RISK ASSESSMENT OF PESTICIDE RESIDUES IN FOOD ON CROATIAN MARKET: SHOULD WE WORRY?

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Abstract
Croatian Food Agency conducted in 2011 a survey on citizen’s perception about the risks in food. Representative sample included 580 examinees, aged 15 - 50 years within entire Croatian territory. Results show that 61% of respondents are very and fairly concerned due to presence of pesticide residues in food. Only small proportions, 26%, are not very worried and 12% not worried at all.

The aim of this study is to assess the acute exposure of consumers from pesticide residues in products that can be found on Croatian market. The assessment was performed based on surveillance (monitoring) results of pesticides in products on market in Croatia for the year 2007, 2008, and 2009. Samples, domestic and imported, belong to the category of fruits, vegetables, cereals and their derivatives. Sampling was conducted through two periods, spring-summer and autumn-winter with respect to availability of products on the market.

From total of 650 samples analysed, 625 samples did not contain measurable values of the active substances and 25 samples showed the presence of some active ingredients of pesticides above the legal tolerance limits. To determine acute risk for different consumer groups, exposure was calculated and compared with values of toxicological limits. Results showed that out of 650 analysed samples MRL exceed 4% and acute risk was found for 1% of the samples. It was concluded that acute risk for consumers in our country can be considered rare, except for oranges and lettuce with high concentrations of pesticides for all consumers groups, especially for children.

Key words: Food safety, Pesticides, Active substances, Risk assessment, Toxicological limits, Risk, consumers.

1. Introduction
Production of safe food and water is a strategic issue and subject of legislation in most developed countries as well as in Croatia. For substances which are permitted in food, as impact of environmental contaminants or as deliberate additives, legislative frameworks define safety margins. Consequently consumers are though usually small amounts subject to an increasing number of synthetic chemicals and in addition to those that occur naturally or under the influence of pollution. At the present time there are sensitive and accurate methods for their determination. Despite that fact it is difficult to establish a relationship and identify health problems arising from specific chemical substances except in cases of high acute exposure. Even in cases where the impact can be determined it can come from several different sources that are difficult to identify and quantify [1]. It should be taken into account the differences among the population in terms of susceptibility to disease. If two individuals exposed to the same amount of harmful agents in the same circumstances does not mean that it will necessarily react in the same way, or be affected by the same degree of severity of the consequences. All mentioned indicate needs for quantification of risk, separately for each individual with varying degrees of sensitivity. This is possible through the steps of risk assessment. Risk assessment, together with Risk management and Risk communication is a part of Risk analysis cycles. At the international level provides the scientific basis for the establishment of Codex standards, guidelines, and other recommendations and includes dietary exposure assessments as an essential component. This ensures that safety requirements for food are protective for public health, consistent among countries, and appropriate for use in international trade [3]. The essential part is dietary exposure assessments. It combines food consumption data with data on the concentration of chemicals in food [2]. Results of estimation are then compared with the relevant toxicological reference value for the food...
2. Materials and Methods

Data were obtained from national monitoring program of pesticide residues in food of plant origin. The program was designed according to coordinated programme for all EU member countries. It performed to ensure compliance with the provisions established in food legislation [17].

For analysis was a used Multiresidue method. Samples were analysed in a mass spectrometer Agilent 6890 GC with 5975 Inert Mass Selective Detector. Positive results were compared with those obtained by gas chromatography (flame photometric and electron absorption detector) [13].

During three-year period (2007 - 2009) a total of 650 different samples of commodity was analysed on the Croatian market. Samples were selected in accordance with the recommendations of the European Commission for a coordinated monitoring program in the EU 2007/225/EC 2008/103/EC 1213/2008. In addition importance was given to products of nutritional importance for population in our country or products with residue found in previous research.

Sampling in all three years was carried out in markets, retail shops, and big malls. The 50% samples were originating from individual producers on green market and 50% from large centres. As well, half products were domestic and another half imported. Considering spatial distribution eleven Croatian cities were included.

Samples were collected in two time periods, spring-summer and autumn-winter with respect to the availability of products on market.

Table 1 gives an overview of total number of species analysed product and total number of cities and patterns for each year of monitoring. It is visible that the sampling comprises one town more each year. This means increased spatial coverage of the study, and higher number of included retails.

<table>
<thead>
<tr>
<th>Monitoring program</th>
<th>Year</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of analysed products by category</td>
<td></td>
<td>9</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>Number of towns</td>
<td></td>
<td>5</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>112</td>
<td>246</td>
<td>292</td>
</tr>
</tbody>
</table>

Analysis was performed on 76 active substances in 2007, or 87 in 2008, and 88 in 2009 year. Active substance referred to insecticides (69), fungicides (17) and herbicides (2).

Sampled commodity by type was as follows:

a) Fruit (8 species): apples, oranges, peaches, grapefruit, pears, bananas, grapes, strawberries;

b) Vegetables (13 species): tomatoes, cabbage, onions, lettuce, potatoes, green beans, spinach, peppers, cucumbers, eggplant, cauliflower, peas, and carrots;

c) Cereals (2 types): rice, wheat;

d) Processed product (3 types): bread, pasta, orange juice.
Table 2 presents the number of analysed samples for all four categories of products for each year of monitoring.

It is worth to emphasize that, during three years of investigation, in samples of cabbage, onions, spinach, peas, peaches, 100% orange juice, wheat, rice and bread residues are not detected.

Table 2. Overview of the total number of samples analyzed by categories of products in the monitoring of pesticide residues in Croatia

<table>
<thead>
<tr>
<th>Products Category</th>
<th>Year</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2007</td>
<td>2008</td>
</tr>
<tr>
<td>Fruits</td>
<td>35</td>
<td>70</td>
</tr>
<tr>
<td>Vegetables</td>
<td>66</td>
<td>121</td>
</tr>
<tr>
<td>Cereals</td>
<td>11</td>
<td>36</td>
</tr>
<tr>
<td>Processed products</td>
<td>-</td>
<td>19</td>
</tr>
<tr>
<td>Total of samples</td>
<td>112</td>
<td>246</td>
</tr>
</tbody>
</table>

To determine the risk, short-term exposure (in one meal or a period of 24 hours) assessment was performed for each sample with MRLs exceeding. For the purpose of risk estimation “EFSA PRIMO-Pesticide Residue Intake Model rev.2.0” for acute exposure calculation was used. Computer model is created, published and revised by EFSA [14, 16]. According to Kroes et al. [12] assessment of exposure dietary components usually require some degree of modelling to attempt to create a representation of real-life exposure situation.

The models used for the calculation of intake are based on the premise that intake is a function of the concentration of pesticide in food (usually referred to as the residue level) and the amount of food consumed [2].

Since exposure is relative to body weight there is simple equation is used to calculate intake (Tucker [18]):

Exposure to pesticides in the diet = Concentration of pesticide in food X Food consumed/Body weight.

The equation is base for calculation of the short-term intake according on International Estimation of Short Term Intake (IESTI) equations, described by JMPR [19, 20]. In acute (short-term) quantitative risk assessment, estimated dietary exposure is compared with the relevant toxicological reference values Acute Reference Dose (ARfD) and respectively acceptable daily intake (ADI). The ARfD and ADI are derived after a full hazard characterization of a compound. Consumer is considered to be adequately protected provided that the estimated dietary intake of a pesticide residue does not exceed the ARfD or the ADI [16].

Statistical basement of IESTI calculation is deterministic approach. Kroes et al. [12] states that deterministic modelling involves using a single ‘best guess’ estimate of each variable within a model to determine the model’s outcome(s). In the context of exposure assessments refers to a method whereby a value for food consumption (average or high level consumption value) is multiplied by determined value of residue concentration (over MRL) in food item [12].

IESTI equation respect following variables: U (unit weight), HR (highest residue), V (variability factor), LP (large portion), BW (body weight). A key feature of equation is that it uses for calculating an estimation of individual product and it cannot be estimated intake in case of complex foods where every single component may contain a certain amount of residues. Nevertheless EFSA [14] concludes that the calculations were carried out using the equation often for a particular product sufficient to provide an adequate level of consumer protection. This is explained by the fact that very little probability of consuming two or more different products in a short time, large quantities and high concentrations of residues in excess of the statutory limit [21, 22].

There are three derivatives of IEST depending on type, size and weight of the sample. The equation and all its derivates are embedded in a computer model created as Excel applications. Model is composed of nine spread sheets with different purposes. Since Croatia don’t have data about dietary habits designed for purpose of given model, for the aim of this investigation the data that are already in the model was used. Table 3 gives an overview of all products and data that was used in the Model used for calculations. Presented data was combined with all results above regulates MRL found in eleven commodities during national monitoring (2007 - 2009). That means that for eleven products and 28 combination products/pesticides risks could not be excluded. Risk evaluation was carried out for two consumer groups, children and adults.

Dietary habit values used in model refers to specific EU country that reported largest food portion for children and adult population, or in some cases, specific food subgroups (e.g. vegetarians) in 24 hours. This is related to “worst case” or “high end” assumption scenarios and it is part of the internationally recognized approaches for risk assessment [19].

Given results are expressed as percentages and compared with acute reference dose (ARfD) for a given active substance:

- If the result is less than the acute reference dose (up 100%), the risk is considered acceptable.
- If the result is greater than the acute reference dose (> 100%) the risk is considered unacceptable.
Table 3. Dietary habit values of certain consumer group in EU member states in model and type of IESTI used

<table>
<thead>
<tr>
<th>Food type</th>
<th>Portion size (g)</th>
<th>97.5 percentiles of largest portion (g)</th>
<th>Body weight (kg)</th>
<th>Type of IESTI equation</th>
<th>Variability factor (ν)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(ch)</td>
<td>(ad)</td>
<td>(ch)</td>
<td>(ad)</td>
<td>(ch)</td>
</tr>
<tr>
<td>Oranges</td>
<td>160</td>
<td>160</td>
<td>193.8</td>
<td>746.7</td>
<td>8.7</td>
</tr>
<tr>
<td>Potatoes</td>
<td>216</td>
<td>216</td>
<td>191.1</td>
<td>694.4</td>
<td>8.7</td>
</tr>
<tr>
<td>Lettuce</td>
<td>534.7</td>
<td>558</td>
<td>86.9</td>
<td>146.6</td>
<td>16.5</td>
</tr>
<tr>
<td>Pod</td>
<td>-</td>
<td>-</td>
<td>194</td>
<td>334</td>
<td>17.10</td>
</tr>
<tr>
<td>Apple</td>
<td>112</td>
<td>131.8</td>
<td>180.3</td>
<td>780</td>
<td>8.7</td>
</tr>
<tr>
<td>Pepper</td>
<td>154.9</td>
<td>160</td>
<td>145.3</td>
<td>155.7</td>
<td>16.15</td>
</tr>
<tr>
<td>Carrot</td>
<td>80</td>
<td>74.6</td>
<td>78.8</td>
<td>300</td>
<td>8.7</td>
</tr>
<tr>
<td>Aubergine</td>
<td>271</td>
<td>272.4</td>
<td>102.5</td>
<td>478</td>
<td>20.5</td>
</tr>
<tr>
<td>Banana</td>
<td>100</td>
<td>100</td>
<td>127.3</td>
<td>260</td>
<td>8.7</td>
</tr>
<tr>
<td>Strawberry</td>
<td>-</td>
<td>-</td>
<td>251.8</td>
<td>333</td>
<td>16.5</td>
</tr>
<tr>
<td>Grape</td>
<td>581.5</td>
<td>581.6</td>
<td>211.5</td>
<td>400</td>
<td>16.5</td>
</tr>
</tbody>
</table>

(ch) children; (ad) adults

3. Results and Discussion

Over the three years of monitoring (2007 - 2009) in total 650 samples was analysed and 25 of them exceeded legislatively set up MRLs. Although the number of samples with MRL exceedance in 2008 was increased (up to 12%) compared to the previous year 2007, in 2009 decreased in comparison to both years. Exceeding frequency in somewhat higher percentage was determined in samples (52%) from domestic production compared to imported products (48%).

In samples of oranges, apples and lettuce residues were found each year, although in most cases (82% - 88%) were below the MRL. According to given frequent occurrence it may be assumed that these products may pose a risk to some or all consumer groups. This contributes to the fact that oranges in 2007 have the largest recorded and measured values of concentrations above recommended exposure.

Active substances analysed in monitoring program for pesticide residues in and on products of plant origin during the three-year mostly belonged to the group of insecticides (79%), followed by fungicides (19%) and of herbicides (2%). High percentage of insecticides analysis has resulted in a relatively high percentage of finding active substances from this group. Small number of active substances from two other groups resulted with a small numbers of samples in which are identified. Although that it was analysed relatively few active substances from the group of fungicides (16), finally they are determine in absolute high percentage (43%). Aggregate results indicate that from a total of analysed samples for the 25 (4%) and 28 combination active substances/products risk could not be excluded. After conducted model calculations and evaluation of acute exposure it was determined that 1% of the products from total number exceeds the toxicological limits. It means that these products can pose risk and some kind of adverse health effects in children and adult population.

In 2007 was generally registered largest number of samples in which exposure assessment determined risk for all or just some consumer groups (children). In the coming 2008, major decline of risk patterns was recorded and particularly in 2009 when for all excess of MRL risk could be excluded.

The Figure 1 presented trends in number of samples above regulatory limit for each year in relation to the number of samples in which the risks was identified.
For risky combinations, oranges/imazalil/thiabendazole, lettuce/procymidone/iprodione an additional calculation was performed with available data for Croatia. For the children population assessment was performed for the age of 3, 7 and 15 years, with body burden of 14.6 kg, 22.85 kg and 56.7 kg [23]. Data used for the adult population, 68 kg for female and 82 kg for male [24]. For orange two average sample weights were used. Amount of 160 g, as it states in the PRIMo Model and for orange sample without peel (portions) 95.23 g (according to internal data from the Institute of Public Health, Osijek-Baranya County). Calculations for all consumer groups carried out by two variability factors (v) 7 and 5. 2a type of IESTI equation was used for all samples and consumer groups. It was determined that combination orange/thiabendazole will not cause any risk. On the other hand combination orange/imazalil could pose acute risk for all consumer groups.

In the case of iprodione/lettuce and procymidone/lettuce in total, over the three years of monitoring, 57 samples were analysed. Every year in detected samples presence of pesticides above (9%) or below (91%) permissible limits was determined. The risk is observed in 5% of cases by using dietary habits data from EFSA Model. The portions size was 534.7 g for children body weight 16.5 kg (3 - 5 years) and 558 g for adults (UK vegetarians) weight 66.7 kg. Considering available data in RH average daily amount of vegetables consumed is around 160 g. Assuming that this is the weight of lettuce consumed in one or more meals a day, eating salads for our conditions was 3.3 and 3.4 times lower comparing to results from Model data. These findings imply the fact that potential acute risk in our terms could lead to overestimation. But in case of consumers with low body weight or those which eating large amounts (e.g. vegetarian) risk could not be excluded.

Another consideration is the fact that because of absence of toxicological values ARfD for iprodione was used ADI value. ADI is estimated amount of a chemical substance in food, expressed on a body weight basis that can be consumed daily over a lifetime without considerable risk to consumers. As well, consumption of salad is preceded by rinsing with water and due to the dilution the amount of pesticides can be reduced but only to a certain extent (22 - 60%) [25].

In order to identify or eliminate the risks for consumers in the Republic of Croatia exposure assessment calculations were carried out with available data for the consumer group of children 14.6 kg, 22.85 kg and 56.7 kg and adults 68 kg for female and 82 kg for male. Results are showed that values of exceeding for combination salad/procymidone in children with lower (14.6kg) weight in relation to weight values given by EFSA Model (16.5 kg) model increased and decreased for children whose weight is higher (22.85 and 56.7 kg). For the adult population the same combination
does not pose a risk. The occurrence of increase concentrations of procymidone [17] explained by the fact that are, in comparison to 2007, from mid-2008 stringent measures in force for this active substance. Due to transitional period across EU markets throughout whole 2008 year were still able to find products with a higher concentration than allowed. This is probably also was the case when in domestic market, in 2008 found a sample of lettuce imported from Italy with an increased concentration of procymidone. For RH analysis of samples of lettuce for that year is not proposed in accordance with international recommendations, but as a product where in previous research (2007) was found residues that exceeding the MRL.

The combination salad/iprodione, according to data in the EFSA Model (portion size 534.7g, children body weight 16.5 kg and adult 66.7 kg), concentration of 10.57 and 11.57 mg/kg) represented risk for all groups. Assessment of exposure with available data for RH shows that risk was found for all consumer groups except for children aged 15 years and men with the use of a smaller variability factor.

Samples with MRL exceedances in domestic production may be associated with violation of instructions on the proper use of pesticides.

Statistically, Croatian consumer’s exposure to pesticide residues checked through three years of monitoring is very small but almost twice higher than in the same period in the EU shown in Table 4.

Compared with the cumulative results of the same program implemented in the Member States it can be seen increase trend in the number of samples analysed in our country and declined the number of samples in the member countries. In [16, 17] reports stated otherwise specified combinations of product/active substance which exceeding MRLs and pose some risk than is the case in the Republic of Croatia in the same monitoring period (2007 - 2009). A similar situation EFSA (2009) is applied only in the case of a combination of lettuce/procymidone on the EU market in 2007. In EU market in 2008 lettuce is not sampled in accordance with the recommendations of the European Commission for a coordinated monitoring programme in the EU.

Opposite, lettuce was analysis on Croatian market in 2008 and 2009 due to detection of residues above the MRL in previous research. Similar situation EFSA reported for the 2007. EFSA (2009) states that the legal boundaries exceed in lettuce samples salads with imidacloprid combination, but the greatest potential to exceed short-term exposure by consumption of salads (expressed as a percentage exceeding the ARfD) were combination: metomyl/thiodicarb/salad (6.241%), methamidophos/salad (2.242%), procymidone/salad (1.683%). For the largest determined concentration of (7.5 mg/kg) procymidone in lettuce, EFSA state that acute health risk will be rarely expressed, except in the case of vulnerable consumers.

In the 2008 oranges, according to the Commission’s recommendations, were included in the monitoring program as required pattern. In our country were analysed in 2007 as well in 2009 as a result of MRL exceeding. EFSA [17] in its report stated that in 2008 the 3% of samples exceeding the MRL established for oranges and the risk was determined for a combination of orange/methomyl/thiodicarb (1644% ARfD). In the same report, for the Spain which represents the country of origin for a proportion of risk patterns in our country have been analysed 68 samples of orange. The 2.9% of samples exceeded the MRL. Some samples contained imazalil, but the risk for orange/imazalil combination has not been determined. None of the other EU member states identify orange/imazalil combination as risk. The greatest ARfD value for 2008 reported United Kingdom for pre-school age children (87.53% ARfD).

Table 4. Comparison of the monitoring results in RH and EU (2007-2009)

<table>
<thead>
<tr>
<th>Program</th>
<th>Year</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total samples</td>
<td>RH</td>
<td>112</td>
<td>246</td>
<td>292</td>
</tr>
<tr>
<td></td>
<td>EU</td>
<td>17575</td>
<td>11610</td>
<td>10553</td>
</tr>
<tr>
<td>Without residues</td>
<td>RH</td>
<td>70%</td>
<td>73%</td>
<td>70.9%</td>
</tr>
<tr>
<td></td>
<td>EU</td>
<td>52.7%</td>
<td>62.1%</td>
<td>61.4%</td>
</tr>
<tr>
<td>Below MRL</td>
<td>RH</td>
<td>23%</td>
<td>23%</td>
<td>27.1%</td>
</tr>
<tr>
<td></td>
<td>EU</td>
<td>45%</td>
<td>35.7%</td>
<td>37.4%</td>
</tr>
<tr>
<td>Over MRL</td>
<td>RH</td>
<td>7%</td>
<td>4%</td>
<td>2.05%</td>
</tr>
<tr>
<td></td>
<td>EU</td>
<td>2.3%</td>
<td>2.2%</td>
<td>1.2%</td>
</tr>
</tbody>
</table>
4. Conclusions

With respect to the results obtained from acute dietary risk assessment for Croatian consumers it can be concluded:

- From total of 650 analysed samples (fruit, vegetables, cereals, derivate) for 4% product (non-compliance with MRL) risk could not be excluded.
- Potential risky samples belong to group of fruit and vegetables.
- Frequency of exceedance was 52% for domestic products and 48% imported products.
- “EFSA PRIMo-Pesticide Residue Intake Model rev 2.0 model” - very useful as a tool for determining the pesticides that can potentially pose a risk to different consumer groups.
- From total number of analysed products, 1% of products exceeds toxicological limits and can pose risk with negative health effects for population (adults and children).
- In general, with regard to the overall result of exposure assessment, it can be conducted that acute risk to consumers in our country can considered rare except for orange and lettuce and consumers with low body weight.
- Based on the results of this investigation and due to the identified risks and the origin of high-risk samples, increased surveillance of oranges and other citrus from imports may be recommend. In situations of finding samples with residues above MRL, for acute risk assessment is recommended to use EFSA PRIMo Model because it represents a high level of consumer protection. Its application provides information about necessarily measure should include recall. The recall involves not only the removal of affected products from the market, but also alert to consumers of existence of the risky products as soon as possible (through media, especially those that are available for a wide range of people). In the case of risky product from domestic production (e.g. lettuce), education of producers about the importance of good agricultural practices adherence can be recommended.

5. References


