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Pesticide residues in fruits and vegetables of the argentine domestic market: Occurrence and quality

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ABSTRACT

The presence of pesticides in fruits and vegetables has been a growing concern in Argentina. Only three of the major marketplaces there have the necessary infrastructure to determine pesticide residues in produce. The aim of this study was to investigate the presence of such residues in nationally produced fruits and vegetables for domestic consumption in order to evaluate the present state of the market. A total of 135 of the most widely consumed fruits and vegetables were analyzed for 35 pesticides. The analyses utilized a *QuEChERS*™ multi-residue-extraction kit along with tandem gas chromatography–mass spectrometry. The results were evaluated according to maximum residue limits (MRLs) for each commodity and pesticide according to national regulation. Pesticides were detected in 65% of the total samples, in 44% of the positive samples at or below the MRLs, and in 56% above the MRLs. Oranges had the highest pesticide concentration detected, but carrots had the highest frequency of noncompliance among the produce items sampled. Five pesticides were detected at frequencies above 10%, the highest being chlorpyrifos in 25.9% of the total samples. In other countries, the percentage of samples above the MLR is 4 times lower than our findings, and 7 times lower for exported products. An implementation of programs designed to facilitate awareness, capacitation, and monitoring is urgently recommended.

1. Introduction

Horticulture and fruticulture in Argentina are characterized by a wide geographical distribution and a diversity of produce types. At an estimated annual production of 8.3 million tons of fruits and 10 million tons of vegetables (MAGyP, 2014; ME, 2010), those two agrarian aspects of the social and economic sector have the capacity to satisfy the domestic demand and strongly contribute to the daily food requirements of the nation's population.

The national production of fruit (in millions of tons) mainly involves grapes (3), citrus fruit (2.7), pomaceous fruit (1.5), and stone fruit (0.4); with the remainder of the production consisting of tropical crops (avocado, banana, mango) plus nuts and fine fruit (strawberries, blueberries). Argentina is the eighth largest citrus-fruit producer internationally and the world leader in the production of lemons (AAIyCI, 2017). Citrus fruits constitute the main class within the national fruit industry, representing about 50% of the total fruit of the country. The destination of sweet citrus is mostly the domestic market, accounting for about 60% of the volume of orange and mandarin produced. The internal consumption of orange is 13.2 kg/person/year and mandarin 5.2 kg/person/year (MHyFP, 2016).

The provinces with the highest horticultural production (by cultivated area) are Buenos Aires (19.7%), Mendoza (15.0%), and Córdoba (10.4%). Root vegetables (potatoes, onions, carrots), tomatoes, and lettuce represent 65% of the total production; total zucchini, eggplant, and bell pepper 20%; and other vegetables the remaining 15%. The main destination of these products is the domestic market (> 93%). On the average, an estimated 85% of the volume of vegetables produced is consumed fresh, with only 8% being industrialized (Colamarino, Curcio, Ocampo, & Torrandell, 2006). Potato represents one-third of the total vegetable consumption in kg/person/year at 25.6; while tomato (at 13.5), onion (at 9.9), carrot (at 4.7), and lettuce (at 2.8) make up almost the other two-thirds (Zapata, Rovirosa, & Carmuega, 2016). The latter breakdown is significant within the present context because most of that consumption is fresh. Bell pepper is almost exclusively grown in greenhouses in Argentina, with an apparent domestic consumption of

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1.1 kg/person/year (SINAVIMO, 2014).

As the global demand for fresh food grows steadily—and an increase of 13% is anticipated over the 2015–2020 forecast period (IFT, 2016)—the application of new production technologies, mainly those based on the use of pesticides, has likewise increased (Bakırcı & Hişil, 2012). This approach to production requires the use of pesticides on a large scale—up to 20 times more than routinely used in the extensive monoculture of grains and oilseeds (DP, 2015, p. 533). Both upon direct application and through the environmental dynamics of pesticides, fruits and vegetables can incorporate those substances (Trapp & Legind, 2011). The incorrect use of pesticides can result in high and detrimental concentrations of these compounds in the final produce (Bakırcı, Yaman Acay, Bakırcı, & Ötleş, 2014). This contamination leads to possible routes of exposure to the population, both as a result of those environmental dynamics and through food-consumption habits, the latter being the greater source of risk for human health (Boobis et al., 2008).

Pesticides are known to be a public-health issue and have been linked to a wide spectrum of human illnesses, ranging from acute ailments to chronic diseases, such as cancer, reproductive disorders, and endocrine-system dysfunctions (Weisenburger, 1993). Thus, the levels of such contaminants should be frequently monitored. Nowadays, food-control programs for pesticides are carried out worldwide in order to protect consumer health, improve agricultural-resource management, and prevent economic losses (Arias, Bojacá, Ahumada, & Schrevens, 2014). That surveillance focusses on compliance with maximum residue limits (MRLs). An MRL is the maximum concentration of a pesticide residue (expressed in $\mu g.kg^{-1}$) legally permitted in or on food commodities (MSAL, 2013). These MRLs limit the types and amounts of pesticides that can be legally present in foods, typically based on the proper application of pesticides according to good agricultural practices in controlled field experiments (Fothergill & Abdelghani, 2013). Nevertheless, in order to properly evaluate food safety, the limits should be set upon consideration of the consumption patterns of different foods and the toxicologic-endpoint values, such as the acceptable daily intake or the acute reference dose. In addition, the norm does not take into consideration the cooccurrence of different residues in the same food item, where possible effects (additive or synergic) as a result of exposure to more than one pesticide have not yet been demonstrated (Hjorth et al., 2011). For any of these reasons, the overall quality of the produce could be affected (Arienzo, Cataldo, & Ferrara, 2013).

In Argentina, since only three of the large wholesale fruit and vegetable markets have the infrastructure to determine the presence or absence of pesticide residues, the rest of the larger urban conglomerates cannot perform controls in their markets. Moreover, with the Central Market of Buenos Aires serving approximately half of the demand of the Metropolitan Region, the ability to properly control the quality of fresh produce becomes greatly diminished since producers that knowingly do not comply with legislation can direct their fruits and vegetables to those remaining wholesale markets operating within Greater Buenos Aires (MSAL, 2014). In view of the minimal control and lack of available relevant information with respect to the most commonly used pesticides (DP, 2015, p. 533), the objective of this study was (1) to investigate the presence of such contaminants in fruit and vegetables so as to establish the true present state of the national market, (2) to ascertain whether or not adequate agricultural practices are being employed, and (3) to compare this domestic situation with the corresponding circumstance in other markets abroad. The information generated can be used as a reference point for future monitoring programs and national health policies.

2. Materials and methods

In 2015, we collected 135 samples from local markets and for the screening selected the active substances from 35 commonly used pesticides including several organochlorine (aka *legacy*) compounds (DP, 2015, p. 533). The samples were analyzed by tandem gas chromatography–mass spectrometry (GC-MS) to determine if the products were in compliance with the existing national regulations limiting the total amount of pesticide residues legally allowed on food crops to be used for human consumption.

2.1. Fruit and vegetable samples

The products analyzed were produced in different regions of Argentina and were not intended for export, but rather for domestic consumption. A total assortment of samples of different fruits and vegetables (28 lettuces, 41 oranges, 23 peppers, 10 tomatoes, 33 carrots) were purchased from randomly selected greengroceries from La Plata (population of 899,520) and the Autonomous City of Buenos Aires, the Federal Capital (population 13,592,000), both cities from the Metropolitan Area of Buenos Aires (INDEC, 2010). We chose different types of samples taking into consideration that since produce has a wide national consumption, those products had followed conventional routes of commercialization and that such produce is often not cooked before being eaten (Chen et al., 2011). After purchasing, the samples were immediately transported to the laboratory and thereafter kept at 4 °C for no longer than 24 h before performing the analysis (FAO, 1993).

2.2. Chemicals and reagents

Pesticide-residual-grade n-hexane, HPLC grade acetonitrile and glacial acetic acid were obtained from J. T. Baker (Phillipsburg, NJ, USA). A Sartorius Arium™ water-purification system (Sartorius AG, Göttingen, The Netherlands) was used to obtain nanopure water in the laboratory. Isotopically labeled atrazine (ATZ-D_5) was acquired from Sigma Aldrich (St. Louis, MO, USA). Certified standards of pesticides as standard stock solutions at 1000 $\mu g.L^{-1}$ in n-hexane were obtained from AccuStandard, Inc. (New Haven, CT, USA). *QuEChERS*™ kits (*DisQuE*™, product #176001676) and graphitized carbon black were purchased from Waters Associates, Milford, MA.

2.3. Extraction procedure

One kilogram of unwashed sample with the skin intact (Bakırcı et al., 2014; FAO, 1999) was first comminuted then homogenized in a blender to obtain thoroughly mixed homogenates. The homogenates were analyzed according to the Official Method 2007.01 of the Association of Official Analytical Chemists (AOAC, 2011). The procedure stated in brief: 15 g of homogenized sample were weighed in a 50-mL polypropylene tube. ATZ-D_5 was used as an internal quality standard (Anastassiades, Maštovská, & Lehotay, 2003). Next, 15 mL of 1% (v/v) acetic acid in acetonitrile were added along with 6 g anhydrous $MgSO_4$ + 1.5 g anhydrous sodium acetate. The closed tubes were shaken manually for 1 min and centrifuged for 10 min at 3000 g. One mL of supernatant was transferred to a 2-mL polypropylene mini-centrifuge tube containing 150 mg anhydrous $MgSO_4$ + 50 mg primary-secondary amine + 50 mg graphitized carbon black for clean-up. The extract was shaken manually for 1 min and centrifuged for 5 min at 3000 g. An aliquot of the extract ($\approx$0.5 mL) was transferred to GC vials, dried under a stream of nitrogen, and finally resuspended in the same volume of n-hexane (Maštovská & Lehotay, 2004).

2.4. GC-MS instruments and equipment

Pesticides were identified and quantified in a Perkin Elmer Clarus 580 gas chromatograph coupled to a Clarus SQ 8S single quadrupole mass spectrometer (Perkin Elmer, Wellesley, MA, USA). The GC system was equipped with a Phenomenex Zebron ZB-SemiVolatiles™ column (30 m × 0.25 mm i.d. x 0.25 μm film thickness). A volume of 2 μL of sample was injected in the splitless mode (injector temperature, 270 °C) with temperature-gradient separation: accordingly, the oven ramp was

set at an initial temperature of 80 °C that was held for 2 min, then increased to 300 °C at a rate of 10 °C min^{-1}, and finally held for 3 min to give a total running program of 27 min. The chromatographic conditions were as follows: a helium flow of 1 mL min^{-1} with the transfer line set at 300 °C and the source at 180 °C. The ionization was carried out by electronic impact in the positive mode at 70 eV with the mass range set between 1.0 and 1200 atomic-mass units for pesticide characterization (scanning mode) and pesticide quantification (selected-ion-monitoring mode).

2.5. Quality control and quality assurance

The recovery, limit of detection (LOD), and limit of quantification (LOQ) were evaluated at 10 and 100 μg.L^{-1} upon instrumental injection on samples of the different fruit and vegetable matrices fortified with all the pesticides to be analyzed (Lehotay, de Kok, Hiemstra, & van Bodegraven, 2005; SANTE, 2015). Reagent blanks, duplicates, and such spiked samples were used for quality control and quality assurance during the analysis of each sample batch. Accordingly, in each sample, ATZ-D_5 (1000 μg.L^{-1} in methanol) was added as an internal quality standard at nominal concentration for the instrumental detection of 100 μg.L^{-1}, to evaluate extract holding time and global recovery throughout the pesticide-analysis procedure (Anastassiades et al., 2003). The quantification was carried out by an external calibration curve of pesticide standard solutions in a range of 5–200 μg.L^{-1}. The analytical criteria applied for the identification and confirmation of pesticide molecules in GC-MS were the same as in previous works (Mac Loughlin, Peluso, & Marino, 2017).

2.6. Legal-comparison criteria

Even though a newer MRL listing from August 2016 was available (SENASA, 2016), a the previous one, from May 2015 (SENASA, 2015) was employed to establish the compliance of the produce, as that law was the one in force when the samples were acquired from the local markets. According to the national legislation, when an MRL has not been established in the national MRL listing—and furthermore no MRL has been approved by the *Codex Alimentarius* for a given product—a default value of 10 μg kg^{-1} is operative (SENASA, 2010). Table 1 lists the MRLs for the pesticides analyzed (SENASA and *Codex Alimentarius* when not available in the former) for each produce, the abbreviation used, and the pesticide type, and maximum and minimum concentrations found.

3. Results and discussion

3.1. Verification of the analytical procedure

On the basis of the two levels of spiked standards in the different produce samples (n = 5), the recovery values ranged from 78% to 113%; and the instrumental LODs and LOQs were below 10 μg kg^{-1} for all the pesticides analyzed, with that value being established as a limit by a government resolution and also in concordance with other studies where the same so-called *QuEChERS* (*i.e.*, quick, easy, cheap, effective, rugged, and safe) methodology had been used (Arienzo et al., 2013; Bakırcı et al., 2014; Lehotay et al., 2005). The calibration curves for all the pesticides analyzed were linear, with interday Pearson correlation coefficients between 0.960 and 0.998 (n = 4, $\alpha = 0.05$, $r_{critical} = 0.950$) in the range 5–200 μg.L^{-1}. The results from the reagent blanks were subtracted from the calculated values for each sample, and isotopically labelled internal standards were used to compensate for matrix effects (SANTE, 2015).

3.2. Percent of samples containing pesticide residues

Of the 35 pesticides analyzed, 21 were detected at concentrations ranging from detectable but not quantifiable to above 7800 μg kg^{-1}. A total of 88 samples tested positive for the presence of the residue for at least one pesticide. The remaining 47 samples were below the instrumental detection limit (LOD_{ins}) for the pesticides analyzed; which finding, however, does not necessarily confirm complete freedom from pesticide, as not all possible pesticides were analyzed. Of those 88 positive samples, 38 were contaminated at concentrations at or below the established national MRLs, but the other 50 were not. That is, of the produce analyzed, over 57% (*i.e.*, 50 out of 88) of the positive detections were for nonauthorized pesticide levels: with lettuce, for example, except for one sample, all the detections indicated pesticide contents above the respective MRLs (n = 27). As LOD_{ins} and LOQ were below the default MRL of 10 μg kg^{-1}, we could establish that certain samples were between the LOD_{ins} and that MRL for nonreported pesticides. Consequently, those samples were considered to be at or below the MRL. Now, with respect to pesticides unlisted among the *Codex Alimentarius* and the SENASA criteria (Table 1), 39 of the samples were at or below the MRLs (≤MRL), while 49 were above the MRLs. Fig. 1 illustrates the percent compliance with the regulation for each vegetable and fruit item analyzed in the study.

The produce items where pesticide residues were found at the highest percentages of detection can be arranged in the following descending order: orange > carrot > tomato > pepper > lettuce. About seven out of ten oranges, carrots, and tomatoes contained pesticide residues. Whereas almost half of those carrot samples were detected at values above the MRLs, only 30% of the oranges and 20% of the tomatoes were in noncompliance. Although half the samples of pepper and lettuce were positive, only 30% of the former and 40% of the latter had residue concentrations above the MRL threshold. The produce items arranged in order of noncompliance with the MRLs is thus: carrot > lettuce > orange > pepper > tomato.

The pesticide concentrations found in this study were all higher than those previously reported, and out of the 135 samples 49 were above the MRLs (36.3%). Other studies (Bakırcı et al., 2014; Chen et al., 2011; Hjorth et al., 2011; Poulsen, Andersen, Petersen, & Jensen, 2017), whose surveys included items sampled in this manuscript, reported that fewer than 10% were above the MRLs—but there, according to their respective national regulations. In the Arabian Peninsula, 20% of analyzed samples contained pesticide residues above the MRLs (Jallow, Awadh, Albaho, Devi, & Ahmad, 2017; Picó, El-Sheikh, Alfarhan, & Barceló, 2018). By comparison, the percentage of samples above the MRLs in the present work proved to be at a 4-fold greater degree of noncompliance than that of those other studies. In contrast, 8 out of 157 of the samples exported from Argentina, as analyzed by Hjorth et al. (2011), or only 5%, were found to be above the MRLs; which value is 7 times lower than that of the produce for local consumption, thus demonstrating that the local producers carry out different pest-management practices and/or have different levels of control than those operative with the international suppliers (MSAL, 2014).

Half of the lettuce samples were positive for pesticides, with 11% at or below the MRLs and the remaining 39% above that threshold. In Italy, Arienzo et al. (2013) found that 51.7% of the leafy greens analyzed were positive, with 6.9% being above the MRL; while in Turkey Esturk, Yakar, and Ayhan (2014) found pesticides in all the samples analyzed, with 45% above the MRLs, similar to the present findings. Oranges had a higher tally of positives at 30 out of 41 of the samples analyzed (73%) with 13 above the MRLs (32%). In China, Chen et al. (2011) reported that all the orange samples were residue-free, whereas in Spain Fernández, Picó, and Mañes (2001) found residues in almost 8 out of the 10 oranges assayed, but with only 6 of those samples being above the respective MRLs (4%). Pesticide residues in oranges in the Danish market, mainly from foreign origin, were found in 98% of the samples (Poulsen et al., 2017).

Table 1
Maximum residue limits, minimum and maximum concentrations found, expressed in μg.kg^{-1}, for analyzed pesticides and produce and abbreviations used for the pesticides and pesticide types.

Compound	Abbreviation	Pest. Type	Lettuce		Orange		Pepper		Tomato		Carrot	
			MRL	Min-Max	MRL	Min-Max	MRL	Min-Max	MRL	Min-Max	MRL	Min-Max
Atrazine	ATZ	Herb	–	–	–	34.7–63.7	–	–	–	–	–	–
Acetochlor	ATC	Herb	–	–	–	129.6	–	166.0	–	–	–	DNQ
Trifluralin	TRF	Herb	50	–	50	–	50	–	50	–	–	DNQ-92.9
Pendimethalin	PEN	Herb	–	99.8	–	–	–	–	50	–	50	DNQ-19.2
Chlorpyrifos	CLP	OP Insec	–	DNQ-1524.5	300	DNQ-76.8	500	5.2–168.0	500	9.0–12.7	100[a]	4.0–231.2
Diazinon	DZN	OP Insec	500	–	50	84.4–304.3	50[a]	32.7	50	–	500[a]	–
Malathion	MAL	OP Insec	–	33.1–105.4	2000	37.5	100[a]	–	3000	30.0–47.9	–	–
Parathion	PAR	OP Insec	–	–	–	–	–	–	–	–	–	–
Methyl parathion	Me-PAR	OP Insec	–	–	–	–	–	–	–	–	–	–
Fipronil	FIP	Insec	–	–	–	DNQ-37.4	–	10.8	–	–	–	19.2–95.7
Lambda-cyhalothrin	λ-CYAL	Pyr Insec	–	1.3–155.3	300	23.2–184.0	40	2.4–181.0	700	–	10[a]	8.7–449.9
Cypermethrin	CYP	Pyr Insec	700[a]	3229.7	300[a]	DNQ-698.8	100[a]	5.2–1024.3	1000	–	10[a]	DNQ-1658.7
Permethrin	PER	Pyr Insec	2000[a]	20.6–105.2	500[a]	–	1000	–	1000	41.4–89.4	100[a]	–
Bifenthrin	BIF	Pyr Insec	–	91.2	50[a]	–	500[a]	–	50	8.7	–	–
Deltamethrin	DEL	Pyr Insec	2000[a]	–	20[a]	–	100	–	100	–	20[a]	–
Endosulfan (α + β)	END	OC Insec	–	5.2–211.0	–	4.4–473.1	–	5.6–166.3	500[a]	–	–	4.4–288.2
α-Lindane	α-HCH	OC Insec	–	–	–	–	–	–	–	–	–	–
β-Lindane	β-HCH	OC Insec	–	–	–	–	–	–	–	–	–	–
γ-Lindane	γ-HCH	OC Insec	–	–	–	–	–	–	–	–	–	–
Methoxychlor	MXCl	OC Insec	–	15.3	–	11.8–17.4	–	–	–	10.2–16.2	–	–
Aldrin	ALD	OC Insec	50[a]	–	50[a]	–	–	–	–	–	100[a]	–
Dieldrin	DLD	OC Insec	50[a]	–	50[a]	–	–	–	–	–	100[a]	–
Endrin	EDN	OC Insec	–	–	–	–	–	–	–	–	–	–
p,p'-DDT	p,p'-DDT	OC Insec	–	–	–	–	–	–	–	–	200[a]	–
o,p'-DDT	o,p'-DDT	OC Insec	–	4.5	–	3.6	–	–	–	–	–	5.3–5.3
p,p'-DDE	p,p'-DDE	OC Insec	–	–	–	21.4	–	8.2	–	–	–	–
o,p'-DDE	o,p'-DDE	OC Insec	–	10.6–20.2	–	DNQ-4.5	–	–	–	–	–	–
p',p-DDD	p',p-DDD	OC Insec	–	–	–	–	–	–	–	–	–	–
Heptachlor	7Cl	OC Insec	–	–	10[a]	12.0–21.4	–	–	–	–	–	–
Heptachlor epoxide (isomer A)	7ClE(A)	OC Insec	–	–	–	–	–	–	–	–	–	–
Heptachlor epoxide (isomer B)	7ClE(B)	OC Insec	–	–	–	–	–	–	–	–	–	–
Epoxiconazole	EPX	Fung	–	5.6–29.6	–	9.1–122.5	–	9.0–116.1	–	–	–	18.7–138.8
Tebuconazole	TEB	Fung	7000	16.0	–	7.1–7821.5	100	40.9–210.1	100	–	400[a]	143.2
Azoxystrobin	AZX	Fung	3000	–	500	–	150	37.9–85.4	500	18.9	50	DNQ-208.2
Pyraclostrobin	PYR	Fung	2000[a]	–	1000	–	500	–	200	–	500[a]	–

[a] Maximum residue limit (MRL) from *Codex Alimentarius* (FAO/WHO, 2017). Pest. Type, Pesticide type; Herb, herbicide; Insec, insecticide; OP, organophosphate; Pyr, pyrethroid; OC, organochlorine (also known as legacy pesticide); Fung, fungicide. Blank spaces indicate that no MRL was found in the national regulations or *Codex Alimentarius* (FAO/WHO, 2017). In these examples, 10 μg kg^{-1} is employed as the MRL. DNQ, detectable but not quantifiable.

3.3. Pesticides most often detected

Fig. 2 depicts the total frequencies at which the 21 pesticides detected out of the total of 35 investigated were present among all the produce samples analyzed and further demarcates the subpercentages for the five individual positive items. The compounds most frequently detected among the 135 samples analyzed were chlorpyrifos in 35 (25.9%), epoxiconazole in 21 (15.6%), the endosulfans in 21 (15.6%),

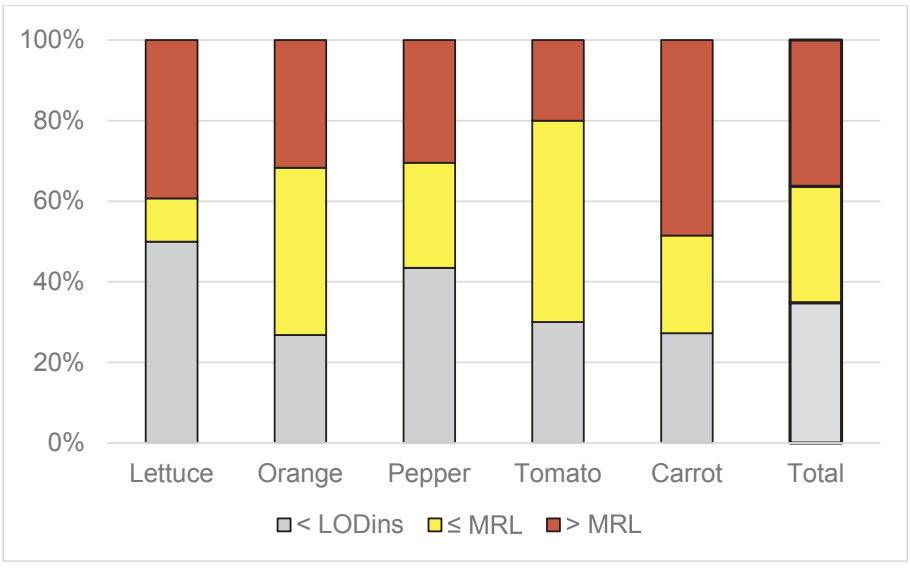

Fig. 1. Percentage of samples in compliance or non-compliance with the MRLs established by SENASA or Codex Alimentarius. The percentage of samples below the instrumental limit of detection (< LODins) is indicated in gray, at or below the maximum residue limit (≤MRL) in yellow, and above the maximum residue limit (> MRL) in red. In the figure, this percentage distribution is plotted on the ordinate for each of the produce items and for the total, as indicated on the abscissa. For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.

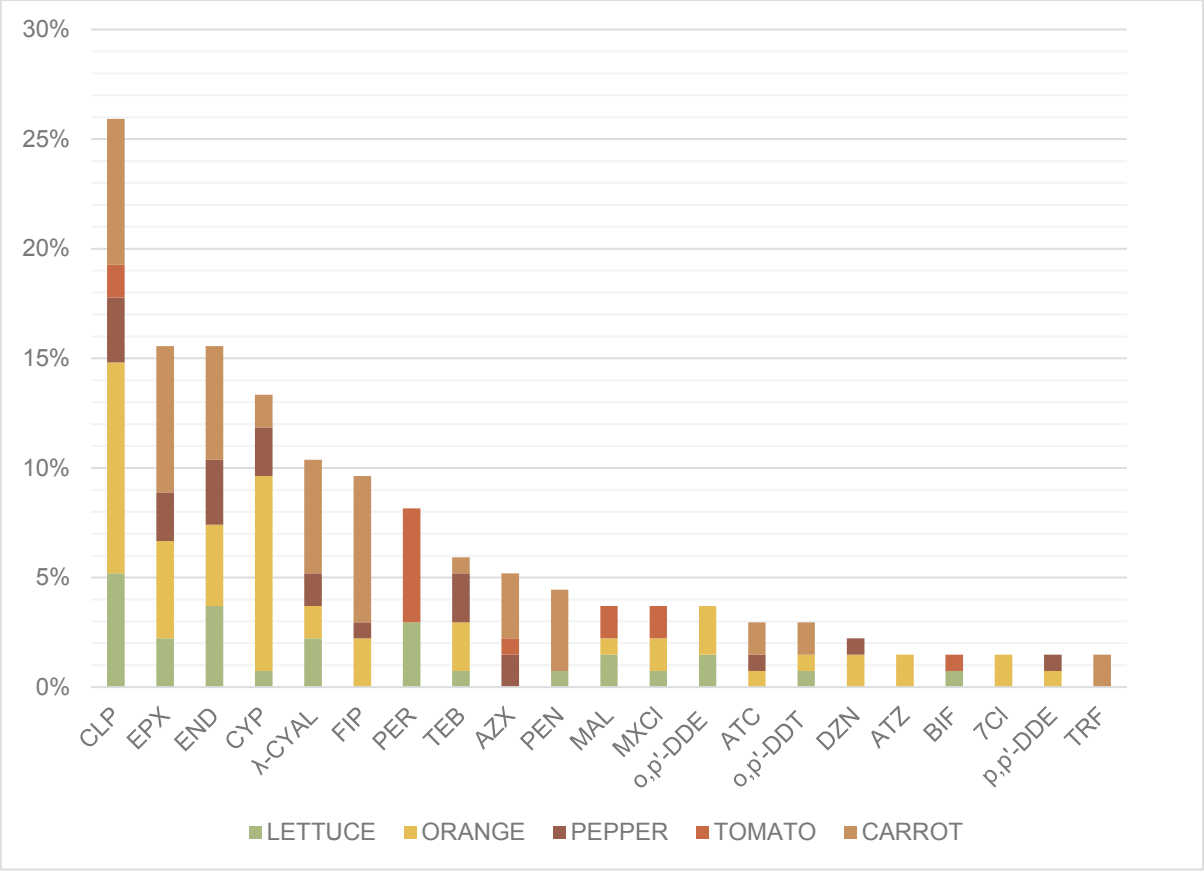

Fig. 2. Frequency of the 21 pesticides detected in samples of the different produce items analyzed. In the figure, the percentage of positive samples of the indicated produce items is plotted on the *ordinate* for each of the pesticides listed on the *abscissa*. Key to the color code: green, lettuce; light orange, orange; dark red, pepper; red, tomato; dark orange, carrot. Key to the abbreviations in Table 1. For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.

cypermethrin in 18 (13.3%), and λ-cyhalothrin in 14 (10.4%). Fig. 3 indicates the corresponding subpercentages of the samples containing each of the pesticides where the compound was present at a concentration above *versus* at or below the MRLs.

The top five most often detected pesticides were all present at a frequency above 10%. Chlorpyriphos was the most frequently detected, being present in all five of the positive produce items (Fig. 2). Epoxiconazole, that along with the endosulfans was the second most detected pesticide in this study (Fig. 2), is not under any form of regulation, either by national legislation or by the *Codex Alimentarius*. Consequently, that compound was present above the default MRL in a greater percentage of the items than even chlorpyrifos (Fig. 3). Though relatively rarely detected, three of the four herbicides analyzed (*cf*. Table 1) were either mainly (*i.e.*, acetochlor, pendimethalin), or exclusively (*i.e.*, trifluralin), found in carrot samples—with atrazine, however, being present in only oranges—while the insecticide permethrin was most frequently detected in tomatoes (Fig. 2). Of the quantifiable concentrations of fipronil that were detected (*i.e.*, 12 out of 13 samples)—with that compound also not under any regulation— were above the MRL.

Other publications have reported similar findings, with chlorpyrifos and other pyrethroids being the most frequently detected pesticides (Alamgir Zaman Chowdhury et al., 2013; Bakırcı et al., 2014; Blankson, Osei-fosu, Adeendze, & Ashie, 2016; Hjorth et al., 2011; Jallow et al., 2017). In particular, in the present work, oranges and carrots were the commodities with the highest level of pesticide detection, with a total of 59 samples between the two being found positive. Of the oranges, 13 samples contained chlorpyrifos and 12 cypermethrin, with the possibility also of random cooccurrence. Moreover, oranges also exhibited the highest frequency of organochlorine pesticides and metabolites, which incidence is further discussed below. In Argentina, this occurrence is a consequence of the chemical management of pests in horticulture and fruit growing wherein these commercial pesticides are the most frequently employed (DP, 2015, p. 533).

3.4. Pesticide profile and relevant concentrations

From the total of 135 samples that were analyzed for 35 different pesticides, a bank of 4725 concentration data was generated. Out of that collection, 190 individual concentrations were above the instrumental limit of detection. Fig. 4 summarizes the number of pesticide-residue detections within discrete concentration ranges and further denotes the fraction of samples within each range having a concentration either above or else at or below the MRL.

If the MRLs approved by SENASA (2015) were applied to our overall results; of the 190 detections, 41 were at or below that value and 8 above, while 141 pesticide-residue concentrations had no MRL specified. Nevertheless, upon applying the *Codex Alimentarius* (FAO/WHO, 2017) and the SENASA (2010) regulations for unlisted pesticides (*i.e.*, 10 μg kg^{-1}), the final result was 99 at or below and 91 above the MRLs. In the 100–250 μg kg^{-1} range (Fig. 4), the detections at or below the MRLs all had an MRL between 300 and 2000 μg kg^{-1}. The highest concentration recorded was 7821.5 μg kg^{-1} of tebuconazole on an orange, for which compound no MRL had been specified and the 10 μg kg^{-1} limit is applied; therefore the concentration was more than 750 times higher than that *ad-hoc* MRL. The second highest concentration was 3229.7 μg kg^{-1} of cypermethrin in a lettuce (4.6 times the specified MRL). In both examples, those two produce items

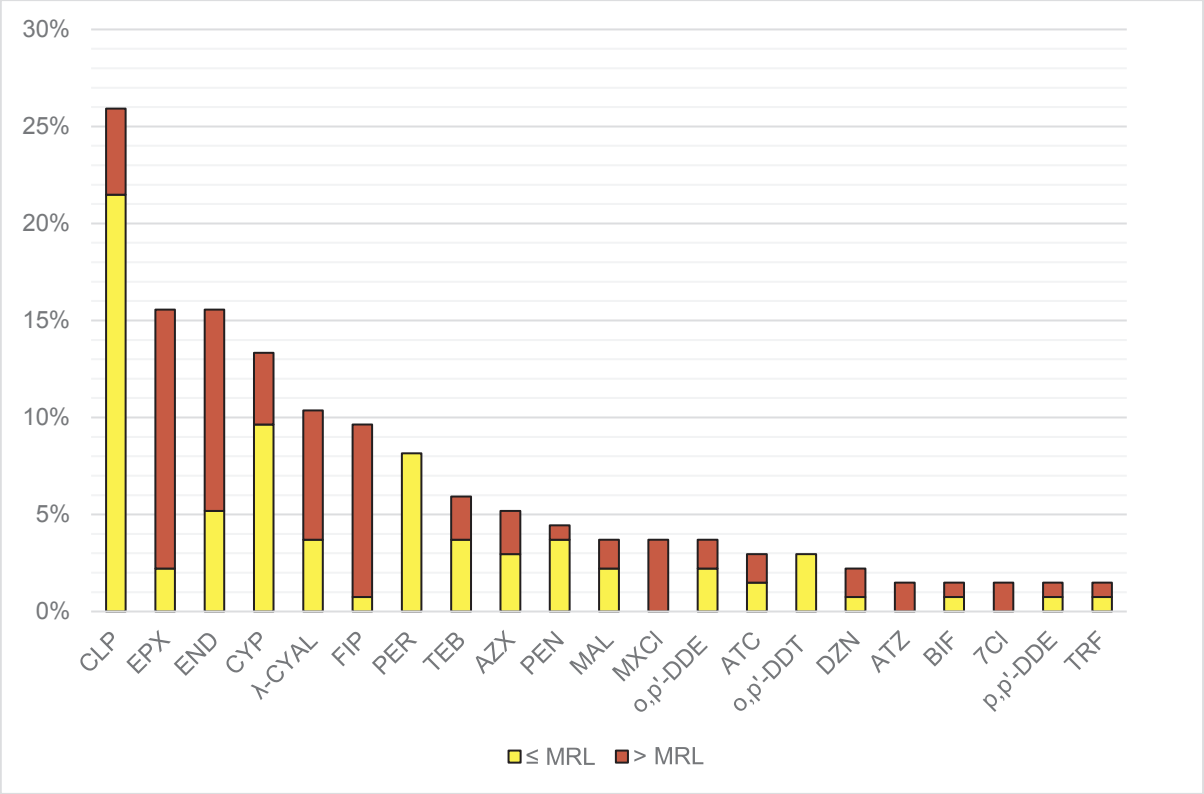

Fig. 3. Total detection frequency and percent compliance with the maximum residue limits for the 21 pesticides detected among the samples of the different produce items analyzed. In the figure, the total percentage of positive samples among all the produce items is plotted on the *ordinate* for each of the pesticides listed on the *abscissa*. Key to the color code: yellow, at or below the maximum residue limit (≤MRL); red, above the maximum residue limit (> MRL). Key to the abbreviations in Table 1. For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.

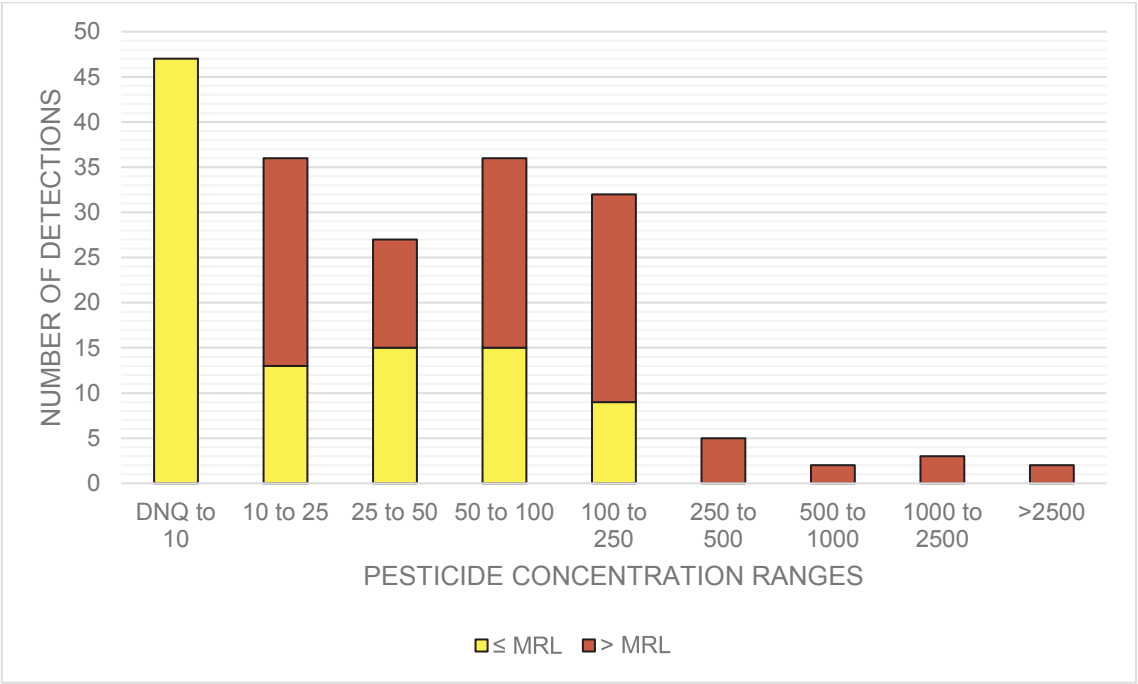

Fig. 4. Number of pesticide-residue detections and fractional compliance with the maximum residue limits within discrete concentration ranges. In the figure, the number of positive detections is plotted on the *ordinate* with respect to values at or below the maximum residue limit (MRL; yellow bar or bar fraction) or above the MRL (red bar or bar fraction) for each of the pesticide-concentration ranges in $\mu g.kg^{-1}$ indicated on the *abscissa*. DNQ, detectable but not quantifiable. For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.

Table 2
Pesticides at the highest concentrations among those with the greatest detection frequency and maximum pesticide load (sum of pesticide concentrations in a single sample), expressed in μg.kg^{-1}.

c order	d freq											
	CLP		EPX		END		CYP		λ-CYAL		maximum pesticide load	
	25.9%		15.6%		15.6%		13.3%		10.4%			
1	L	**1524.5**	C	**138.8**	O	**473.1**	L	**3229.7**	C	**449.9**	O	**9093.3**
2	C	**231.2**	C	**131.5**	C	**288.2**	C	**1658.7**	C	**345.0**	L	**3410.1**
3	C	**196.6**	C	**122.6**	L	**211.0**	P	**1024.3**	C	**217.7**	C	**1962.2**
4	P	*168.0*	C	**122.5**	P	**166.3**	O	**698.8**	P	**184.0**	L	**1615.7**
5	P	*131.8*	C	**116.9**	O	**96.5**	O	**588.3**	O	*181.0*	P	**1366.7**

d freq, detection frequency; c order: concentration order.
*Text format represents a concentration at or below the MRL (*italic*) or one above the MRL (**bold**). The first letter only of each product is indicated (L = lettuce, O = Orange, P = pepper, T = tomato, C = carrot).

contained 4 other pesticides (*cf*. Fig. 2). Of the pesticide cypermethrin, the highest concentrations were in the pepper and carrot and the second highest in the orange. When the sampling was conducted, the pyrethroid insecticide permethrin was not included in the national MRL legislation but was listed in the *Codex Alimentarius*. In tomatoes the highest concentration of this compound was at 89.4 μg kg^{-1} (MRL = 1000 μg kg^{-1}).

For the five pesticides with the highest frequency of detection (Fig. 2) those five concentrations were further evaluated. In addition, the five maximum-pesticide loads—*i.e.*, the sum of the pesticide-residue concentrations detected in a single sample—are presented in Table 2. Out of this 5 by 5 matrix of data summarized in Table 2, 88% of those most frequent detections constituted concentrations in the indicated produce items that were above the MRLs. Almost half of those instances involved pesticide residues in carrots (all above the MRLs); moreover, the 5 highest concentrations of epoxiconazole were detected in carrots (Table 2). This occurrence might be a result of the greater chance of absorption of soil-derived pesticides into the root tissues of carrots than into those of other plants (Mattina, Iannucci-Berger, & Dykas, 2000).

The produce items with the highest accumulated load of pesticide residues (Table 2) were all above the MRLs for at least one of the compounds detected. All but one sample contained 5 pesticides, with one of those compounds being a fungicide and furthermore with at least 3 of those 5 contaminants being present at concentrations above the respective MRLs. All the samples contained chlorpyrifos and at least one pyrethroid insecticide, though in most instances λ-cyhalothrin and cypermethrin simultaneously.

3.5. Organochlorine pesticides: endosulfans

The use of the organochlorine pesticides (OCPs) that were analyzed in this study is prohibited in Argentina (MSAL, 2016). Nevertheless, 37 samples (27.4%) contained these compounds. Since the OCPs are prohibited, no MRLs for those pesticides were listed. With 10 μg kg^{-1} as an *ad-hoc* regulatory limit, the OCP concentrations in 13 samples were assayed at below that threshold, whereas 24 were above. Two samples, one lettuce and one orange, contained two organochlorine pesticides.

The endosulfans, banned from the market since 2013, were the second most frequently detected pesticide (at 15.6%). Fig. 5 summarizes the endosulfan concentrations in the 21 produce items in which that OCP was detected and illustrates that while 8 samples contained concentrations of the compound below that arbitrary MRL (the horizontal red line), the concentrations in the remaining 13 were in excess; with 4 values—1 each from pepper, lettuce, carrot, and orange; with tomatoes, however, never being contaminated with these pesticides—being greatly so, at concentrations between 166.3 and 473.1 μg kg^{-1}.

A plant can accumulate OCPs through different pathways, one being via root uptake and transport to the shoot (Lichtenstein, 1959; Trapp & Legind, 2011). The detection of metabolites of pesticides assumed to be no longer in use could occur through translocation from soils where those persistent pollutants had been previously used. The literature on the translocation of pesticides from the soil to fruits and vegetables is, however, scarce. Gonzalez, Miglioranza, Aizpún De Moreno, and Moreno (2005), though, were able to determine that the incorporation of pesticides from soil depends on several details—such as the plant species, the nature of the pollutant, and the prevailing environmental condition. In a previous study reported in 2003, those same authors had analyzed the incidence of OCPs in tomatoes grown on a farm where agrochemicals had never been used (Gonzalez et al., 2003). The findings presented demonstrated that tomato plants were able to accumulate OCPs from soils, resulting in an average background concentration in the fruit of 15.2 μg kg^{-1}. Some concentrations of OCPs, and especially endosulfan (at up to 473.1 μg kg^{-1}), were above what could be expected to be incorporated into the produce by translocation. On most fruits and vegetables, 50% of endosulfan is broken down to the corresponding sulfate metabolite within 3–7 days (Kidd & James, 1991). Since endosulfan-sulfate (screened but not quantified) was not detected, it stands to reason that, in the instances where endosulfans were detected, such concentrations (up to 30 times the background concentration) were a consequence of the recent applications of those types of banned pesticides.

3.6. Multiple residues detected

Because in 88 positive samples a total of 190 pesticide residues were detected, many of those items did not contain only a single pesticide residue (Table 3). Indeed, two or more pesticides were present in more than half of those positive samples (*i.e.*, 53). Carrots and oranges were more prone to such cooccurrences, with those products involving 18 and 17 samples, respectively, with at least 2 pesticides detected simultaneously.

Furthermore, the organophosphate insecticide chlorpyrifos, indicated above as being the most frequently detected pesticide at 35 out of 135 samples—25.9%; *cf*. Fig. 2—was almost half the time (*i.e.*, 16 out of 35 samples) present along with at least one pyrethroid insecticide as well. In addition, in 11 out of 35 samples, chlorpyrifos, was detected along with the OCP endosulfan and in 10 out of 35 samples in combination with at least one fungicide. Finally, we found 7 instances where chlorpyrifos was detected with endosulfan, plus at least one pyrethroid and one fungicide (*i.e.*, chlorpyrifos + endosulfan + pyrethroid + fungicide)—a total of 4 pesticides in the selfsame samples.

Though many of the samples that contained multiple pesticides were above the respective MRLs for at least one of the agents detected, the existing regulations do not contemplate such instances of cooccurrence. To weigh how multiple detections affect the quality of the produce, we applied the index of food quality for residues (IqR; Arienzo

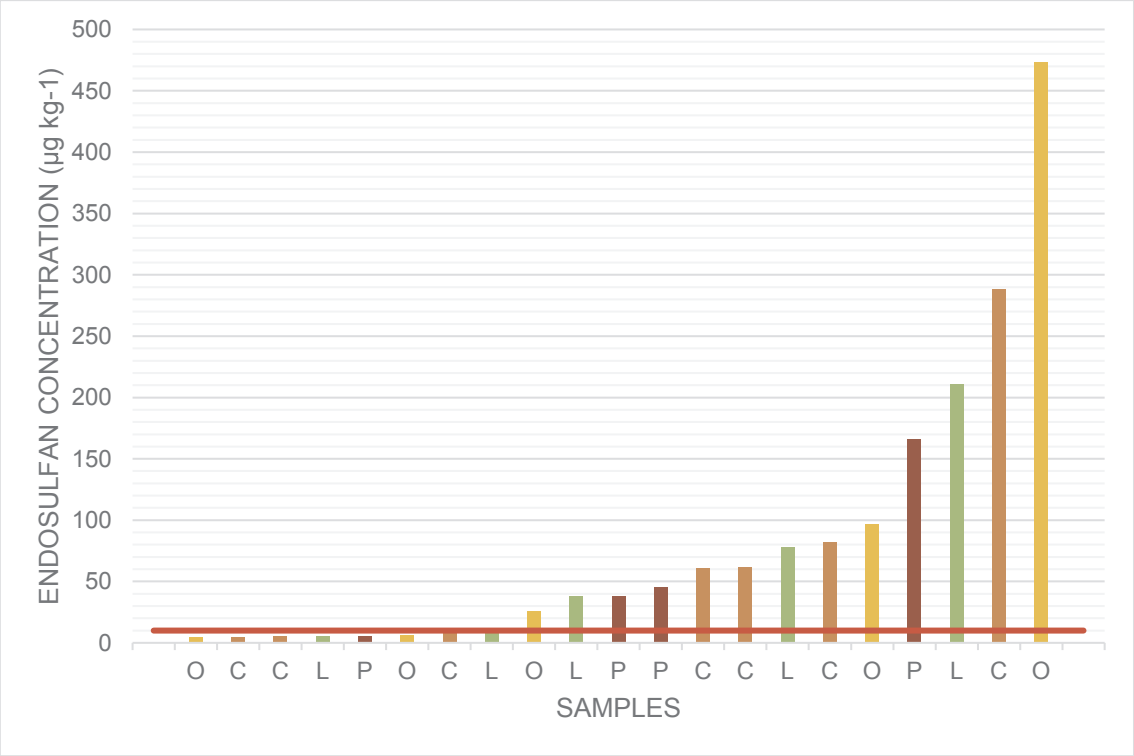

Fig. 5. Endosulfan concentrations in different produce samples. In the figure, the concentration of endosulfans in $\mu g.kg^{-1}$ is plotted on the *ordinate* for each of the 21 positive samples listed in order of increasing concentration on the *abscissa*. The solid horizontal red line demarcates the arbitrary maximum residue limit ($10\ \mu gkg^{-1}$) used. Key to letter (colour) code: O (light orange), orange; L (green), lettuce; P (dark red), pepper; C (dark orange), carrot. For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.

Table 3
Number of pesticide residues in an individual sample.

No. of findings	No. of samples	%
0	47	34.8
1	35	25.9
2	27	20.0
3	9	6.7
4	11	8.1
5	6	4.4

et al., 2013) to the findings for each of the samples analyzed (Fig. 6). This index is calculated for each sample as the sum of the ratios between the pesticide concentrations and the respective MRLs (Equation 1). The IqR contains four categories: excellent (IqR = 0), good (0–0.6), adequate (0.6–1.0), and inadequate (> 1.0). For nonquantifiable detections, a value of half the LOD_{ins} was used to calculate the contribution to the IqR.

$$IqR = \sum_{i=1}^{n} concentration_i / MRL_i \quad (1)$$

After calculating the IqR with our findings, all the samples were at least one pesticide above the MRLs (*i.e.*, 49) were rated at inadequate. Most of the samples were concentrations were at or below the MRLs (*i.e.*, 39) had an IqR category of good (*i.e.*, 31 out of 39) and 4 out of 39 samples had a rating of adequate. The remaining four samples that were at or below the MRL for each of the pesticides detected in those items nevertheless had an IqR rating of inadequate (*cf.* the circled points in Fig. 6). The four samples in question were 2 oranges, 1 pepper, and 1 carrot; with 2 pesticides being detected in each, except for one of the oranges that contained 4 residues (chlorpyrifos, cypermethrin, endosulfans, and the fungicide tebuconazole). Within the inadequate category (*i.e.*, 49 above MRLs + 4 from cumulative presence of pesticide residues at or below MRL), 26 out of 53 samples had an IqR between 1 and 10—meaning that, cumulatively, the product's decrement in quality was between 1 and 10 times beyond the MRL. Additionally, 25 out of 53 samples were rated at between 10 and 100, while 2 out of 53 had values greater than 100—thus ranging in assessed unsuitability from 100 times beyond the MRL to almost 1000 times beyond that cutoff point.

Since MRLs do not take into consideration toxicologic effects, and furthermore because possible enhanced or even synergistic actions of various pesticides in combination have not been well documented (Hjorth et al., 2011), the IqR is a useful indicator for the overall quality of foodstuffs. Moreover, since different countries and regions have individual MRL-regulation values, the criteria of IqR enable a normalization of the data that allows for easy and objective comparisons to be made.

4. Conclusions

One hundred and thirty-five samples were purchased from green-groceries, extracted via a rapid and efficient multiresidue procedure, and analyzed for 35 commonly used pesticides by GC–MS: Of the samples tested, 65% were positive for at least one pesticide. In many instances, a pesticide was not regulated for a specific product. Of the total samples, 29% were at or below a specified MRL, while 36% were above that threshold; nevertheless, according to the index of food quality for residues, 39% of the samples were deemed inadequate for consumption. Chlorpyrifos was the most frequently detected pesticide and was usually accompanied by at least one other compound. Endosulfans were found at concentrations that consequently indicated the recent use of this pesticide despite its having been previously banned. Two or more pesticide residues were present likewise in 39% of the total samples, where no information has as yet been garnered on the possible combination effects of these agents and no regulation exists

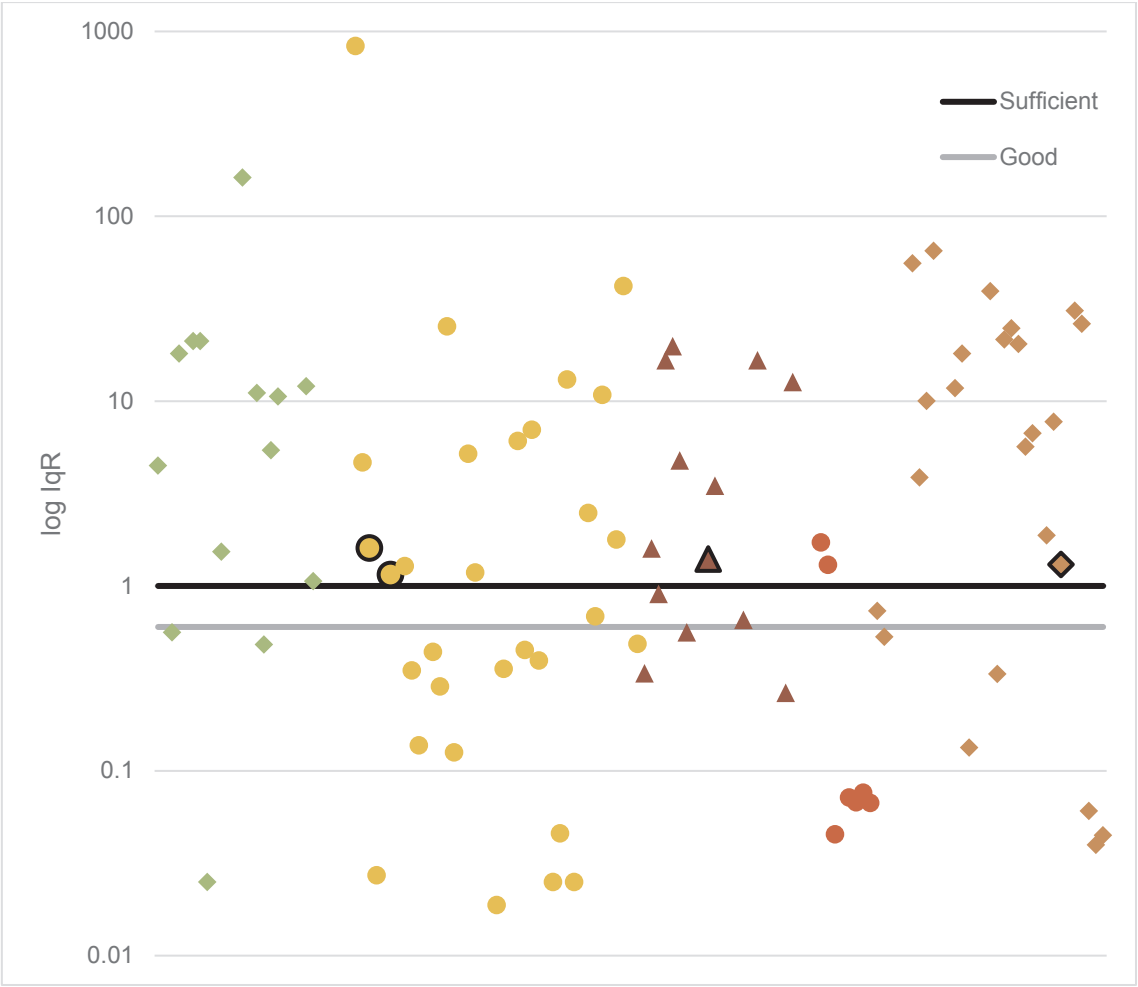

Fig. 6. Index of food-quality for residues of the produce samples analyzed. In the figure, the index of food quality for residues (IqR) is plotted on the *ordinate* on an exponential scale for each of the individual samples displayed above the *abscissa* from the produce sources indicated by the colour and symbol code starting from the *origin* with lettuce (green diamonds) and proceeding sequentially thereafter through orange (light-orange circles), pepper (dark-red triangles), tomato (red circles), and carrot (dark-orange diamonds). The upper solid horizontal black line and lower solid horizontal gray line demarcate the range of adequate among the four quality categories: excellent (IqR = 0), good (0–0.6), adequate (0.6–1.0), and inadequate (> 1.0). The highlighted points depict samples with pesticide levels at or below the MRLs, but that nevertheless had an IqR value higher than 1 and were thus deemed inadequate. For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.

contemplating such cooccurrences.

These results demonstrate that in Argentina the systems regulating the use of pesticides are fraught with an appreciable degree of permeability because of the lack of monitoring programs and the failure to update the MRL listings regarding the commercially available and currently used pesticides. Since the products analyzed were of high consumption nationwide and at a much greater frequency exceeded the MRLs than in other countries, or than even in the domestic exporting market; these conditions create a scenario in which the people of Argentina are regularly exposed to a complex mixture of pesticides in their routinely consumed fruits and vegetables.

The pesticides analyzed did not cover all of the active compounds available in the market. Future studies must address the high diversity of pesticides applied by growers as well as the use of nonregulated and even prohibited compounds for certain fruits and vegetables. The results here clearly indicate the need for the establishment of a national monitoring program oriented toward locally consumed fruits and vegetables, as well as the processed foods based on those products, in order to take the appropriate measures for insuring that pesticide residues are reduced to within the permissible limits for safe consumption, thus minimizing the health risks involved. The study reported here constitutes the first report presenting extensive information regarding pesticide residues contaminating fruits and vegetables for local consumption in Argentina.

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