide residues for plant-based infant formulas. Thus, a 10-year survey was carried out evaluating samples available on the market in order to quantify GLY and its metabolite AMPA in SBF. The determination of residues of glyphosate and AMPA was based on post-column reaction with o-phthaldialdehyde and fluorescence detection⁶.

A total of 126 samples, with composition between soy extract or protein isolated, were collected from January 2012 to December 2020 in the Brazilian retail market were analyzed. GLY residues were detected in 42% of them with a maximum quantified at 1.08 mg kg⁻¹. The AMPA metabolite was detected in only 25% of the samples with a maximum residue of 0.23 mg kg⁻¹.

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M-07

APPLICATION OF UNKNOWN AND SUSPECT SCREENING ANALYSIS FOR THE IDENTIFICATION OF VOLATILE CO-FORMULANTS IN DIFFERENT PLANT PROTECTION PRODUCTS BY GAS CHROMATOGRAPHY – HIGH RESOLUTION MASS ACCURACY SPECTROMETRY

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Plant protection products (PPPs) are widely used technical formulations containing one or more pesticides (active substances), in addition to several co-formulants responsible for improving the properties of the mixture. In spite of the current analytical focus on active substances, the importance of co-formulants is often overlooked, as these compounds are usually undisclosed, even though they have been proved to enhance pesticide toxicity.¹ Thus, co-formulants in PPPs need to be characterised so that they can be monitored in samples to ensure food safety.

In the present study, 11 difenoconazole and 3 chlorantraniliprole-based PPPs comprising several types of formulations, such as emulsifiable concentrates (EC), suspension concentrates (SC), dispersible concentrates (DC) and ZC, which is a mixture of capsule suspension (CS) in SC, were analysed. The selected analytical technique was gas chromatography coupled to Q-Orbitrap high resolution mass spectrometry (GC-Q-Orbitrap-MS), providing efficient separation and detection of all identified compounds. Unknown analysis was performed by NIST database, whereas suspect screening was carried out by literature review, with several criteria including a matching fragmentation pattern and a mass error lower than 5 ppm. The combination of high resolution mass spectrometry and mass accuracy conferred a high degree of reliability in the identification of co-formulants, which would have not been attained in low resolution mass spectrometry.

Finally, 42 benzene and naphthalene derivative compounds were tentatively identified, and 12 of them (3 suspect and 9 unknown) were confirmed and quantified using available analytical standards. Confirmed compounds were: 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 2-methylbiphenyl, 3-methylbiphenyl, 4-ethyltoluene, biphenyl, ethylbenzene, isopropylbenzene, naphthalene, n-propylbenzene, pentamethylbenzene and tert-butylbenzene. Results showed that the applied methodology was able to detect these co-formulants at concentrations as low as 0.03 g/L (tert-butylbenzene), encompassing a wide of range of concentrations, up to 9.63 g/L (pentamethylbenzene). Pentamethylbenzene was the only compound detected in all studied samples. Overall, EC formulations showed the greatest number of confirmed co-formulants, with a mean value of 8 co-formulants per sample.

Keywords: Plant protection products, GC-Q-Orbitrap, unknown analysis, suspect screening

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M-08

MULTIRESIDUES PESTICIDES MONITORING IN FRUITS AND VEGETABLES IMPORTED BY ARGENTINA.

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An abundant and safe food supply for the world's growing population frequently requires the use of many pesticides for the control of insects, fungi, or other plants. Concern naturally arises over the safe and proper use of these toxic agents¹. More than 1000 active pesticide ingredients have been or are in current use throughout the world. Many of these pesticides can be expected to appear on imported foods even if not registered or banned for use¹. The aim of this work was collect information about the sampling and analysis of pesticides residues of fruits and vegetables imported by Argentina through the last four years, to establish a statistical knowledge about the presence of some pesticides residues in food commercially available, and if they are within the currently law Reg. 934/2010 SENASA². The present work shows the results of multiresidue pesticides analysis, including a wide range of insecticides, fungicides and herbicides.

Different sort of fruits and vegetables were collected periodically by SENASA through Official National Sampling over the last four years, and a total of 1675 samples of this Official Sampling were analyzed by JLA Argentina SA, member of SENASA Official Laboratory Network.

QuEChERS extraction³ in combination with LC-MS/MS and GC-MS/MS, and the determination of Dithiocarbamates (through carbon disulfide, LC-MS⁴) were used, in order to extract and measure pesticides in multiresidues chromatographic runs. As a quality controls of MRM and SIM method, reference materials and/or spiked samples were introduced in each batch of analysis. For the purpose, fruits and vegetables were grouped as follows: *Stone Fruits* (as plum, peach, blueberry, grape), *Pome Fruits* (apple and pear), *Citrus Fruits* (orange, tangerine, lemon, lime and grapefruit) and *Fruits and Vegetables* (not included in the characterization mentioned before, as lettuce, tomato, potatoes, banana, melon, onion, carrot, kiwi, pineapple, squash, mango, eggplant, etc).

Through this 4 years: tomatoes, grapes, lemons, pineapples and bananas were the fruits and vegetables in which pesticides appearance was most common, with a maximum of 14 different pesticides detected higher or equal to 0.010 mg/kg in the pool of samples analyzed. In this sense, considering $n \geq 20$ samples, of all the commodities tested, and in relation with the number of pesticides analyzed, a positivity of approximately 6% was observed, of which an average of 50% was a deviation to the current law Reg. 934/2010 SENASA². Under this condition, along this 4 years, the main deviations occur in Fruits and Vegetables Group, with Prochloraz, Thiabendazole and Fludioxonil (fungicides), and Methamidophos and Imidacloprid (insecticides). CODEX Reg.⁵ was not considered in this deviation analysis.

Overall, it can be seen that the occurrence of positive pesticides exceeding or equal to 0.010mg/kg has been decreasing over the years, showing that there is greater awareness on the agricultural and manufacturing practices.

Keywords: Pesticide Monitoring, Fruits and Vegetables Analysis, Quechers.

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M-09

ASSESSMENT OF THE PRESENCE OF THE CARCINOGENIC PESTICIDES-LINDANE, ALDRIN AND DDT- IN THE GENERAL POPULATION OF ARGENTINA (2005 – 2019)

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Organochlorine pesticides (OCPs) are persistent organic contaminants (POCs). There are adverse effects associated to them; among them human carcinogenicity. Aldrin, Lindane and DDT have the major importance at this point. The International Agency for Research on Cancer (IARC) has classified Lindane as a carcinogen (Group 1) because of its association to non-Hodgkin lymphoma². Aldrin, DDT, and their metabolites are considered as probably carcinogens (group 2A). Dieldrin and Aldrin have shown a positive association to breast cancer³ and DDT have a positive connection to cancers of the liver, testis, and non-Hodgkin lymphoma². Despite their use and production have been banned since many years, they can still be found in the general population, who are chronically exposed to OCPs through environmental pollution and the diet.

To carry out an epidemiological evaluation of the presence of Aldrin, Lindane and DDT and their metabolites in the general population of Argentina, 681 blood samples which were derived to CENATOXA during 2005 to 2019 were analyzed. The samples extraction was performed according to Dale et al¹ and they were analyzed by GC- μ ECD, with dual injection. The investigated compounds included: Aldrin, Dieldrin, Lindano (γ -HCH), opDDD, opDDE, opDDT, ppDDD, ppDDE, and ppDDT.

The percentage of detectable results Lindane was 4% (Limit of detection OCPs: 0,1 ng/mL). The pediatric population had the highest levels of them 83% with a mean concentration of ND-0,06 ng/mL. Aldrin showed 26% of detectable results, meanwhile dieldrin had 10%. Adults were the main affected population in both cases (89% and 69% respectively). The mean concentration of Aldrin was ND-0,11 ng/mL and its metabolite's one was ND-0,06 ng/mL. Isomers opDDT and ppDDT had 20% and 4% respectively of detectable levels. Adult population showed the highest percentage of them (96% and 52%), whose values were ND-0,11 ng/mL and ND-0,06 ng/mL. Main metabolites opDDE and ppDDE were detected in 8% and 22% of the population respectively. Adults had the highest number of results with detected opDDE (58%), whose mean concentration was ND-0,06 ng/mL. However, ppDDE was the main detected compound in children (64%) whose mean was ND-0, 09 ng/mL. Metabolites, opDDD and ppDDD, had 4% and 11% of detectable concentrations. Both were the most important in pediatric patients (35% and 90%) and ranges of mean concentration were ND-0,08 ng/mL and ND-0, 05 ng/mL respectively.

The analysis request and OCPs concentration shows a clear decrease indicating scarce recent exposures. It is related to the long period of time these pesticides prohibition exists. The results indicate exposure to Lindane in children that could result in harmful effects due to their greater vulnerability and the possible adverse effect of this OCPs. It must be noticed the importance of the chronic exposure to these carcinogens in both populations. New evaluations are recommended in the general population of Argentina.

Keywords: Organochlorine pesticides, carcinogens, adult and pediatric populations, Argentina. **References:**

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M-10

DETERMINATION OF MULTIPLE EMERGING POLLUTANTS IN EFFLUENTS FROM DAIRY PRODUCTION.

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Emerging pollutants (EPs) refer to compounds of different origin and chemical nature, whose presence in the environment can generate alterations or adverse effects on biotic and abiotic systems. Its presence was not previously known as they were unnoticed. These compounds reach the environment through domestic and industrial wastewater (treatment plants, hospital effluents, agricultural and livestock activities). The intensification of livestock activity can cause contamination of soils and water (surface, underground and drinking water) and can generate public health problems. The fate of substances used in animal production for health purposes has been little studied. Animal manure and effluents generated from livestock are commonly used in agriculture as fertilizers. To assess the health risk of the presence of these EPs (veterinary drugs), proper identification and quantification in various environmental matrices is necessary, which is why it is important to have analytical methodologies and equipment of high specificity and sensitivity such as coupled liquid chromatography-tandem mass spectrometry (LC-MS / MS).

In the present work, multiple EPs were identified and characterized in effluent water samples from dairy activity.

Thirty samples of effluent waters were taken from dairy farms in the Northwest region of the province of Córdoba during the period September-December 2020. The analysis of the effluent samples was carried out in an LC-MS / MS; the parameters of each were optimized. Compound on the mass spectrometer, the potentiality of the linear ion trap instrument (QqLIT) employed was exploited, including enhanced scans such as enhanced product ion spectra (EPI), enhanced resolution (ER) and MS³ experiments.

Due to the wide variability of physical and chemical properties that these molecules present, the analytical procedure was based on a treatment of the effluent with organic solvents, 0.1M disodium EDTA, 0.1M dibasic potassium phosphate buffer and pH 8.5, membrane filtration and subsequent quantitative determination by LC-MS / MS.

Veterinary drugs investigated were antiparasitics, anti-inflammatories and antibiotics of the family of beta-lactams, quinolones, macrolides, tetracyclines, sulfonamides. The concentrations detected and quantified in the effluent were found within the range 0.1-20 µg.L⁻¹, with recoveries for the different analytes between 50% and 130%.

These initial results provide information for the development of knowledge for the generation of future regulations in the province of Córdoba on the use and disposal of livestock waste.

Keywords: Veterinary drugs, LC-MS / MS, Effluents, Dairy activity.

M-11

OCCURRENCE OF ORGANOCHLORINE PESTICIDES AND CHLORPYRIFOS IN *BOMBUS PAULOENSIS* FROM AREAS WITH DIFFERENT LAND USES IN BUENOS AIRES, ARGENTINA

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Bees, especially those from Apidae family, constitute a key component in global biodiversity but also in the ecosystem stability and in the productivity of crops for human consumption. Among native bees inhabiting Argentina, the social bumblebee *Bombus pauloensis*, has a wide distribution and abundance. In recent years, it has been observed a decrease in populations of several bee species around the world, partly as a consequence of agricultural intensification with high use of agrochemicals. In this sense, bees are continuously exposed to environmental disturbs and therefore are very useful biomonitors of environmental pollution. The aim of this study is to evaluate the impact of land use (conventional agriculture, ornamental plants agriculture, and natural reserve) on the Organochlorine Pesticides (OCPs) and chlorpyrifos levels in *B. pauloensis*. Females (workers) and males from three areas near Mar del Plata city (Argentina), characterized by different land uses were assessed: a conventional agriculture production area (A1), an ornamental plants field adjacent to an urban solid waste disposal site (A2) and a natural reserve with organic crops production (A3). The higher pesticide concentration was found in both conventional agriculture areas in relation to the reserve area. Females and males from A1 showed the highest chlorpyrifos levels, as a consequence of the extended current use of this insecticide, particularly in this zone dedicated to intensive agricultural production. In spite of their prohibition worldwide, OCPs were present in both sexes from all sampling areas, as a result of their extended use in the past. It was not observed a clear pattern on OCPs distribution across the areas, although Drins and DDTs groups prevealed. According to our knowledge, the present work represents the first analysis of OCPs and chlorpyrifos bioaccumulation in wild bees in Argentina and highlights their potential as environmental pollution biomonitors.

Key words: OCPs, chlorpyrifos, wild bees, land use.

M-12

REVIEW OF PESTICIDE RESIDUES IN CROPS IN THE CARIBBEAN.

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Agrochemicals are widely used across the Caribbean region, although many countries lack adequate and up-to-date legislation regulating pesticide use as well as consistent long-term monitoring programmes. One particularly growing concern has been food safety issues related with pesticide residues on food commodities. A limited number of studies have been published in the English-speaking Caribbean on pesticide residues in crops. This poster presents results from a focused literature review of studies carried out in Trinidad and Tobago, Saint Lucia, Guyana and Suriname, between 1998 and 2020, on pesticide residues in crops. Results from the review indicate that pesticide residues are detected on a wide range of crops, of which the majority are above MRLs. Overall, pesticide residues were detected in 23% of the total samples collected, where 73% of these were found to be above the MRLs, noting that in several instances these were hundreds of folds the MRLs. Many samples contained multiple pesticide residues, including banned active ingredients, and crops with pesticide residues above MRLs included celery, lettuce, cabbage, tomato, tannia and bean. Organophosphates, organochlorines, neonicotinoids and pyrethroids are some of the chemical classes detected above MRLs. It is important to highlight the need for consistent long-term monitoring of pesticide residues in food crops to reduce potential threat to the environment and public health. Further analysis of pesticide residues in locally produced crops is essential for a solid baseline to develop a long-term monitoring strategy adapted to the local context.

Keywords: Pesticides, residues, crops, Caribbean.

M-13

BEES AS ENVIRONMENTAL INDICATORS OF THE USE OF FIPRONIL

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People tend to associate bees with honey production, however the main service provided by bees is the maintenance of biodiversity through the pollination of natural ecosystems and agricultural cultures. Recently, the decline and disappearance of different species of bees have been worrying beekeepers, who are looking for solutions to this problem.

In Brazil, there are no maximum limits for pesticide residues and veterinary medicines established for bee, honey, or any bee product (wax, propolis, royal jelly), as there are no products registered for use in hives and bees. However, in recent years, several bee death events have been reported. Because of this, this work aimed to evaluate the presence of pesticide residues in bees found dead in the State of São Paulo, Brazil. Sampling was carried out from March 2020 to February 2021.

The QuEChERS method was used to analyze pesticide residues and the detection was made by liquid and gas chromatography with a mass detector, 120 pesticides were evaluated in 22 samples. Of the samples evaluated in 31,8%, none of the active ingredients analyzed were found, in 40,9 %, fipronil was found; cypermethrin, thiamethoxam and lambda cyhalothrin was found too.

Fipronil is the active ingredient that has caused the most death in bees. Fipronil is forbidden to use in European countries, it is allowed in the United States, Australia and in many South American countries. In Brazil, fipronil is authorized for use in 13 crops and 5 ornamental plants for application in seeds, soil and seedlings. Also, the application on leaves is allowed for cotton, rice, eucalyptus and soy.

The state of São Paulo has 30,5% of its territory occupied by agriculture and livestock and is a great producer of sugarcane and eucalyptus, crops in which the use of fipronil is allowed. Besides, according to the Pesticide Residue Analysis Program-PARA, fipronil is one of the active ingredients in which unauthorized use for culture is observed. It was concluded that a more effective control in the application of fipronil is necessary to prevent the disappearance of the bees.

Keywords: pesticide, monitoring, risk analysis

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M-14

WHEN CHEAP BECOMES EXPENSIVE: MONITORING OF FORMULATED PESTICIDES PRODUCTS TRADED IN THE SOUTHERN REGION OF BRAZIL.

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Pesticide formulation trade moves millions of dollars every year and has a significant participation in world's economy. According to the Food and Agriculture Organization of the United Nation (FAO) [1] Brazil was the country that most imported pesticides in 2018. That huge demand for formulated pesticide products resulted also in many imitation products entering in the market and illegal products coming from other countries to Brazil. The extensive frontier that Brazil has with the Latin America countries, facilitate the illegal trade of these products, since they are cheaper in comparison to the legal formulated pesticide product. The Brazilian PRF (Federal Highway Police) presented data exposing pesticides seizures reached 90 tons in October 2020, over 30 tons higher than the same period in 2019. While in 2017 the sum of losses in the productive sector and tax evasion reached R \$ 3.1 billion, the amount reached in the following year was R\$ 8.9 billion and R\$ 11.2 billion in 2019[2]. The goal of this study was to evaluate the composition of formulated products analyzed by LC-MS/MS in the Center of Research and Analysis of Residues and Contaminants (CEPARC)/Federal University of Santa Maria – Brazil, from March 2017 to March 2021.

A total of 326 samples (319 fungicides and 7 insecticides) of formulated products were analyzed. Considering those 217 formulations containing trifloxystrobin and prothioconazole as active ingredients, just 14% were in accordance with the acceptable concentration limits ($100 \pm 6\%$) established by the Brazilian legislation (Portaria nº 45/1990) [3]. The second most analyzed formulation was the one containing pyraclostrobin as active ingredient (41 samples). Results showed that just 24% of those products were within the acceptable limits of concentration by legislation ($100 \pm 5\%$) and in 34% of samples pyraclostrobin concentration was below the detection limit (2.5 g L^{-1}). Regarding the formulate products that presented azoxystrobin as active ingredient (29 samples), just 7% of the samples were in accordance with the specified concentration ($100 \pm 5\%$) and for 28% of thosesamples the active ingredient was below the detection limit (2.5 g L^{-1}).

In a nutshell, results indicated that 82% of the analyzed products was in disagreement with label specifications in terms of active ingredient presence and concentration and show the importance of a stricter enforcement and control of commercialized pesticide formulations.

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Keywords: Formulated products monitoring, LC-MS/MS, pesticides, Brazilian legislation.

M-15

GLYPHOSATE RESIDUES DETECTION IN HONEY BEES FROM URUGUAY PROTECTED AREAS

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Beekeeping in Uruguay is present throughout the territory and honey despite being a prominent exporting product still miss differentiation that could increase its value. On the other hand, the country has a national system of protected areas (SNAP) where native fauna and flora are preserved. It is in these areas where a different honey could be achieved both for its botanical originality and for its environmental quality. The potential for producing a differentiated product of selected region from the SNAP was explored. Four regions of Uruguay were environmentally monitored through honey samples obtained over a year. Three of the regions belong to the SNAP: Valle del Lunarejo (North), Quebrada de los Cuervos (East) and Esteros de Farrapos (West). The fourth, Los Cerrillos (South), being a region of agricultural and fruit production outside the SNAP, with no special restrictions to pesticides applications. The relative abundance of each TAXA was determined by counting pollen grains (Louveaux), separating between native, exotic and cultivated. Glyphosate and AMPA residues were determined by LC-MS/MS. 37 different plant origins were found; the most diverse region was the South with 28 origins. Only in the eastern region were no cultivated species found, in addition to being the least diverse area. Glyphosate residues was detected in the North and East regions but below limit of quantification (LOQ), for one of the honey crops. Both areas, belonging to the SNAP, are surrounded by livestock and forestry activities; in the West region was detected glyphosate residues above LOQ (0.014 mg/kg), also belongs to the SNAP, this area is surrounded by agriculture. In the Southern region, glyphosate residues average was detected for both crops above LOQ (0.019 and 0.079 mg/kg). The established MRL for glyphosate in honey is 0.050 mg/Kg. AMPA residues were not detected in any of the studied areas. Crop's presence and their associated (exotic) weeds is detected by palynology and is related to glyphosate presence. Due to the flight range of bees the environment of the protected areas must be considered. Rethinking the geometry and size of these areas could be necessary. This work confirms the role of bees in detecting pollutants and the risk posed by agricultural activities.

M-16

CASE STUDY: AQUATIC BIOMONITORING IN AMARILLO STREAM IN URUGUAY.

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When evaluating pesticide residues in surface waters as a compartment in environmental studies, it is usual to find several non-detects. However, this fact is not conclusive about the presence of pesticides in the environment. It needs a deeper look at the data and how the study was performed to ascertain the presence/absence of pesticides within it. The analytical parameters such as the scope, analytical instrumentation and limits of quantitation of the methodologies that were used for the pesticide residue analysis are highly important. Also, the dynamic characteristics of these ecosystems make sampling a huge challenge. On the other hand, when the composition of aquatic macroinvertebrate communities is studied in streams, the effects caused by diverse contaminants that reach surface waters can be integrated in a time period, but little is known about the chemicals or the distortion that caused a particular community composition. Combining ecotoxicological observations with chemical analysis of the biota and the water where this biota lives could bring some light on the overall phenomenon. The usual approach used for this type of study, is to select a reference site upstream that does not have the alterations of the evaluated site and to compare them. The reference site should have a more diverse macroinvertebrates community than the site of interest. In the present work we present an unusual result of this approach. During a pesticide monitoring study in the Queguay river basin in Uruguay, 4 sites with different land use and their corresponding reference sites were selected, visited and sampled 6 times during one year from February 2019 to February 2020. Three of the streams showed the expected behavior regarding the difference in the aquatic macroinvertebrates communities but one of them did not. It was Amarillo stream which presented in all samplings biological indexes showing a lower diversity upstream (reference site). When pesticide residue analysis was performed (LC&GC-MS/MS) in odonate nymphs samples, among other currently used pesticides, the highly toxic organochlorine compounds hexachlorobenzene, chlordane, mirex and DDT metabolites were found. The water samples analysis only showed a positive result of DDT in the evaluated site and all non-detects in the upstream site. Further research confirmed that in this site agricultural activities have been performed since decades ago when these pesticides used to be applied. This hints at the cause of the positive findings due to the persistence of the organochlorines detected. Possibly through surface runoff these pesticides reach the stream, contaminating it and negatively impacting the biota. Water analysis alone give us only a photograph of what is running in the stream, whereas this type of interdisciplinary approach gives a broader vision of the situation of the environment. The complementary study of biological indexes and chemical determinations shows its utility to understand pesticide dynamics and effects in the environment.

M-17

STUDY OF THE PRESENCE OF THE INSECTICIDES MALATHION AND DELTAMETHRIN IN CORN FOR DIRECT OR INDIRECT CONSUMPTION, HARVEST 2020

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The industrialization of corn is one of the agroindustrial activities that in Argentina generates a high added value, since it allows obtaining a large number of products that are consumed directly or are inputs from other industries. The applications of agrochemicals in the storage of corn grains, cause greater problems of residues in the grains than the applications in the crop. However, in most cases following the recommendations for use, according to GAP, the residues are below the Maximum Residue Limits (MRLs). In Argentina, MRLs are established by SENASA. The active principles approved for use in grains stored by SENASA, belong to the organophosphate and pyrethroid families. The presence of pesticide residues in products for human and animal consumption can compromise their safety, and is one of the aspects of agrochemicals that currently concern the most due to the sensitivity of public opinion regarding the quality and safety of food.

The objective of this work was to detect, identify and quantify the presence of insecticides, malathion and deltamethrin in samples of corn grain treated during storage. A standardized methodology (SANTE/12682/2019.UNE-EN 15662 AENOR) was selected and verified for both active principles in corn samples. The methodology is based on the extraction and purification technique using the dispersive SPE-QuEChERS method and detection by gas chromatography with a negative chemical ionization mass spectrometry detector.

The following parameters were evaluated for each analyte: linearity, intraday and interday precision, recovery percentages, detection limits (LOD) and quantification (LOQ). The results obtained for deltamethrin were: linear regression analysis between 0.01 - 1.3 mg / kg, LOD: 0.04 mg / kg; LOQ: 0.12 mg / kg, for malathion linear regression between 0.01 - 0.6 mg / kg, LOD: 0.02 mg / kg; LOQ: 0.06 mg / kg. For the recovery, a range between 70-110% was established. The identity of the analytes was confirmed by checking the relative abundance of the characteristic ions compared to that of the standard. The influence of the matrix effect on the quantification of each analyte was determined.

A total of 50 samples corresponding to untreated corn, corn after 24 hours of application, broken kernels, sieve rejection and marlo rejection were analyzed.

In the initial corn samples, the presence of deltamethrin was detected below the MRL, while after the application, deltamethrin and malathion were detected, only one sample exceeded the value of the established MRL for deltamethrin. Deltamethrin and malathion were detected in the other three types of samples. The results obtained show the importance of analytical measurements as an instrument for subsequent monitoring of insecticide applications in grains destined for human and / or animal consumption.

Keywords: Insecticides, Corn, Food Safety.

M-18

PESTICIDE POLLUTION FROM THE AGRICULTURAL ACTIVITY IN THE GUALEGUAY RIVER BASIN, ENTRE RÍOS, ARGENTINA.

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Agriculture in Argentina has undergone major transformations in recent decades with the incorporation of biotechnological packages. Despite the agro-industrial relevance of the province of Entre Ríos. Few studies evaluate the entry and dynamics of pesticides in waterbodies of the region, considering their contribution to the Paraná Delta, the second largest wetland in Latin America. The objective of this work was to study the occurrence of pesticide residues in surface waters and bottom sediments in the lower zone of the Gualeguay River, a representative basin of the region.

Four sampling campaigns were carried out over 2 years, covering the 4 seasons. Samples were collected from 7 tributary streams to the Gualeguay River and from 6 sites on the main course. Water samples were extracted by LLE with dichloromethane and sediments by QuEChERS. Multi-residue analysis was carried out on a Perkin Elmer GC-MS¹. For glyphosate (GLY) and AMPA, 1 mL of water was adjusted to pH 9 with borate buffer and derivatized with FMOC-Cl. For sediments, 7 g were extracted with borate buffer by sonication and 1 mL of the supernatant was derivatized. Instrumental analysis was performed using a Waters ULPC-MS/MS².

GLY was detected in 71% and 97% of the water and sediment samples, while AMPA was detected in 63% and 87%, respectively. While atrazine (ATZ) was detected in 73% of the waters. The spatial analysis regarding the origin of the sample revealed that there were no statistically significant differences between the concentrations in the tributaries and those quantified on the main course for GLY and AMPA in water and sediment, and for ATZ in water. Still, the maximum concentrations were found on the tributaries: water: GLY=10.90 $\mu\text{g}\cdot\text{L}^{-1}$, AMPA=9.60 $\mu\text{g}\cdot\text{L}^{-1}$, ATZ=2.113 $\mu\text{g}\cdot\text{L}^{-1}$; sediment: GLY=208.6 $\mu\text{g}\cdot\text{kg}^{-1}$, AMPA=104.7 $\mu\text{g}\cdot\text{kg}^{-1}$. The GLY:AMPA relationship provides information on the source, destination, and transport of glyphosate in the environment. In the water samples, most of the GLY:AMPA ratios were >1. These results suggest short transport times and mobilization distances from the application zone to the analyzed waterbodies.

Pyrethroids insecticides bifenthrin, cypermethrin, deltamethrin and λ -cyhalothrin were detected in water, with frequencies lower than 10%. Nevertheless, concentrations were above their respective guideline for the protection of aquatic life, up to more than 200 times the guideline, even in samples from the main course.

The homogeneity in the distribution of pesticide concentrations shows not only the large volume of these that is used in agriculture, but also the mobility of pesticides in the environment, being able to be quantified in water bodies with flows greater than 200 $\text{m}^3\cdot\text{s}^{-1}$, such as that of the Gualeguay River.

Keywords: glyphosate, pyrethroids, mass spectrometry, tributary.

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M-19

INFLUENCE OF THE AGRICULTURAL LANDSCAPE SURROUNDING APIS MELLIFERA COLONIES ON THE PRESENCE OF GLYPHOSATE AND ITS METABOLITE AMPA IN HONEY

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During foraging flights, honey bees settled in agricultural ecosystems may encounter glyphosate residues on flowers of both cultivated and native plants growing in semi-natural habitats within the landscape. This product has been considered non-toxic to bees based on acute contact and oral toxicity tests ($> 100 \mu\text{g}$ / per bee) performed mostly under lab conditions; however, several authors have described various deleterious effects of this herbicide on honeybee's behavior and survival. The configuration and heterogeneity of the landscape and the agricultural management in which the bee colonies are located, have direct and indirect implications on the presence and survival of bees. In this work, we were interested to analyze the relationship between landscape configuration and the presence of pesticides in honey. In particular, we tested the relationship between the presence of glyphosate and AMPA residues in honey and some metrics of habitat configuration. We expect a higher presence of glyphosate and AMPA as the proportion of crop lands in the landscape is increased and the connectivity of semi-natural habitats is decreased. A total of 30 honey samples belonging to the 2019 and 2020 harvests were analyzed in various areas of the southeast of the province of Buenos Aires and a frequency of 50% of glyphosate positivity was found in the analyzed samples meanwhile AMPA was found in 30% of the samples using a method of analysis of residues of Glyphosate and its main metabolite of degradation to Aminophosphoric Acid (AMPA) in honey developed using UPLC MSMS. We identified a total of 24 different sites to test the relationships between habitat configuration and residues of pesticides in honey because six of the samples were obtained in the same apiary (during the same of different season; see below). The range of values found in the samples was between 2 – 27,5 $\mu\text{g}/\text{kg}$ for Glyphosate and 1,9 – 18,1 $\mu\text{g}/\text{kg}$ for AMPA. The metrics for the near landscape (1000m ratio) surrounding the apiaries showed negative higher correlations than those for the larger one (2225 m ratio), particularly with AMPA residues. Nevertheless, these correlations were weak and thus the amount of crop lands with industrial agriculture is not enough to clear explain the values of glyphosate and AMPA residues detected in the honey bee colonies. Based on the pesticide prevalence in the environment, as well as our findings of its presence in honey samples, we propose that detailed studies at the apiary scale should be conducted in Argentina to determine if glyphosate is in fact a contributing driver to the colony losses. Geospatial analysis like the performed in this study can help honey producers to estimate risks to pesticide exposure in landscapes with intensive agriculture.

Keywords: Apis mellifera, Honey, Glyphosate, Agricultural.

M-20

STUDY OF THE EFFECT OF *AZOSPIRILLUM BRASILENSE* AZ39 ON THE RESIDUALITY OF GLYPHOSATE USED IN CORN CROPS

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Currently, there is an increasing need to expand to the maximum the knowledge of the physical-chemical characteristics, the form of action and the environmental impact of herbicides, in order to make a rational use of them¹. In the development of an herbicide, aspects such as its chemical formula, its behavior within the plant to the impact on the environment should be studied, in order to offer the farmers effective and safe tools. Thus, studies related to forms of degradation of herbicides that remain as residues are important to achieve a minimum environmental impact¹.

The time that an herbicide remains active in the soil, after it produced its effect, is called persistence. Any factor that alters the disappearance or decomposition of herbicides affects their persistence. Nowadays, different strategies are being developed to eliminate these substances in an economic and ecological way. Numerous studies have shown that soils contaminated with pesticides can be decontaminated by the action of specific microorganisms².

In this work, an in vitro study was carried out on the interaction between the Rizo bacterium *Azospirillum brasilense* Az39 and glyphosate in order to determine if the microorganism was capable of reducing the accumulation of glyphosate's residues.

For the study, a bacterial inoculum was prepared using the *Azospirillum brasilense* Az39 strain, grown in LB liquid medium. From it, in vitro survival tests of the bacterial culture against glyphosate were performed, as well as its ability to use it as a carbon source. In the first case, a selective medium for nitrogen-fixing bacteria was used: NFb (nitrogen free broth), to which glyphosate sources were added. While for the second case, the same culture medium was prepared but without the addition of the carbon source, which was replaced by glyphosate. The concentration of glyphosate and AMPA was determined in these treatments where the culture medium conserved all the nutritional sources for the growth of *A. brasilense* Az39, representing the availability of nutrients that the bacteria usually have. Their quantification was carried out using HPLC chromatography with MS / MS detection after derivatization with FMOC³.

The obtained results showed a 30% decrease in the glyphosate concentration in the culture medium inoculated with *A. brasilense* compared to the treatment without bacterial inoculation. The treatment in which the Az39 culture was inactivated did not show significant differences with respect to the treatment without Az39. In the control treatment (-), neither glyphosate nor AMPA was detected. The ability of *Azospirillum brasilense* Az39 to use glyphosate as a carbon source was demonstrated, even in the presence of all its nutritional sources, which is promising for its degradation in the soil.

Keywords: *Azospirillum brasilense* Az39, glyphosate, degradation of herbicides, HPLC-MS/MS.

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M-21

BIOMONITORING IN INTERTIDAL ECOSYSTEMS: THE SEA ANEMONE *BUNODOSOMA ZAMPONII* AS A CASE STUDY.

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Legacy pesticides such as organochlorine pesticides (OCPs) have long been studied due to their ubiquitous and persistent nature. Even though these compounds were prohibited in 2001 and are regulated by the Stockholm Convention, they are still of major environmental concern given their lipophilic and volatile properties. Chlorpyrifos is a current use organophosphate pesticide, one of the most widely used pesticides in Argentina. Biotic and abiotic processes may cause the mobilization of these compounds, which can then be transported by streams and rivers, reaching coastal and marine environments. In this sense, coastal environments are heavily influenced by anthropogenic pollution throughout the world.

The aim of this work is to study pesticide levels in two populations of the sea anemone *Bunodosoma zamponii*, in Mar del Plata city (Buenos Aires, Argentina). Samples were collected on four occasions throughout a year, following a seasonal periodicity, at two locations (Punta Cantera (PC) and Las Delicias beach (LD)). PC is regarded as a reference site and LD is an impacted area, since it is adjacent to a wastewater plant. A total of 19 compounds (18 OCPs and chlorpyrifos) were analyzed by GC-ECD.

The greatest diversity of compounds took place over summer (16 compounds in PC and 15 in LD). Chlorpyrifos, α -HCH and *p,p'*-DDE had a detection rate higher than 85%. Higher pesticide levels occurred during winter in LD ($8.43 \pm 0.50 \text{ ng.g}^{-1}$), and were significantly greater than PC ($4.42 \pm 1.22 \text{ ng.g}^{-1}$). PERMANOVA analysis also revealed differences among sites during winter. Principal Coordinates Analysis (PCoA) indicated that samples from LD had higher levels of endosulfans, HCHs, DDTs and chlorpyrifos.

There was a clear disparity in pesticide levels among sites, which could be a starting point to further inquire about the biological and ecological aftermaths of such asymmetry. It is also noteworthy to mention that being *B. zamponii* a sessile organism and tolerant to such compounds, it is useful as a sentinel specie and could also be considered for toxicity assays. To our knowledge, this would be the first study on the occurrence of pesticides in a sea anemone. Hopefully this work will raise concern in protecting cnidarians and encourage researchers to dive into their diverse world.

Key words: anemone – organochlorine pesticides – chlorpyrifos – multivariate analysis.

M-22

EVALUATION OF THE TUMOR SUPPRESSOR GENES TP53 AND P16 AS POTENTIAL BIOMARKERS OF EPIGENETIC DAMAGE DUE TO OCCUPATIONAL EXPOSURE TO PESTICIDE MIXTURES IN AGRICULTURAL WORKERS FROM NORTHERN SINALOA, MEXICO.

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Agriculture is the economic activity with greater relevance in the state of Sinaloa, because of this they are used on average 223 tonnes of pesticides annually and has triggered serious consequences on ecosystems and the health of agricultural workers, A oday, the DNA methylation monitoring has emerged as a novel way of evaluating the influence that pesticides ³ have on the presence of cellular damage caused by the movement of these compounds within the body. The **objective** of this study is to demonstrate that the specific PCR-methylation technique presents viability for detecting diseases. we conducted an MS-PCR study with people with and without exposure to pesticides. According to the **results** , bands corresponding to 193bp for the TP53 gene and 150bp for the P16 gene were evidenced, which indicates that 27 (65%) of the workers exposed to pesticide mixtures presented methylation in both genes evaluated, while that 5 participants without exposure (23%) also resulted with a potential epigenetic damage, according to the Chi square tests, the variables referring to direct exposure to pesticides (hours of exposure, mixing, etc.) showed a strongly significant association at a confidence index of 0.05. Similarly, the MS-PCR test showed a sensitivity of 0.85 and a specificity of 0.43, therefore, the results obtained are viable to be used in the timely diagnosis of genetic damage caused by exposure to multiple toxic agents, such as pesticides. Based on the results of this study, we propose to carry out subsequent tests focused on the specific search for the methylated nucleotides within the affected fragments, as well as the search for polymorphisms linked to a greater or lesser susceptibility to being affected by induced methylations. of pesticides. In the same way, it is proposed to carry out genetic expression tests in TP53 and P16 in order to relate the level of methylation with damage to the genome.

Odds ratio complex mixtures of pesticide	Value	95% confidence Interval Low	High
Yes/No	5.100	1.656	15.702
Cohort TP53 methylation	2.070	1.290	3.321
Cohort TP53 partian methylation	0.406	0.197	0.837
Number of cases	65		

Keywords: Pesticide Methylation Epigenetic Monitoring

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M-23

ORGANOCHLORINE RESIDUES IN FOOD AND ENVIRONMENTAL MATRICES IN MERCOSUR COUNTRIES. A REVIEW.

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The Dietary Exposure to Neurotoxic Substances in Latin America Is Limited, Which Can Affect the Neurological Development of Children, Especially Through Breast Milk and Food From Contaminated Water and Soils. OCPs Were Widely Used in the Region, Due to Their Low Cost and Their Wide Spectrum of Toxicity. Industries, Agricultural Activities, and Complex Ecosystems Can Promote Food Contamination Through the Food Chain. Organochlorine Pesticides (OCPs) Are Part of the POPs Mostly Regulated by the Stockholm Convention Since 2004 and Have Mostly Been Limited in Agriculture, However, There Is Evidence of its Presence in Different Environmental Matrices Such as Water, Soil and Sediments. In This Work, a Systematic Review of the Evidence of Contamination by Organochlorines in Food Matrices, Water, Soil and Sediments in Countries of the MERCOSUR Region (Paraguay, Uruguay, Brazil and Argentina) in the Last 10 Years Was Carried Out. Certainly, Very Few Studies Have Focused on Organochlorines, Just Under 15 Studies Have Been Found. However, This Review Highlights the Overwhelming Evidence That These Pesticides Are Still in Force in Food and Environmental Matrices, at Levels That Can Be Dangerous and Harmful to the Population in MERCOSUR Countries. It Was Observed That Water Is One of the Most Studied Matrices To Evaluate Contamination With OCPs. Biomonitoring Studies Have Been Carried Out, These Establish the Risk of Toxic Exposure To Biota and Human Populations. It Can Be Seen That Brazil Is One of the Countries With the Best Monitoring System. It Is Suggested To Evaluate the Contamination of Food Matrices Such as Milk, Can Provide Useful Information on Temporal Trends From Inherited Pesticides and Other Lipophilic Contaminants. It Was Observed Too That In All the Water Samples and in Similar Studies Carried Out in the Region, There Was a Prevalence of Endosulfan Sulfate in Water Bodies, Which Could Be Due to the Persistence of This Metabolite in the Soil After Fumigation, or the Current Illegal Application, Especially in Countries With a Dry Border, Which Means That Eventually Surface Waters May Contain This Pesticide. In This Sense, Permanent Monitoring of Surface Waters Is a Good Alternative for Surveillance Programs. The Presence of DDT, HCH, Chlordane and Endosulfan Indicated That the Residues of Most of the Compounds Would Have Their Origin in the Historical Application. There Is no Reduction in the Levels of Certain OCI Such as Endosulfan After the Ban Came Into Force in the Countries of the Region, but the Reduction in the Levels of Heptachlor, DDT, Dieldrin and Chlordane Can Be Verified From 2007 to 2015. It Seems That the Implementation of Periodic Monitoring Systems and the Use of Biomonitoring To Assess Contamination Are the Most Efficient Alternatives To Prevent the Exposure of Residual Organochlorines in Water and Food Through the Food Chain. This Is 17 Years After the Entry Into Force of the Stockholm Convention.

Keywords: Organochlorines Pesticides, Pesticides, Residues, Foods, Environmental Matrices.
Please Indicate How Do You Want To Present Your Work Poster...X..... Oral Communication...

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M-24

DETERMINATION AND QUANTIFICATION OF ORGANOCHLORINE PESTICIDES IN SOILS OF CROPS FROM THE DEPARTMENT OF CÓRDOBA.

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For several decades, a large part of the agricultural society worldwide has been knowing and making use of a varied amount of products or chemical agents destined to eradicate pests and microorganisms that threaten the quality of a harvested food or in more extreme cases, threaten the health of consumers, these products are what we know as pesticides. These caused such an impact in the eighties that they were even used to combat tropical diseases ¹. However, with the passage of time and its indiscriminate use, it was subsequently verified, due to its main characteristics as an exterminating agent, they caused irreparable damage due to its high toxicity and its ability to last over time ². Among these substances we find organochlorine pesticides (OC's), which are chlorinated pollutants, which were banned years ago and which to date are widely distributed in all environmental matrices, given their physicochemical properties, allowing their entry into the food chains and can bioaccumulate, which leads to generating public and environmental health problems such as carcinogenesis, immunological and reproductive disorders in living beings ³.

In the present research work, organochlorine pesticides were determined and quantified in crop soils, whose sampling was carried out in an area of 10 farms in the department of Córdoba. To determine these chlorinated pollutants, a cleaning was carried out on the sample and the subsequent extraction of the pesticides present in them, extraction that was carried out with a primary standard (PCB-209), by the ultrasound method. Subsequently, it was completely dried with a stream of nitrogen and restored with a related solvent with an added standard, which is a solution that was made based on a mixture of OC's pesticides, among which were the following (HBC, Lindane, Metallochlor, 4,4'-DDT, 4,4'-DDE, Endrin) in order to quantify said components by means of Gas Chromatography coupled to the Mass Spectrophotometer (GC / MS), using as methodology of calibrated, adding standard (or standard). As a result of the quantification, it was found that the organochlorine pollutants in the highest proportion in the analyzed soils were (hexachlorobenzene (HBC), and Lindane), with concentrations at trace levels ranging from 0.785 ± 0.0036 ppb to much higher concentrations. as 165.970 ± 0.0015 ppb (in the case of HBC), and for lindane concentrations between 4.38 ± 0.0015 ppb and 123.711 ± 0.002 , on the other hand, the pesticides with the highest concentration reported were HBC and 4,4, '- DDT, with values of 1904.483 ± 0.017 ppb and 2924.166 ± 0.11 ppb respectively, which indicates that despite not being present in large quantities, these values

obtained represent an alarming factor in the area, due to the risks that this type of pollutant generates to health and the environment.

Keywords: Contamination, Organochlorine, Environment.

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Miscellaneous

MI-01

INTERACTION BETWEEN PESTICIDE, DRYING TECHNIQUE AND FRUIT MATRIX ON PROCESSING FACTOR ESTIMATION

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Pesticide residues present in fruits or other agricultural products are commonly concentrated during the drying process. Knowing this, when a MRL is defined for one pesticide that will be use in some raw materials, which will be utilized to elaborate dried products, is fundamental to estimate the processing factor (*Pf*) for the utilized pesticide. However, to obtain dry products the raw material could be subjected to a different method, like sun drying (direct or indirect), oven air drying, microwave drying, vacuum drying, freeze drying, and some mixture of these procedures. The question are if the *Pf value* would be affected by the drying technique and if the raw material, under the same drying process, could affect the *Pf*.

A study was performed to determine the effect of dried processes (sun and oven) and fruit matrix on the pesticides *Pf*. Plumes, table grape bunches, and apples were dipped for 1 minute in 100 L pesticide solution containing buprofezin, methidathion, pyriproxyfen, indoxacarb, acetamiprid, thiacloprid, and spiroidiclofen. Thirty minutes after the raw materials were remove from the solution, half of each treated raw fruit was distributed on a polyethylene film placed over the soil and exposed to sunlight during 22 days. The other half was put into an air dryer oven at $75\pm 2^{\circ}\text{C}$ for 24 h. In the case of apple, before drying, fruits were sliced (0.5 cm-thickness). After the sun and oven dry process, the water contents were as follows: prunes 12.5% and 11.3%, raisins 14.8 and 11.3%, dried apple slices 11.2.% and 12.3%.

The results showed that the averages of estimated *Pf* for each of the fruit matrix under sun-dried (*Pfs*) were 21% lower than the values obtained under oven-dried (*Pfo*) conditions. This difference depended on the matrix, being the ratio *Pfo/Pfs* was 1.1 for plums to prunes, 1.3 for grapes to raisin, and 1.2 for apple to dried slice apple. However, the case-by-case analysis showed important differences between pesticides. For example, thiacloprid apple *Pfo* was 1.9 and *Pfs* 0.7. With these values the Pre-harvest interval should be 29 days and <1 day to achieve the MRL for this insecticide in EU (0.3 ppm) under oven and sun-dried conditions, respectively. Methidathion was the only compound that showed the same *Pfo/Pfs* ratio (0.8) in all fruit matrices.

The correlation analysis indicated that the *Pfs* were related to pesticides $\text{Log}K_{ow}$, photolysis, Henry constant, molecular density, and soil K_{oc} and for *Pfo* were $\text{Log}K_{ow}$, vapor pressure, molecular weight, sediment DT_{50} , and K_{oc} .

According to these results, it is possible to say that pesticides *Pf* are related to the drying process, the fruit matrix and finally, with some physicochemical pesticide properties. For that reason, if the goal is to obtain *PPF* values that will assure low or non-detectable residues, the *Pf* should be estimated considering the interactions pesticide/raw materials/drying processes. (Study supported by ANASAC Chile S.A)

Keywords: PPF, food safety, transfer factor, agroindustry.

MI-02

ATRAZINE BIOACCUMULATION AND BIOTRANSFORMATION IN CATTAIL (TYPHA LATIFOLIA) OVER THE EXPOSURE TIME.

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Atrazine (ATZ) is a widely used herbicide primarily applied to genetically modified corn fields for weed control. Due to its ubiquitous occurrence in water resources, it is considered a recalcitrant pollutant in aquatic ecosystems. Vascular macrophytes play an essential role in structuring the physical, chemical, and biological characteristics of aquatic ecosystems. *Typha latifolia* is an emergent macrophyte widely used in phytoremediation process, due to its ability to bioaccumulate contaminants. Some reports have described ATZ bioaccumulation and biodegradation pathways in terrestrial plants¹ but there is scarce information for aquatic macrophytes.² Research goals were to (1) analyze ATZ bioaccumulation and distribution patterns in *T. latifolia* tissues over the time; and (2) determine ATZ biodegradation metabolites in tissues, as desethyl atrazine (DEA) and desisopropyl atrazine (DIA). Cattails were hydroponically exposed to 20 µg/L of ATZ (18 exposed plants and 18 non-exposed control plants) at 7, 14, 21, 28, 35 and 42 days. The plants were separated into root, rhizome, stem, and base, middle and upper leaf sections. Atrazine was determined by LC-MS/MS analyses, and DIA and DEA were determined by LC-DAD. Atrazine bioaccumulation pattern, expressed as bio-concentration factor was (in L/kg): middle leaf (81.8 ± 4.8) > upper leaf (66.1 ± 4.3) > base leaf (52.8 ± 2.2) > stem (8.2 ± 0.4) > root (7.2 ± 0.3) > rhizome (5.3 ± 0.2). In belowground tissues DEA and DIA was detected. In leaves, DIA was the main metabolite rather than DEA. Results indicated *T. latifolia* has the ability to take up ATZ from the media, translocate it from root to shoot, bioaccumulate it in tissues (mainly leaf), and biodegrade via different metabolic pathways. In this sense, *T. latifolia* could be used in water phytoremediation to bioaccumulate and biodegrade ATZ.

Keywords: herbicide, biodegradation in vivo, aquatic macrophyte, phytoremediation

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MI-03**EFFECT OF THE ADDITION OF MONOAMMONIUM PHOSPHATE ON THE LEACHING OF GLYPHOSATE IN A COLOMBIAN INCEPTISOL****M. Dotor**^a, J.A. Guerrero, M.J. Martínez^b.^a *Departamento de Agronomía. Universidad Nacional de Colombia* ^b *Departamento de Química. Universidad Nacional de Colombia* mydotorr@unal.edu.co

From the beginning, glyphosate has been considered an environmentally safe pesticide due to its strong binding to soil minerals. Nevertheless, under certain environmental and agronomical conditions, for example, soils with low sorption and degradation capacity and where fertilizers and other soil amendments are applied, glyphosate can also reach water resources^{3,4}. The impact of phosphate on glyphosate adsorption in soil has been previously investigated, but an information gap exists in Colombian soils where is widely used for rice cultivation, usually inceptisols.

In this study, a rice field soil, classified as a typical Ustortheps was collected from specific region in Colombia (Espinal). The main physicochemical properties were: Organic Carbon 1.1%, clay 49.9% and pH 5.9. Infiltration assays were performed on six soil columns (30 cm length: 9 cm i.d.). A pulse was added to the columns containing non labeled herbicide (dose equivalent to 4 L ha⁻¹) and 0.312 μ Ci of C¹⁴-glyphosate. One day after herbicide pulse, a monoammonium phosphate (MAP), dose equivalent to 60 kg ha⁻¹, was applied in three of the columns. Simulated rainfall consisted in water at flow rate of 100 mL day⁻¹. The leachates were collected at the bottom of the column at 24 h intervals. The samples were analyzed using a Liquid Scintillation Counter, by mixing 1.5 mL aliquots of the effluents with 5 mL of scintillation liquid. To obtain breakthrough curves (BTCs), the relative herbicide concentration (C/C₀) versus the relative pore volume (V/V_P) was represented (Figure 1).

The results show that when glyphosate is applied alone the maximum peak in the BTCs is in average 3.4 ± 0.3 V/V_P and in presence of MAP, the maximum peak is displaced to the left, with an average value of 1.8 ± 0.1 V/V_P. The herbicide mass balance in the effluents were 5.1 ± 0.1 % and 6.2 ± 0.1 % with and without MAP respectively. Thus, the addition of MAP improved the leaching of glyphosate in the Colombian rice soil, this result agrees with other previous studies in templated soils⁵.

Key words. Leaching, soil, glyphosate, fertilizers.**References:**

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MI-04

GLOBAL RESIDUE DATA PACKAGE

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The ideal global residue package is characterized by a harmonized GAP in different geographies, number of trials that meets national and global requirements, robust representative data of different climates zones resulting in globally harmonized MRLs. This concept brings benefits for the growers who can buy new and safer technologies sooner, and trade products easily; for the regulators who can share the regulatory reviews, improve efficiency, assess robust data packages, work with mutual acceptance and rely on consistent global decisions and harmonized MRL's; and for the registrants to reach the market faster, achieve registrations in more countries, work with harmonized safety standards and achieve fewer trade issues.

However, several countries have their own legislation for Magnitude of Residues (MoR) studies with some dis-harmonization of requirements around the world. By making a comparison between the Latin America and other relevant global guidelines, differences are highlighted across different geographies such as: the number of required trials, number of at-harvest and decline trials, crop grouping, crop extrapolations, representative raw agriculture commodities (RACs) and good agriculture practices (GAPs). Since the requirements are not fully harmonized, studies targeting multiple country guidelines could provide different information and the resulting Maximum Residue Levels (MRL) can be different, triggering potential trade issues.

Another consideration when comparing Latin America legislation with other relevant legislations is the requirement for studies beyond MoR studies, for example, studies of residues in processed commodities, bee products, livestock commodities and rotational crop commodities. Requirement dis-harmonization may result in multiple residue data packages instead of a global residue data package. Ideally, all legislation will follow the OECD recommendations permitting global residue data packages that can support/complement submissions in all countries.

Keywords: Residues, Global, Package, MRL.

MI-05

ESTIMATION OF THE PESTICIDES TRANSFER RATE DURING THE PREPARATION OF *CALENDULA OFFICINALIS* PHARMACEUTICAL USE EXTRACTS

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Background: The residual content of pesticides, even in herbal medicinal materials, is of increasing concern to consumers. Pesticides are present in herbs' raw materials due to possible applications during cultivation and preservation. For the estimation of pesticide's exposure to consumers via herbal drugs, it must be required the determination of the transfer rates (TRs%) of the residual pesticides from raw herbal to the pharmaceutical preparation.. In this work, the TR% of 40 pesticides belonging to different chemistry groups (including organophosphates, carbamates, neonicotinoids, triazines, pyrethroids, imidazoles, strobirulines among others) was investigated in *Calendula officinalis*. **Work methodology:** A pesticide residues transfer simulation was performed. The pharmaceutical hydroalcoholic extracts (1:10 herb-solvent) were prepared by 24h dynamic maceration in the dark with ethanol 50% and 70% V/V (called extract and tincture, respectively) following the Brazilian Pharmacopeia. An analytical methodology was adjusted and validated for the determination of the pesticide residues in the extracts using liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS). Merit figures were evaluated; the quantification limits were between 2 and 10 $\mu\text{g L}^{-1}$ with the exception of imazalil, thiamethoxam and dicamba that have a LOQ of 25 $\mu\text{g L}^{-1}$. An important suppression matrix effects (ME) was observed for all analytes in both preparations, where around 45% of the compounds presented a strong ME (>50%), 45% present a moderate ME and only 10% show an insignificant ME. **Findings:** The relationship between the transfer data thus obtained and physicochemical properties like water solubility (Ws), octanol-water coefficient (Kow) was evaluated. The extractability of the pesticide residues from *C. officinalis* can be correlated with log Ws and log Kow. The fate of pesticide in *Calendula officinalis* extract and tincture was mainly dependent on the chemical nature of the pesticides. However, among the two prepared extracts, the tincture showed the most universal extracting capability for the all tested pesticides, due to the higher proportion of alcohol in it. The lowest TR% average ($\leq 8\%$), was obtained from biphentrin in the extract. **Improvements/Application:** This TRs% of residual pesticides could be used for the establishment of herbal drug monitoring system in the future. As *Calendula officinallis* based pharmaceuticals are widely used in breastfeeding women creams and lotions, the safety of such preparations must be strictly assessed. Hydro-alcoholic extracts are used in this type of formulations, similar to the tested in this work. Pesticide residues in *C. officinalis* should be considered by health authorities to assess safe consume of this type of over the counter products.

Keywords: herbs; pharmaceutical extracts; pesticide transfer.

MI-06

REMEDIATION OF AGRICULTURAL WASTEWATER CONTAMINATED WITH THE FUNGICIDE/NEMATICIDE FLUOPYRAM BY ABSORPTION ON DIFFERENT MATRICES

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Fluopyram is a novel broad-spectrum fungicide from the pyridinyl-ethyl-benzamide class. It has been found effective against nematodes and was registered as nematicide, too. As an extensively used pesticide, could be easily distributed in environment causing toxicity in non-target organisms or contaminating drinking water. The washing/loading sites of spraying equipment are potential point sources pollution by pesticides. Usually, the topsoil of these sites is removed and replaced by gravel and sand layers. Thus, the risk of leaching of pesticides to surface water and groundwater is increased because of poor biodegradation and sorption capacity. Consequently, the most efficient solution is removing pesticides before they are released to the ecosystem. Adsorption has been considered an effective method for pollution control. Zeolite, attapulgite, bentonite and biochar have been reported as an environmentally friendly, low cost and efficient absorbents due to their high absorption capacity. According to our knowledge there are not studies about the fate of fluopyram in these absorbents. The aim of this study is to investigate absorbents' ability to prevent the contamination of natural waters with fluopyram, coming from point sources pollution due to agricultural activity. Batch equilibrium experiments were carried out to investigate the effects of different experimental factors such as initial concentration of fluopyram and contact time between fluopyram and each absorbent. The absorption capacities were calculated by matching the results to isotherms equations. An analytical method was developed and validated for the efficient extraction of bound fluopyram residues with recoveries between 70-110%. The efficacy of the absorbents was estimated at the highest environmental relevant concentrations. The results showed that the adsorption capacity is higher in zeolite with removal efficiency of 64%. Bentonite, attalpugite and biochar reached 56%, 41% and 38%, respectively.

Keywords: absorbents, fluopyram, pollution, removal.

MI-07

WATER DECONTAMINATION BY SELECTIVE FORMATION OF MOLECULAR INCLUSION COMPLEXES OF CLORDECONA AND β -HEXACHLOROCICLOHEXANE WITH NATURAL CYCLODEXTRINS: THEORETICAL STUDY

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Surface water contamination with persistent organic compounds, including organochlorinated pesticides, is a global problem. While there are procedures for the treatment of these waters today, such as filtration in activated carbons, the search for new procedures, such as precipitation by formation of inclusion complexes, is a priority in research and development. On the other hand, mathematical modelling of the interactions of pollutant-decontaminating agents is a recently used tool to facilitate the management of water resources in the environment. This work studies the interactions between two pesticides of high environmental stability that cause serious health involvements: clordecona (CLD) and β -hexachlorocyclohexane (β -HCH), with the most common cyclodextrins (α -, β -, and γ -CD's) and the formation of their nanoaggregateds by host-receptor inclusion complexes. The training reaction of these molecular inclusion complexes is addressed in this research, as well as the main types of complexes that could be obtained. The Methodology of Multiple Minimum Hypersurfaces, quantum chemistry calculations based on Functional Density Theory, and a topological study of electron density were used to characterize the interaction space of the two contaminants with the symmetrical formulae of the three cyclodextrins (CD's). Finally, for the β -HCH@CD's complexes, a study of load distribution, load transfer and dual descriptor was used to clarify the forces involved in the formation of these nanogroups. The formation of nanoaggregates was also experimentally addressed. Three types of fundamental interactions were observed: total occlusion, partial occlusion, and external interaction (non-occlusion). The most stable complexes were obtained when γ -CD is the host molecule, as it was experimentally confirmed by spectroscopic analysis and electron microscopy results. These results suggest the usefulness of these nanoaggregates in the separation of these contaminants and the possibility of using CD's for water management, purification and treatment.

Keywords: *molecular inclusión complexes, pesticides, cyclodextrin, DFT, molecular dynamic.*

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MI-08

EFFECTIVENESS OF 2,4-D PHYTOREMEDIATION

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Plectranthus neochilus tea is used in traditional medicine for stomach pains and liver problems. This plant promoted the 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide phytoremediation in water¹. However, the technique's effectiveness, in terms of plant destiny and aqueous waste toxicity, has not been proven. Thus, this study aimed to verify the *P. neochilus* tea toxicity and water toxicity (aqueous waste) after 2,4-D phytoremediation.

Drosophila melanogaster (fly) mortality was used for tea toxicity analysis. The tea was prepared by decocting the leaves for 10 minutes, followed by cooling, filtering with cotton, and drying (rotary evaporator, 40°C). The dry extract was dissolved with 1% sucrose in distilled water (5 mg/mL). *D. melanogaster* toxicity groups (Figure 1): Control: 1% sucrose (water); Treatment: *P. neochilus* tea (plant after 2,4-D exposition in water) with 1% sucrose; Blank: *P. neochilus* tea (plant after water exposition) with 1% sucrose. *D. melanogaster* (n = 20) received the continuous liquid feed of each group every 24 hours, for seven days. The mortality was verified in triplicated with ANOVA One-Way with Bonferroni post-test. Aqueous waste toxicities were investigated with *Artemia salina* by median lethal dose (LD50) and *Allium cepa* toxicity by roots growth (cm). *A. salina* (n = 30 nauplii) concentrations: 0.1; 1; 10; 100 and 500 µg/mL. And they were analyzed in triplicated by a logarithmic curve. *A. cepa* groups (Figure 1): Positive Control (PCG), glyphosate 15%; Negative Control (NC), distilled water; Treatment 1 (T1), 2,4-D (aminol) waste after 30 days in water without the plant; Treatment 2 (T2), 2,4-D (aminol) waste after 30 days in the water with the plant; Blank Negative Control (BNC), water waste after 30 days with the plant. Significant difference between T1 and T2 were concerning PCG, NC, and BNC in duplicated by ANOVA One-Way with Bonferroni post-test. The 2,4-D (aminol) concentration used at day zero was 0.604 g/mL, equivalent to 1,209 Kg/ha of aminol. The sequence SPE-HPLC was used to verify the 2,4-D in aqueous wastes percentages after 30 days (T1 and T2) by analytical curve ($y = 60.6x - 15.824$, $r^2 = 0.9975$).

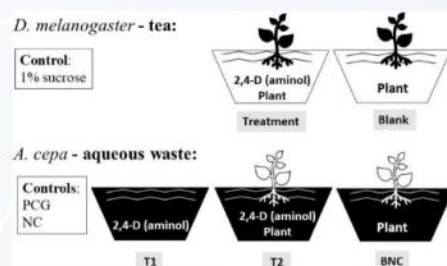


Figure 1. Experimental groups.

The treatment and blank tea groups were more toxic than the control. Moreover, the treatment group was a higher lethal than the blank group, with 100% *D. melanogaster* mortality. The LD50 of *A. salina* was 5.6 µg/mL ($r^2=0.9567$), which was greater than the 2,4-D aqueous waste detection (5.18 µg/mL and 4.42 µg/mL in T1 and T2, respectively). *A. cepa* roots growths were lower at T1 (3.35 cm) and T2 (4.63 cm) than the NC (8.56 cm). However, T1 had higher toxicity than T2 because T1 had a difference in root elongation concerning BNC (7.13 cm). Besides, just T2 had a difference in root elongation regarding PCG (1.1 cm). Therefore, tea consumption after phytoremediation is not safe. Furthermore, phytoremediation proved its efficiency by decreasing the toxicity of the aqueous medium.

Keywords: Aminol; Water waste; Toxicity; Plant.

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MI-09

PERINATAL EXPOSURE TO GLYPHOSATE AND PROPICONAZOLE IMPAIRS THE DEVELOPMENT OF THE MALE RAT MAMMARY GLAND

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Exposure to Glyphosate (GLY) during critical developmental periods induces adverse effects on the reproductive system of male rats, and we have shown that glyphosate-based herbicides produce endocrine-disrupting effects on the male rat mammary gland. On the other hand, propiconazole (PRO) has been shown to cause alterations in steroidogenesis and to be a hepatotoxic compound, which could alter the hepatic response to xenobiotics and, therefore, modify the effects induced by GLY when a mixture of both agrochemicals are used. Here, our aim was to evaluate whether developmental exposure to PRO, GLY or both (PROGLY) alter mammary gland development in postpubertal male rats. Pregnant rats were orally exposed to vehicle (saline solution), 4 mg/kg/day of PRO, 4 mg/kg/day of GLY, or a mixture of PRO and GLY (each 4 mg/kg/day), from gestation day 9 until weaning. On postnatal day 60, male offspring were euthanized, and mammary gland samples were collected. Total area, perimeter, longitudinal growth, number of terminal end buds and mammary developmental score were analyzed in mammary gland whole-mounts (WMs). Lobuloalveolar development and the presence of hyperplastic structures were evaluated in histological sections, as well as proliferation (Ki67) and protein expression of estrogen receptor alpha (ESR1), androgen receptor (AR) and aromatase (ARO). In addition, the mRNA expression of ARO, cyclin D1 (Ccnd1) and Wnt5a was assessed. Among the parameters evaluated in WM, only the total area of the mammary gland was affected in the exposed animals and it was reduced in the males exposed to GLY (Control: 492±16 mm², GLY: 419±21 mm², PRO: 436±17 mm², PROGLY: 473±19 mm²; Control vs GLY p<0.05). Regarding the morphology of the mammary gland, PRO animals presented an enhance lobuloalveolar development (p<0.05), and 27% of the animals developed lobular hyperplasias, whereas no differences were observed in the percentage of hyperplastic ducts between the experimental groups (p>0.05). In GLY males, the protein expression of ESR1 was lower (Control: 15.3±0.72%, GLY: 11.0±0.74%, PRO: 15.5±1.4, PROGLY: 12.6±1.0%; Control vs GLY p<0.05), whereas the protein expression of ARO was higher compared to Control animals (Control: 0.32±0.02, GLY: 0.43±0.02, PRO: 0.30±0.04, PROGLY: 0.29±0.02, IOD values; Control vs GLY p<0.05). The proliferation index, AR protein expression and the mRNA expression of ARO, Ccnd1 and Wnt5a were similar between the experimental groups (p>0.05). In summary, both agrochemicals alter the male mammary gland development, PRO induces mammary gland lesions, whereas GLY reduces the mammary gland area. However, these effects are not observed when males are exposed simultaneously to a mixture of both compounds.

Keywords: Male rat, mammary gland, glyphosate, propiconazole.

MI-10

BIOBEDS FOR THE BIODEGRADATION OF PESTICIDES USED IN WINE PRODUCTION

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Grapevine crops dedicated to the production of wine and table grapes are one of the most important ones worldwide. Vineyards are particular ecosystems that can be attacked by several pests and diseases. Therefore, an intensive pesticide schedule is required to meet qualitative and quantitative production standards.¹ Fungicides are the most employed pesticides in the vineyards treatments. Unsatisfactory management can give rise to pesticide residues in surface waters, groundwater and large soil volumes. On-farm practices for pesticides handling and use are the major source of contamination, being the pouring of pesticide concentrates into the spray tank, their dilution, the spraying in the field, as well as pesticide residues left on of the spray tank, the critical steps². The need to prevent the negative impact on human health and the environment has stimulated the research of innovative devices for sustainable agricultural practices. Biobeds are versatile biotechnological solutions to hamper food and environmental point contamination by wastewaters from agricultural activities, but their efficiency must be checked on a case by case basis. With the support of INIA-FPTA 353 Project: "Integrated Wine Production" managed by FUCREA, INAVI and VICCA Cooperative, a biobed was installed in Establecimiento Juanico's vineyard. The on this biobed of 10 pesticides (9 fungicides pyrimethanil, iprodione, boscalid, pyraclostrobin, difenoconazole, carbendazim, thiophanate-methyl, folpet, fludioxonil; and one insecticide: methoxyfenozide) was followed applying a validated analytical methodology. Three types of biobed design were tested in the field: (1) 50:25:25 % of bran, peat and soil respectively, (2) substituting bran for grape stem, and (3) mixture 50:50 % of soil and oat straw. After an ultrasound assisted extraction³ of the samples, and a dispersive cleanup of the extract, the residues were determined by GC & LC-QqQ-MS. The protocol was validated fulfilling the SANTE/12682/2019 guidelines. All pesticides yielded recoveries between 70-120% and RSDs <20%. In the first design, most pesticides had >75% degradation after 4 months but pyraclostrobin, difenoconazole and boscalid, showed lower degradation ratios. Similar situation was observed in the second design, where these three fungicides were not degraded in 4 months. On the other hand, the biomixture of soil and oat reached more than 60% of degradation in 4 months for all evaluated pesticides. However, all pesticides were degraded to at least 92% in the biobed using the traditional biomixture after 6 months.

Keywords: fungicides, biobeds, vineyard

Acknowledgements INIA-FPTA 353.

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MI-11

DEGRADATION OF TEBUCONAZOLE BY THE REACTION OF FENTON AND PHOTO-FENTON MODIFIED WITH GRAPHENE OXIDES

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In wastewater, the organic pollutants present that are not effectively removed by conventional methods can be treated with Advanced Oxidation Processes (POA). Among them, Fenton reactions involve the generation of oxidizing species, mainly the hydroxyl radical (HO•). To overcome the disadvantages of the homogeneous Fenton process, greater attention has been paid to the use of semi-heterogeneous catalysts.¹ Graphene oxide (GO) and related materials, reduced GO (bwGO), have been used as supports in environmental photocatalysis, by improving the adsorption of organic pollutants, increasing the separation and transport of charges for eventual degradation. In the last years the use of pesticides has contributed to improve agricultural production, providing a better quality of crops. The sale of fungicide in Argentina has grown significantly. According to the “Cámara de Sanidad Agropecuaria y Fertilizantes de (CASAFE)”, there was a significant increase in the volume of application. Tebuconazole (TEB), an azolic fungicide, have been found in aquifers in Argentina as a consequence of their intensive use.² In this work, the effect of the addition of GO and bwGO was investigated, for the degradation of TEB by the Fenton and photo-Fenton reaction. This knowledge will allow evaluating its eventual application for the remediation of contaminated environments, as well as its possible elimination of industrial effluents.

The chemical structure of GO and bwGO is dependent on carbon precursor, synthesis, and storage. Uv-Vis spectroscopy was used to identify changes in the chemical nature of the oxides, the possible interaction of the substrate with the oxides, and the degradation of TEB by the Fenton and photo-Fenton reaction in the presence of GO and bwGO. The analysis by FT-IR provided information concerning the functional groups present in the material, and the evolution of the chemical structure during the reaction time. The morphology of the sheets was studied by atomic force microscopy (AFM).

The percentage of TEB degradation by the reaction of Fenton and photo-Fenton with GO and bwGO was determined by HPLC-DAD. For the Fenton reaction, with the addition of GO, the percentage of TEB degradation at 60 minutes was 14.7%, and 42.8% for photo-Fenton. While for the same time with bwGO, the percentages were 29.5% for Fenton, and 50.9% for the photo-Fenton reaction. The rGO has a lower surface charge density, which is why low-polar molecules or AZO could be near the oxides and degrade efficiently.

From the experimental result, it was concluded that the efficiency of the Fenton and photo-Fenton reaction for the degradation of TEB largely depends on the pH, presence and structure of the graphene material used as heterogeneous support.

Keywords: Advanced oxidation processes, Azolic fungicides, Fenton, Degradation

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MI-12

RESISTANCE OF LACTOBACILLUS SPP. TO MALATHION.

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In recent years, the use of pesticides has increased as essential tools for the control of agricultural pests and vector-borne diseases, however, they are one of the main toxic substances in the environment that can contaminate food, representing an important problem of food safety and a serious threat to health¹. Malathion is one of the most widely used pesticides in Mexico and the world, and according to the FDA², it is the main pesticide detected in food products, with a presence of 18% in foods with a sanitary inspection. Its indiscriminate use has placed it as the main pesticide detected in food products, causing health problems. However, so far, there are few studies on how to mitigate the effects of pesticide residues, such as malathion, present in food, and there are no documents that talk about the resistance of *Lactobacillus* spp. to malathion, therefore, the objective of the present study was to determine the resistance of eight species of *Lactobacillus* to different concentrations of malathion and which could be used to reduce the toxic effects of malathion on health. Eight *Lactobacillus* species present in food supplements were isolated and identified by PCR and their resistance capacity to the insecticide malathion 1000® at different concentrations was evaluated using the Kirby-Bauer technique. All *Lactobacillus* species evaluated, except *L. salivarius*, were capable of growing in the presence of malathion at low doses (0.1%, 1%), however, resistance at medium doses (10%, 20%) varies between species, while at high doses (50%, 83.6%) there was no growth or the number of colonies was visibly lower compared to the control group. Taking into account the previous data we can conclude that the resistance of *Lactobacillus* spp. At different concentrations of malathion, it varies according to the species and seven of the eight species evaluated could present a potential beneficial effect when consuming food contaminated with residues of this pesticide.

Keywords: food, malathion, health.

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MI-13

AGRICULTURAL PESTICIDE RESIDUES, SMALL DOSES INDUCE PERSISTENT EFFECTS ON THE REPRODUCTIVE TRACT OF CAIMAN LATIROSTRIS, AN ENVIRONMENTAL SENTINEL SPECIES

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Agricultural pesticides comprise a group of chemical compounds, many of them classified as endocrine-disruptors (EDC) that cause harmful health effects in human and wildlife. Despite of it, the use of agricultural pesticides is the current strategy of choice when dealing with crop pest. Endosulfan (END) is a persistent organochlorine pesticide classified as an immune disruptor and an EDC with xenoestrogenic and antiandrogenic activity¹. END was used worldwide as an insecticide and, despite being banned in most countries, its presence in animal tissue and freshwater evidences its environmental presence and persistence¹. Atrazine (ATZ) is a widespread herbicide used for weed control, classified as an EDC with estrogenic and antiandrogenic activity^{1,2}. Its metabolite, diaminochlorotriazine, has been found in animal tissues and surface waters¹. The increasing transformation of wetlands into agricultural fields increases the risk of exposure to pesticide residues in non-target organisms. Caiman latirostris, a South American crocodylian species, is highly vulnerable to EDC exposure due to its long lifespan and carnivorous food habits that led it to bioaccumulate contaminants at all life stages. Exposure to pesticides is known to cause alterations in the reproductive organs of C. latirostris. The reproductive tract, or oviduct, provides the eggs with white proteins, immune peptides and the eggshell, secreted by glands. Previously, we reported that prenatal exposure to END and ATZ alters the development of the oviduct, measured through histomorphological features such as gland density¹. The aims of this study were to evaluate the long-term effects of in ovo exposure to environmentally relevant doses of END or ATZ on the development of the oviduct by assessing gland formation and their ability to secrete protective immune peptides. To this aim, caiman eggs collected from wetlands with low anthropogenic intervention were exposed to 20 ppm END, 0.2 ppm ATZ or vehicle. Hatchlings were raised under controlled conditions until the prepubertal juvenile stage. At sacrifice, the oviducts were dissected. After DNA extraction and reverse transcription, we evaluated the genetic expression of three proteins involved in gland formation and growth (MMP2, MMP9 and β -catenin) and one peptide involved in egg and oviduct immune protection (Av β D12). For such task, we designed specific oligonucleotides and assessed the genetic expression of the selected proteins by quantitative PCR. Student's t test was performed and $p < 0.05$ was accepted as significant. Results are summarized in Table 1. We demonstrated that in ovo exposure to pesticides induces the expression of proteins that regulate the formation and growth of glands, which may explain the early development of the oviduct of prepubertal juvenile previously reported. Our results highlight the role sensitive species play as sentinels of ecosystem health and that, the effects of pesticides residues cannot be underestimated.

	VEH (n=8)	END (n=8)	ATZ (n=7)
MMP2	3.20 ± 0.98	6.63 ± 2.26*	3.27 ± 0.98
MMP9	2.39 ± 0.47	3.66 ± 0.95*	2.92 ± 0.67*
β -catenin	1.23 ± 0.35	1.95 ± 0.52*	1.25 ± 0.40
Av β D12	26.16 ± 7.46	27.87 ± 5.48	26.44 ± 5.89

Table 1. Genetic expression of proteins involved in the maturation of the oviduct of *Caiman latirostris*.

Table data represent the mRNA expression levels of the selected proteins normalized by the expression of L8, a housekeeping gene. Results are expressed as mean ± SEM. The asterisk indicates significant differences at $p < 0.05$ by Student's t test.

MMP2: matrix metalloproteinase 2, MMP9: matrix metalloproteinase 9, Av β D12: Avian beta defensin 12.

Keywords: atrazine, caiman, endosulfan, oviduct.

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MI-14

INFLUENCE OF TWO COOKING METHODS OF CHARD ON IMIDACLOPRID AND SPINOSAD RESIDUES

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Leafminer flies, thrips, aphids and whiteflies are the most common pests of chard (*Beta vulgaris* var. *cicla*). Intense damage not only reduces chard yield, but also the quality of leafy vegetables. The pesticides widely used against them are imidacloprid and spinosad. The ingestion of small traces of these pesticides for prolonged periods of time can affect the health and well-being of the consumer. The objective of this work was to determine the influence of two cooking methods of chard, microwave and boiling, on the pesticides under study.

Imidacloprid OD 20% (90 cm³.hL⁻¹) and spinosad 48 SC (15cm³.hL⁻¹) were applied in a chard crop in a farm located in Rodeo del Medio, Guaymallén, Mendoza. In order to have enough residue to observe the behavior of the pesticides tested, the harvest was carried out on the same day of spraying. Two tests and uncooked control were performed with three replicates each. Boiling test (H), consisted of a pot with boiling water, added 300g of unwashed leaf chard, left to cook for 8 minutes, then drained and processed. Microwave test (M), consisted of microwave cooking of 300g of unwashed leaf chard in polyethylene bags for a 900-watt microwave oven for 5 minutes. Once cold, it was processed.

For the analysis of pesticide residues, the QuEChERS method (EN 15662) was performed. Imidacloprid and spinosad were quantified by UHPLC (ESI +) - MS / MS. To calculate the influence of the treatments carried out, they were compared to the control. Imidacloprid residues in chard were reduced 80% in treatment H and 12% in treatment M. Spinosad residues increased 33% in treatment H and 6% in treatment M. Imidacloprid assay shown a greater reduction in treatment H compared with treatment M, probably caused by the high-water solubility of this pesticide (610mg. L⁻¹). Regarding spinosad, both treatments revealed that the pesticide concentrated, probably due to the low solubility in water (7.6 mg. L⁻¹). The high level of residues from treatment H could be due to the greater weight loss of chard compared to treatment M.

We conclude that the behavior of the pesticides tested depends on the cooking methods used and their solubility.

Keyword: imidacloprid residues, spinosad residues, chard.

MI-15

OPTIMIZATION OF THE ADSORPTION PROCESS OF EPOXICONAZOLE, PENCONAZOLE AND CYPROCONAZOLE WITH CHITOSAN

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Traditional agricultural techniques involve treatments with different pesticides aimed at maintaining the production quality. Fungal diseases can cause considerable losses when they are not timely controlled. Triazoles such as epoxiconazole, penconazole and cyproconazole, are one of the most frequently used fungicides, and are applied to various crops in the Salto Grande region, Argentina.

Environmental pollution and water quality deterioration are the biggest problems associated with the pesticide usage. To minimize the pesticides levels in water, mainly for human consumption, it is necessary to apply various technological processes to remove these compounds, such as adsorption with powdered activated carbon or other adsorbents.

Activated carbon is commonly used in water purification treatments. However, there are other types of adsorbents with different characteristics. Chitosan is a copolymer obtained by partial deacetylation of chitin from seafood processing industry waste. It has a great adsorptive capacity. The use of this biopolymer emerges as a technological alternative for pesticide's removal. It has been used by various authors for metallic pollutants adsorption. However, there are few studies in the literature about its use for pesticides adsorption.

The objective of this work is to apply a Response Surface Methodology (RSM) for the optimization of pesticides removal from water using chitosan. Type 1 grade water fortified at 20 µg / l with the analytes was prepared. RSM and a factorial design were used with 2 variables: amount of chitosan (400-1800 mg / l) and contact time (20-60 minutes). Water samples with chitosan were stirred in a thermostated bath at 25 °C, with a frequency of approximately 60 movements per minute. Then, samples were filtered, and fungicides residues were extracted by solid phase microextraction, using a 100 µm polydimethylsiloxane fiber. Finally, a gas chromatography with a micro-electron capture detector determination, and a mass spectrometry confirmation were performed.

The statistical analysis of the results indicated that the optimal combination was obtained with 1800 mg / l of chitosan and 60 minutes of contact time, for all pesticides. The % reduction optimized were: 83.0%; 70.7% and 90.1% for penconazole, cyproconazole, and epoxiconazole, respectively. The optimized values were corroborated, and the % reduction obtained were 85.0%; 73.2% and 92.1% for the three compounds, respectively.

We can conclude that the maximization of the removal percentages of these analytes occurs with the highest contact time and adsorbent concentration used.

Keywords: Chitosan – adsorption – Fungicides

MI-16

QA/QC IN BEEHIVE PESTICIDE MULTIRESIDUE ANALYSIS FOR ENVIRONMENTAL BIOMONITORING

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Beehives are currently being used as environmental biomonitors of pesticide residues. Pollen, capped honey, bees and beeswax are from a chemical and analytical point of view challenging matrices. The quality assurance and quality control of their analysis must be performed in order to obtain reliable results for environmental biomonitoring purposes. Nowadays, certified reference materials are not available, neither proficiency tests nor specific guidelines for these matrices and analytes. The aim of the present work was to explore the usefulness of applying the concepts of SANTE guidelines (developed for food and feed) [1] and Shewhart charts for these particular analysis. The Shewhart chart or control chart is a well known tool to evaluate if the process is under statistical control and determine when it is necessary to analyze an eventuality. Following the ongoing quality control recommendations of SANTE guidelines a single recovery experiment of all the studied analytes was introduced in each analysis batch (15-20 depending on the matrix) since the year 2014. When the extension of the scope was performed, new analytes were also included previously conducting the initial validation. Percentage recoveries of these experiments were used to graph the Shewhart chart for each matrix and to calculate the within laboratory reproducibility, RSDwR. Results showed that most of the pesticides recoveries range between 70 and 120% with a RSDwR below 20%. Therefore, 70 and 120 % are the control chart limits which matches with the acceptance range stated in SANTE guidelines. The exceptions which showed lower limits with an acceptable RSDwR < 20% were carbendazim in bees and beeswax; imazalil in beeswax and pollen and clothianidin in pollen. Deviations in punctual batches indicated specific instrumental problems which needed to be addressed and the samples re-injected. For positive findings it is useful to look at the chart and verify that the pesticide in that batch is under control or that the sample needs to be re-analyzed. In short, the statistical tool and SANTE guidelines concepts were applicable for the QA/QC of beehives' pesticide multiresidue methods for environmental biomonitorings.

Keywords: QA/QC, pesticides, beehive.

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MI-17

DEVELOPMENT AND VALIDATION OF AN LCMSMS METHOD FOR THE QUANTIFICATION OF VETERINARY DRUGS IN MUSCLE, KIDNEY, LIVER AND FAT

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The authorization for the commercialization of a new veterinary product in Argentina demands the approval of SENASA. It requires a series of studies, one of which is a depletion study. The present method was developed and validated to be the analytical support for depletion studies of some active substances and their metabolites.

The simultaneous quantification of cypermethrin, spinosad A and D, fipronil, fipronil sulfone, enrofloxacin and ciprofloxacin using deltamethrin, fipronil desulfinyl and enrofloxacin-d5 as internal standards and abamectin as a recovery control standard, in muscle, liver, kidney and fat was achieved. Except quinolones were not included in fat.

A previous QuEChERS method ⁽¹⁾ was modified for the incorporation of quinolones to the scope, which requires the addition of acetic acid to the acetonitrile extraction and the removal of PSA from the clean-up. The determination in fat needs the dilution of the fat in hexane before the extraction with acetonitrile and water.

The extracts were dilute in a 1:5 relation for fat, and 1:2 for the rest of the matrices, and then analyzed in a LCMSMS Acquity Xevo TQD. The separation was obtained with a gradient of methanol and water with 0.1% formic acid and 5 mM ammonium formate. The addition of ammonium formate allows the inclusion of pyrethroids in the scope but decreases quinolones signal. The column used was C18 Acquity BEH 2.1 x 100 mm 1,7µm. The ionization was ESI negative and 0.6 kV for fipronil group and positive with 3.0 kV for the rest of the analytes with N₂ at 900 l/h and 500°C for desolvation.

The quantification strategy adopted was surrogate standards and IS, except for spinosad A+D where the abamectin was used a recovery control only.

Three complete validations in a laboratory working according to ISO 17025 were done for the matrices muscle, kidney and liver and fat for the species bovine and ovine. All the calculated parameters for all the analytes and matrices achieved the required limits for linearity, repeatability, intermediate reproducibility, detection limit, recovery and uncertainty required for these methods.

For example, limited detection and average recovery in muscle: 0.35 µg/kg for fipronil (103%) and fipronil sulfone (97%); 5 µg/kg for cypermethrin (105%), 8 µg/kg for spinosad A+D (93%) and 8µg/kg for enrofloxacin and ciprofloxacin. The repeatability CV% was in the range of 4-18% and the CV% of intermediate reproducibility was 7-18%, depending to analyte and concentration. The expanded uncertainty was from 14 to 36% in muscle.

Keywords: lcmsms, veterinary drugs, quechers, validation

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Risk Assessment

R-01

ARE PESTICIDE RESIDUE LEVELS AND MRLS AFFECTED BY SEASONAL VARIABILITY?

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Pesticide residues present in fruits or other agricultural products are commonly concentrated during the drying process. Knowing this, when a MRL is defined for one pesticide that will be use in some raw materials, which will be utilized to elaborate dried products, is fundamental to estimate the processing factor (Pf) for the utilized pesticide. However, to obtain dry products the raw material could be subjected to a different method, like sun drying (direct or indirect), oven air drying, microwave drying, vacuum drying, freeze drying, and some mixture of these procedures. The question are if the Pf value would be affected by the drying technique and if the raw material, under the same drying process, could affect the Pf.

Variability of pesticide residues obtained from crop field trials is known to be a significant factor in the field of residue chemistry. It is not unusual for pesticide residues in harvestable crops to vary by more than 10X despite identical product use parameters (application rate and timing, pre-harvest interval, etc). Factors that lead to the variability of results can include temperature, rainfall, crop variety and local agronomical practices. It is important to consider if seasonal variations within a region significantly affect pesticide residue levels. Is it necessary to conduct residue trials over multiple seasons or a would greater number of trials in one season be sufficient to capture the full range of residue values needed to set a suitable robust MRL?

This poster investigates the residue profiles of several crop-active ingredient combinations from residue trials conducted in Argentina across single and multiple seasons. Residue variability as demonstrated by parameters such as standard deviation and median are compared within single seasons and across multiple seasons from Argentina, and a comparison from results from the same crops in other regions.

The result of this comparative provides an interesting overview and opens possibilities for future investigations on the behavior of residues and consequently to the MRLs (maximum residue levels) derived from trials conducted across multiple seasons and MRLs derived from trials conducted within a single season.

Keywords: Residue, Variability, Seasonality, Argentina

R-02

EVALUATION OF FIFTEEN LEACHING INDEXES FOR HERBICIDE ENVIRONMENTAL RISK ASSESSMENT IN FORESTRY PLANTATION. LYSIMETER AND FIELD STUDIES.

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Weed control has been one of the most significant factors of establishment practice that can improve large term growth of radiata pine and eucalyptus. Herbicides represent the most effective and convenient way of weed management and they are applied normally just one or twice during the two first years after planting. Thus, the environmental concern about this relevant industry is focused because of the vast herbicide treated area, which is usually located near water reservoirs (i.e lakes) or areas in which rivers and creeks originate. Even though, predictive models can help to determine the environmental dynamic of herbicides used in forestry production; they are highly demanded in data resources and require qualified users to manage them. On the other hand, the *Leaching Indexes (LI)* are easy to use and are useful to perform screening analysis oriented to evaluate compounds according to their relative risk to contaminate groundwater. However, the question is how related are the *LI* estimations with the real herbicides leaching risk under forestry field conditions.

During 2019 and 2020, laboratory studies were performed to determine sorption and degradation coefficients for terbuthylazine, hexazinone, metsulfuron-methyl, triclopyr, glyphosate, indaziflam, flazasulfuron, and fluroxypyr, in five Chilean forestry soils. With the obtained results and physico-chemical herbicide properties, a screening analysis was performed utilizing the following *LI*: Hamaker's *Rf*; *GUS*; Briggs's *Rf*; *LIX*, *LEACH*; *M.LEACH*; *Hornsby Index*; *LIN*; *GLI*; *PLP*; *Rf-EPA*; *AF-Rao*; *AFT-AFR*; *YASGEP*; and *McCall*. Screening results were compared to herbicide leaching obtained from disturbed soil lysimeters experiments (PVC columns: 0.11-m diam. and 0.9-m long) and also to the herbicide leaching under field studies, which were performed in two relevant areas of Chilean forestry production. The results showed good correlations between leaching risk assessment with *M.LEACH* ($r=0.5219$; $p<0.0001$) and *GLI* ($r=0.4941$; $p<0.0001$) and the soil deep reached by the herbicides under disturbed lysimeter experiment, but only *M. LEACH* correlated with the amount of herbicide leached below 30 cm ($r=0.5023$; $p<0.0001$).

When the leaching screening results were compared with the the soil deep reached by the different herbicides under field conditions, only *PLP* showed a significant correlation ($r=0.5247$; $p<0.0001$). However, results from Briggs's *Rf* (0.8078; $p<0.0001$) and *LIN* ($r=0.6711$ $p<0.0001$) showed a significant correlation for the amount of herbicide leached below 30 cm of soil depth.

According to these results, it is possible to indicate that *LI* are a good tools for pesticide leaching risk assessments, but not all of them will offer a good approach to the real herbicide leaching potential under field conditions. For that reason, if the user does not have a validated *LI* under his own conditions, the results obtained from this tool should be considered only as a general reference. (Project supported by CMPC)

Keywords: Leaching, risk assessment, water, contamination.

R-03

ENHANCEMENTS OF CODEX MRLS

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Codex has been setting pesticides MRLs for more than 50 years at a productivity level of 200-400 MRLs per year. However, most advanced national agencies are setting more than 1,000 MRLs per year, which creates an ever-growing gap between national and international MRLs. This presentation is based on an analysis of MRL regulations at Codex and main agencies setting MRLs and is recommending a set of options ('tool-box' concept) for further enhancements of the Codex-system to increase the MRL productivity, and to achieve true global harmonization through a ONE-MRL system. Some of the options can also serve as basis for countries that intend to develop a local system for MRLs and need new, or updated MRL regulation. In addition to stimulating actions towards increasing productivity for missing MRLs, the recommendations will also increase harmonization of MRL values across countries and should increase acceptability of Codex MRLs from about 70 countries currently, to all 188 member countries.

Keywords: codex, enhancements, ONE-MRL

R-04

COMPARATIVE ANALYSIS OF MULTIPLE RESOURCES OF CONSUMPTION DATA

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The present work deals to developing an impedimetric biosensor for the detection of chlorpyrifos using the nanocomposite formed by montmorillonite (SWy-1) clay modified with a molecule that mimics the active site of the enzyme acetylcholinesterase (SWy-1-M). Chlorpyrifos is an organophosphate insecticide widely used in the control of domestic pests and in agriculture in different cultures. However, its use should be cautious, as it can lead to serious damage to human health, since small amounts can quickly inhibit the activity of the cholinesterase enzyme, and block the transmission of

The dietary exposure assessment (DEA) is performed to scientifically estimate the risk to human health due to exposure via diet to food treated with pesticides as a role for authorization of these products. It allows to identify, implement appropriate measures and communicate to all involved about the control of the risks. Some countries have a more advanced legislation and perform a national evaluation, while others use Codex standards as a basis, as most countries in the Latin America, excepted by Brazil, Mexico and Argentina.

An important data basis for exposure assessment is the consumption data, provided by a national survey where the dietary habits are statistically treated. Whereas a national survey is not available, there is the possibility of using the cluster diets from GEMS (Global Environment Monitoring System) implemented by World Health Organization in cooperation with a network collaborating centres and national institutions around the world.

The objective of this analysis was to compare the data from different resources in Latin America (Brazil¹ and Mexico²) with GEMS³ to understand how some differences among countries of a same cluster might affect the exposure when compared with individual national data. Focus was in Latin America countries where the dietary exposure assessment is performed with national data. They take part of G5 cluster diet.

Food of animal origin and feed items were not evaluated since they are not considered in the DEA of the respective countries.

Keywords: dietary risk assessment, national consumption data, GEMS

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R-05

PESTICIDE USE COMPARISON BETWEEN LATIN AMERICA AND EUROPEAN UNION. ARGENTINA AND CHILE AS STUDY CASE

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Bees, the main pollinators of wild and cultivated plants, are suffering for a huge decline in recent decades caused by several factors, including the increase of pesticide use. A wide range of these compounds are used in conventional agriculture to control pests and weeds though they could have numerous negative effects on bees, depending partly on their chemical group, concentration and route of exposure. In Latin America (LA) most countries are food producers but at the same time, pesticide regulation is absent or weak. Conversely, in the European Union (EU) regulation is very strong and they have also adopted a strategy of sustainable use of pesticides. In order to describe pesticide use regulation in developing countries, we explore differences in government authorization between two Latin American countries. For that purpose, we selected five focal crops (i.e. wheat, corn, soybeans, sunflower and apple) and analyzed the active ingredients authorized in Argentina and Chile for each one of them. We considered the number of allowed pesticides, their identity, chemical classification, type, maximum residue levels (MRLs) in honey and honey bee LD₅₀. Then we compared the regulation status of each of these products with the EU one. In the five crops, a total of 385 pesticides are approved in the two American countries (Argentina: 234; Chile: 269), with high differences in the number of pesticides admitted per crop for each country. Among these 385 pesticides, 125 (35.9%) are not approved in the EU, being 30.4% herbicides, 28.8% insecticides and 12.8% fungicides, among others. Regarding the toxicity to honey bees, we found 27 insecticides of high toxicity while herbicides and fungicides present generally slight or low toxicity. However, pesticides of high toxicity are authorized in all studied crops for both countries (range: Argentina 10-21; Chile 4-17). On the other hand, we found that both Latin American countries partially or completely lack national regulations regarding the MRLs in honey for domestic consumption. The backward regulations on pesticide use shown by these two Latin American countries implies a much higher risk for bees and pollinators, and also for humans and improvements on this matter should be urgently taken.

Keywords: Agriculture, *Apis mellifera*, Pesticides regulation, Pollinators decline.

R-06

PRELIMINARY BEES RISK ANALYSIS OF PESTICIDE RESIDUE FINDINGS IN HIVE MATRICES

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Bees are highly valuable because they provide the ecosystem service of pollination. The exposure to pesticides highly used in agriculture may affect human health and the environment in different ways. Agrochemicals might affect bees among other non-target organisms. For these reasons it is very important to study the exposure, effects caused and risks posed by pesticides on bees in real agroecosystems. The principal routes of exposure of pollinators are: direct contact, consumption of contaminated pollen, nectar or water and in some cases contact through contaminated flowers and foliage. EFSA and EPA guidelines have been developed for notifiers and authorities to review pesticides with regulatory purposes. These documents provide guidance for the risk assessment of pesticides on bees within that context. They are both based on the risk quotient approach, which involves comparing through a quotient the exposure with the effects in order to evaluate the risk. Aiming to perform a risk assessment of the pesticide residue findings in beehives placed in different agroecosystems, the same principle was followed. Residue analysis for 104 pesticides was performed in a total of 192 samples of honeybees, beeswax, pollen and honey were performed and 47 findings were assessed. The concentrations ranged from 0.0016 to 0.27 mgkg⁻¹ corresponding to 30 different pesticides. The risk quotients were calculated using the concentrations determined in pollen and nectar. The BeeRex tool from EPA was used to evaluate the exposure of the pesticides because it takes into account bee's food consumption according to their life stage and caste or task in hive. The toxicological values to estimate the effects used were adult contact and oral acute LD₅₀ (worst case from 24, 48 and 72 hour values - µg bee⁻¹) from PPDB database. The results of the risk quotients calculated were below 0.4 which is the Level of Concern defined by EPA and indicates low risks. It needs to be pointed out that this evaluation is performed as if honeybees were exposed to only one pesticide at a time while our results show between 2 to 16 different detections in each sampling. On the other hand, pesticide residues in beeswax were frequently found and also be a source of exposure for bees, particularly for larvae. The quotients between these concentrations and contact acute LD₅₀ were calculated and pesticides were ranked according to them. Cypermethrin and Chlorpyrifos resulted in the ranking top. The obtained results highlight the importance of further research in this field and deliver important information for pesticides risk based prioritization for future studies.

Keywords: Risk, Bees, Pesticides.

R-07

ECOLOGICAL RISK ASSESSMENT OF PESTICIDES IN THE MEDITERRANEAN RIVER BASIN (MIJARES RIVER) IMPACTED BY CITRUS PRODUCTION

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Pesticides are compounds used worldwide in many sectors, especially in the agricultural field. These compounds are necessary in crop production to improve soil performance and increase the quality and quantity of daily product consumed. Then, population growth is associated with the use of pesticides, although a considerable amount of synthetic pesticides can adversely affect the health and the environment 1. The main entry routes of pesticides to surface water ecosystems are runoff, spray-drift and leaching. Additionally, wastewater treatment plants (WWTPs) can also discharge pesticide mixtures 2.

Advances in analytical instrumentation have allowed the detection of extremely low concentrations (ng/L) of these compounds and/or their transformation products (TPs) in different bodies of water 3. The hybrid quadrupole-time-of-flight (QTOF) analyzer has been frequently coupled to both LC and GC for screening of pesticides/TPs. The screening methods based on high resolution mass spectrometry (HRMS) allow the detection of a wide list of compounds and help to prioritize those that are more frequently found in environmental samples. The application of HRMS-based screening methods is of great help to focus the subsequent quantitative analysis, especially for LC coupled to tandem mass spectrometry (MS/MS) with triple quadrupole (QqQ) analyzer.

The aim of this study was to investigate the occurrence and ecological risks of pesticides/TPs in a Mediterranean river basin (Mijares River) sited in Spain and impacted by citrus agricultural production. Nineteen sites (57 surface water samples) were monitored in three campaigns distributed over three different seasons. After a qualitative screening (LC-QTOF MS and GC-QTOF MS), 24 compounds were selected for subsequent quantitative analysis (LC-MS/MS). The lower section of the river was the most contaminated, with a total concentration >5 µg/L in two sites near to the discharge area of WWTPs. The highest concentrations were found in September, after agricultural applications and when the river flow is generally reduced. Ecological risks were calculated using two mixture toxicity approaches: Toxic Unit 'TU' and multi-substance Potentially Affected Fraction 'ms-PAF' calculated on the basis of Species Sensitivity Distributions 'SSDs'. The results revealed high acute and chronic risks of imidacloprid to invertebrates, moderate-to-high risks of diuron, simazine and 2,4-D for primary producers, and moderate-to-high risks of thiabendazole for invertebrates and fish.

This study demonstrates that, while intensive agricultural production is the main source of pesticide contamination in the Mijares River, freshwater biodiversity is primarily threatened in areas near to WWTPs and downstream of post-harvest citrus processing plants. Further actions are needed to control pesticide use and environmental emissions in agricultural areas of eastern Spain dominated by citrus production.

Keywords: Pesticides, Chromatography coupled to mass spectrometry, Ecological risk assessment, Mixture toxicity

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R-08

PESTICIDE REGISTRATION APPROACHES AND TECHNOLOGICAL ADVANTAGES IN THE AGRICULTURAL SECTOR: CAN LEGACY PESTICIDES BE RECONSIDERED IN AGRICULTURAL PRODUCTION?

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Soybean crops are one of the most affected by insects, especially stink bugs and defoliator caterpillars such as *Rachiplusia nu* and *Anticarsia gemmatalis*. Insecticide application is usual as pests exceed the action threshold in almost all crop cycles. This work's aim to study the residual effect of selected insecticides currently used in soybean crops and determine their dissipation curves in leaves and soil, to establish a relationship between the residual concentration and the mortality of a colony of larvae fed with the field-treated leaves. The field experiment was carried out on a soybean crop by randomized plot design with three treatments, chlorpyrifos (900 cc/ha), triflurumuron (90 cc/ha), and control (without application) with four replicates. Leaves and soil samples were collected at different times and taken to the laboratory.

Field control efficacy

Environmental risk assessment of pesticides is usually conducted by applying pre-registration (toxicity tests and fate assessment using predictive models) and post-registration methodologies (toxicity tests and measured concentrations from monitoring studies). Various pesticide registration approaches have been adopted by the different countries with the European and USA's ones being the most popular. The pesticide registration process involves a scientifically-based evaluation of the data provided by the pesticide company, legal requirements, administrative procedures and finally a policy decision based on prevailing safety standards. Latin American countries are currently develop or have been developed complicated pesticide registration and risk assessment process similar or based on European or USAs ones.

Technological advantages in precision agriculture, pesticide application technologies, plant phenotyping and pesticide risk mitigation practices could help in the reduction of the risk of unauthorized or other legacy pesticides. Insights and challenges on the pesticides-based weeds / diseases /pests management, pesticide resistance, pesticide tolerant crops, pesticide environmental fate, pesticide risk assessment, pesticide prioritization and of pesticide registration process will be discussed. The major questions that we are trying to reply is "Can legacy pesticides be considered as alternatives for resistance management under new technological advantages in precision agriculture?"

Stacked multiple-pesticide-resistant crops will expand the use of currently available and maybe few legacy pesticides. Now it is more important than ever to find ways to utilize currently and maybe legacy available pesticides. Despite the high cost to discover, develop, register and commercialize a new pesticide the industry has increased its efforts to find new pesticides with novel mode of action incorporating new technologies during various stage of the development. The results of these efforts are expected in near future, in the meantime, reconsideration of the existing pesticides or re-registration of legacy herbicides for mixture application could be a good resistance management practice. There are various registered or banned (legacy) pesticides that can be used for weed control in various crops. In this presentation we study various scenarios that can be applied in large scale monoculture usually cropped in Latin American countries. Our case studies were assessed in terms of environmental risk resistance management and efficacy. Different scenarios of occupying new technologies have also been taken into consideration.

Keywords: pesticide registration; prioritization; risk assessment; resistance management.

R-09

DIETARY RISK ASSESSMENT – OPPORTUNITY TO IMPROVE CONSUMER SAFETY

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Daily, people worldwide are exposed to a variety of chemical substances through different routes. Many of these are non-intentional exposures, such as metabolites of antibiotics, contraceptives, dyes, toxins and even drugs that can be detected in many sources of exposure. Several efforts are being permanently done by developers and authorities in order to advance in Science and regulations with the aim to assess Safety of compounds which on the other hand have been developed to bring many benefits to the world.

One of the strongest efforts is seen when it comes to pesticides, once active ingredients are exhaustively tested in many fronts: i) toxicological studies are conducted under strict guidelines, so it is possible to understand potential adverse effects at many dose levels and a safe dose can be established along with safety factors that should be applied to assess risks of exposure; ii) metabolism studies are run and their results show if there are other compounds coming from degradation and/or metabolism that should also be taken into consideration when assessing safety, and iii) residues studies in all representative crops that will be applied for registration are available in order to measure concentrations in edible parts. Another critical parameter to be considered in an assessment is the estimates of population food consumption, then the magnitude of exposure can be calculated.

Sometimes, the generation of data is not possible to cover all the specific scenarios; however, international guidelines have been developed in order not to over test unless it is fully reasonable, in order to make the best use of resources and appropriate prioritization. In that sense, extrapolating between different residue studies is routine and assessors can identify most critical scenarios among various doses, crops, number and timing of application, making sure it does not impact the assessment robustness. There are some international guidelines that can be followed as basis for extrapolations^{1,2}.

When considering consumption data, although most of the countries in LatAm does not conduct periodic surveys to address consumption, World Health Organization (WHO) provides 17 cluster model diets in its website³ that represent a pragmatic approach to be used to assess risk coming from different crops.

Even if extrapolation of residue data and estimated consumption are necessary, the combination of these four items ends in a scientifically sound dietary risk assessment, enough to judge whether the intake of a residue is safe or not.

Keywords: dietary risk assessment.

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R-10

A FIRST APPROXIMATION TO THE ADJUSTMENT OF PESTICIDE USE AND THEORETICAL MRL AND ADI ACCOMPLISHMENT IN FRUITS AND VEGETABLES IN URUGUAY

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Pesticide residues in fruits and vegetables (F&V) are of primary concern as these foods can be usually consumed as such. Little if any processing is done before their consumption apart from peeling and washing, depending on the type of F&V considered. Because of that, monitoring programs are performed all over the world to ensure legal MRL's accomplishment. The MRLs pursue two main objectives: to enforce Good Agricultural Practices accomplishment and protect consumers' health. In Uruguay, the number of legally allowed pesticides dropped from 453 to 285 active principles during the past decade. For instance, no pesticide of toxicological Level I is permitted in the country.

In this work, thorough research on the active principles employed in Uruguay in F&V was performed. Of 233 pesticides registered for the 35 most cultured and consumed F&V in the country, 72 are insecticides, 60 are fungicides, and 101 herbicides. Among the insecticides, 20 were OPs, 10 carbamates, 11 pyrethroids, 6 neonicotinoids, and 25 belong to other chemical classes (matrine, azadirachtin, spinosad, abamectin, chlorantraniliprole a.o.). Most of the 60 fungicides active principles belong to the dithiocarbamates, Cyt-P450 inhibitors, and strobilurins chemical classes.

A deterministic approach for evaluating chronic dietary risk for pesticide intake was performed following the recommended procedures by the World Health Organization (WHO) for chlorpyrifos, an insecticide from the organophosphate class, and the two most employed dithiocarbamates in Uruguay: Mancozeb and Ziram. The National Maximum Theoretical Daily Intake (IDTMN) was calculated using consumption data of fruits and vegetables of the National Survey of Household Expenditure and Income (ENGIHS), the Accepted Daily Intake (ADI), and the Maximum Residue Limits (MRL).

As a result of the deterministic analysis, chlorpyrifos theoretical intake represented 92% of the IDA value below the safety limits. Nevertheless, as chlorpyrifos is allowed to be used in other highly consumed commodities such as cereals and grains, the maximum value of IDA for it can be easily reachable.

In the case of dithiocarbamates, the results varied depending on the studied compound. The MRL for the whole chemical class is expressed as mg of CS₂/kg sample, and correction factors for each specific compound must be applied to assess dietary risk assessment. Within this context, Mancozeb represented 48% of the IDA and Ziram 427% IDA.

The results of a monitoring program on a seasonal basis of pesticide residues in fruits and vegetables will be presented to refine the values obtained with the theoretical calculations; aiming to verify the adjustment of the established MRLs to the Uruguayan diet will be presented and discussed.

Keywords: Pesticide residues; MRLs, Uruguayan diet, Risk Assessment.



RALACA

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