HEALTH RISK ANALYSIS OF PESTICIDE RESIDUES IN BERRY FRUIT FROM NORTH-EASTERN POLAND

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A B S T R A C T

The first aim of this paper was to evaluate pesticide residue levels of berry fruit samples. The second aim was to analyze health risks associated with pesticide levels. The monitoring was conducted on samples from producers in north-eastern Poland, during the time period 2005-2010. In total, 241 samples of berry fruit were analyzed using validated and accredited multi residue methods. The studies included 7 commodities (125 strawberry, 59 black currant, 25 raspberry, 23 chokeberry, 7 red currant samples and one sample of elderberry and wild strawberry), and the analysis of 128 pesticides. Residues, mainly insecticides, were found in 47.7% of samples while 40.7% of samples contained pesticide residues below MRLs and 7% above MRLs. The pesticides were found most often in red currant (100%) and black currant (63%) samples. The most frequently detected pesticides were fenazaquin and fenitrothion. Pesticide residues at levels exceeding legally binding MRLs occurred mostly in black currant samples (12 samples).

Violations of the maximum residue limits (MRLs) (15 notifications) and use of a forbidden plant protection product (8 notifications) were found in twenty-three berry samples during the six-year study. For these cases, the RASFF system (rapid alert system for food and feed) procedures were initiated. The highest number of notifications was recorded in 2008 (11 notifications). Only one of the notifications was prepared for berry fruit from an integrated production system – black currant, the remaining were for conventional fruit. Among the RASFF notifications, 17 (74%) were for black currant samples.
The estimated exposure to pesticide residues detected in the analyzed berry fruit samples was shown to be very low for the general population (adults) and for the critical population of small children. Acute and chronic exposure based on residue levels did not adversely affect consumer health.

**Key words:** berry fruit, pesticide residue, RASFF notification, risk assessment, MRL

**INTRODUCTION**

In order to protect human health against adverse effects of plant protection products (p.p.p.) and ensure the safety of the food produced, official control of both the primary and secondary production levels is conducted. Research on pesticide residue and other contaminants in crops and foodstuffs is considered an essential element in each national program. Such research is used to assess the quality of food and to estimate risks to human health.

Berry fruits contain many dietary components: vitamins, minerals, folate and fibre (Seeram, 2008). Residues may be present in berries following pesticide applications. They may not only include the pesticide that was applied but other degradation or reaction products and metabolites that may be of toxicological significance.

Just the eating of berries can represent a significant potential source of human exposure to pesticides and other hazardous chemicals including organophosphorus, organochlorine, carbamate and pyrethroid. Such chemicals are unavoidably or improperly used for protection against pests and putrescence during plant cultivation and the product-manufacturing process.

During recent years, there has been an increasing public concern and scientific investigation related to the presence and control of pesticide residues in plant products. There has been a demand to access the potential risk hazards. Because of high consumption rates and significant health risks of detrimental residues in berries, people from both consumer and producer countries are now paying more attention to berry safety (Yang et al., 2011).

Berry plants are attacked by many pathogens and insects, which is why pesticides are often used in cultivation. Use of plant protection products may be a potential risk to human health, especially the health of young children. To assess the exposure associated with the collection of pesticides in the diet, it is necessary to define consumed food.

An important element of consumer health protection in the European Community is the Rapid Alert System for Food and Feed – RASFF, implemented in Poland since 1 May 2004. Functioning of RASFF is regulated by the European Directive (EC) No 178/2002 (Reg., 2002). The legal basis for the system in the country is the Law of 25 August 2006 for food safety and nutrition (Law, 2006). In the European Union, the RASFF has a network structure. Risk assessment of consumer exposure is being made under the system in the case of prod-
ucts not complying with existing legislation (Struciński et al., 2007). Notification in the RASFF system for pesticide residues in crops, studied at the stage of primary production, include non-compliances arising from: exceeding the maximum residue levels (MRLs), presence of active substances (a.s.) of forbidden p.p.p. in the market, implementation of the p.p.p. threatening human or animal health, or use contrary to the recommendations.

In the case of exceeding the limit values of MRLs and/or use of p.p.p. contrary to the recommendations (Reg., 2005, 2007), the risk was assessed for the general population as well as for small children who are the most vulnerable part of the population.

The aims of this work were to evaluate pesticide residue levels in berry fruit samples and to perform a health risk analysis. The study was conducted under authorized control, in north-eastern Poland in 2005-2010.

MATERIAL AND METHODS

Material for the study (Tab. 1) consisted of 241 berry fruit samples (51.9% – strawberry, 24.5% – black currant; 10.4% – raspberry, 9.5% – chokeberry, 2.9% – red currant, elderberry and wild strawberry at 0.4%). Samples were collected in 2005-2010, from three provinces in north-eastern Poland (Podlaskie, Warmińsko-Mazurskie and Lubelskie) by appropriate inspectors under an authorized control program (Łozowicka et al., 2010). Samples were produced in three systems: organic – 22 samples (9.1%), integrated – 72 (29.9%) and conventional – 147 (61%).

The research program included 128 a.s. commonly used as p.p.p. and relatively persistent in the environment (45 fungicides, 12 herbicides, 67 insecticides and 4 acaricides).

Validated and accredited (PN-EN ISO/IEC 17025) analytical methods were used for pesticide residue determinations. These methods allowed for simultaneous multiresidue analysis of interesting compounds, in accordance with the applicable standards (SANCO, 2009) and proven in international proficiency tests (FAPAS, EU) (Medina-Pastor et al., 2010).

Pesticide residues were isolated using the technique based on matrix solid-phase dispersion MSPD. Extraction was carried out at the same time as the purification step using adsorption column chromatography with silica gel (Łozowicka, 2012).

Quantitative and qualitative analysis of prepared extracts from samples were performed by gas chromatography (GC) using two selective detectors EC (electron capture) and NP (nitrogen-phosphorus) and high performance liquid chromatography (HPLC) with a UV and fluorescence detection system. Dithiocarbamates expressed as CS₂ was determined by a spectrophotometry method (Chmiel, 1979).

Incompliances related to the exceeding of MRLs assessed in relation to national and EU legislation (Reg., 2005, 2007). In the case of detection of a.s. of forbidden p.p.p. on the market, assessments were done according to the plant protection act (Law, 2004) and current preparation label.
Table 1. Number of analyzed samples in 2005-2010

<table>
<thead>
<tr>
<th>Berry fruit</th>
<th>Number of samples analyses</th>
<th>Number of samples with residues</th>
<th>RASFF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td>Conven.</td>
<td>Integr.</td>
</tr>
<tr>
<td>Black currant</td>
<td>59</td>
<td>37</td>
<td>20</td>
</tr>
<tr>
<td>Chokeberry</td>
<td>23</td>
<td>13</td>
<td>-</td>
</tr>
<tr>
<td>Elderberry</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Raspberry</td>
<td>25</td>
<td>15</td>
<td>9</td>
</tr>
<tr>
<td>Red currant</td>
<td>7</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Strawberry</td>
<td>125</td>
<td>75</td>
<td>31</td>
</tr>
<tr>
<td>Wild strawberry</td>
<td>1</td>
<td>1</td>
<td>-</td>
</tr>
</tbody>
</table>

n* – number of samples with forbidden active substance
Conven. – conventional, Integr. – integrated, Organ. – organic
MRLs – maximum residue levels

To assess the risk associated with the consumption of berries containing residues, the results of the research were used. The evaluation was conducted for the general population of consumers (adults) and the critical population; children aged from 1.5 to 4 years, as the group most vulnerable to the effects of pesticide residue exposure (Łozowicka, 2009).

Short-term exposure was estimated by comparing a single intake of the highest detected residue of plant protection products to a set volume ARfD (Acute Reference Dose).

Long-term exposure was estimated by comparing the daily intake of residues, calculated from the average pesticide residues detected in fruit to set value of the tolerable daily intake ADI (Acceptable Daily Intake). In cases where the compounds were not detected above the limit of quantification, the calculation of the average residue values of the limit of quantification were assumed.

The risk assessment of consumer health exposure associated with consumption of crops containing pesticide residues was based on the available epidemiological studies. These were studies conducted for the two sub-populations in the database of food consumption: the British model, Pesticides Safety Directorate (PSD, 2006), for consumption at the 97.5 percentile. In Poland, there is no complete data for these populations, hence there was a need to use other available sources.
The values of ADI and ARfD are elaborated by the European Food Safety Authority (EFSA) of the European Union (EU) (EFSA, 2008) or the Federal Institute for Risk Assessment (BfR), Germany (Grenzwerte, 2006).

RESULTS AND DISCUSSION

Based on studies of 241 berry fruit samples, the presence of pesticides was estimated and 115 of them contained chemical contamination (47.7%). Distribution of pesticide residues in selected berry fruit is shown in Figure 1.

The highest percentage of detected pesticide residues was shown in red currant samples (100%), a lower percentage was seen in black currant (63%), raspberry (52%) and strawberry (46%) samples. Chokeberry, elderberry and wild strawberry samples were free from residues.

Pesticide residues were reported in 59% of black currant samples from the conventional system and 75% from the integrated system. The largest number of active substances was detected in one black currant sample derived from a conventional production, with 5 residues (cypermethrin 0.03 mg/kg; dithiocarbamates 0.19 mg/kg; fenazaquin 0.24 mg/kg; fenitrothion 0.03 mg/kg; flusilazole 0.01 mg/kg). In addition, 11 multi-residue samples from conventional systems containing from 2 to 4 a.s and 5 samples with 2 a.s. in the integrated. There were also cases where a.s. of fungicidal p.p.p. not authorized for use in strawberry cultivation which were detected (procymidone and tolylfluanid) (Tab. 2).

Raspberry samples with residues were noted in 40% of the samples from the conventional production while 78% for integrated production. There were three multi-residue samples detected: 2 from conventional system containing 2 to 3 residues, and 1 from the integrated with 2 compounds.

From 2005 to 2010, twenty-three cases were reported in which consumption could pose a significant health risk to consumers (Tab. 1). Special attention should be focused on non-compliances associated with detection of active substance of p.p.p. not authorized for use in a given crop: endosulfan (IC), procymidone (F) (above NDP) and also azoxystrobin (F), endosulfan (IC), flusilazole (F), tolyfluanid (F) (below NDP) (Tab. 2).
Figure 1. Pesticide residues in selected berry fruit: a) black currant, b) red currant, c) raspberry and d) strawberry.
### Table 2. Crops with RASFF notification

<table>
<thead>
<tr>
<th>Year</th>
<th>Berry fruit</th>
<th>Pesticide group</th>
<th>System production</th>
<th>Active substance</th>
<th>Concentration ± uncertainty [mg/kg]</th>
<th>MRLs PL* or EC**</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006</td>
<td>black currant</td>
<td>IC</td>
<td>conven.</td>
<td>endosulfan</td>
<td>0.03±0.009</td>
<td>0.05*</td>
</tr>
<tr>
<td></td>
<td>black currant</td>
<td>I</td>
<td>conven.</td>
<td>fenazaquin</td>
<td>0.25±0.075</td>
<td>0.10*</td>
</tr>
<tr>
<td></td>
<td>black currant</td>
<td>IF</td>
<td>conven.</td>
<td>fenitrothion</td>
<td>0.06±0.018</td>
<td>0.01*</td>
</tr>
<tr>
<td></td>
<td>black currant</td>
<td>F</td>
<td>conven.</td>
<td>procymidone</td>
<td>0.02±0.006</td>
<td>0.02*</td>
</tr>
<tr>
<td></td>
<td>red currant</td>
<td>IF</td>
<td>conven.</td>
<td>fenitrothion</td>
<td>0.03±0.009</td>
<td>0.01*</td>
</tr>
<tr>
<td></td>
<td>red currant</td>
<td>F</td>
<td>conven.</td>
<td>flusilazole</td>
<td>0.29±0.087</td>
<td>0.20*</td>
</tr>
<tr>
<td>2007</td>
<td>black currant</td>
<td>I</td>
<td>conven.</td>
<td>fenazaquin</td>
<td>0.22±0.066</td>
<td>0.10*</td>
</tr>
<tr>
<td></td>
<td>black currant</td>
<td>I</td>
<td>conven.</td>
<td>fenitaquin</td>
<td>0.24±0.072</td>
<td>0.10*</td>
</tr>
<tr>
<td></td>
<td>black currant</td>
<td>IF</td>
<td>conven.</td>
<td>fenitrothion</td>
<td>0.03±0.009</td>
<td>0.01*</td>
</tr>
<tr>
<td></td>
<td>black currant</td>
<td>IP</td>
<td>conven.</td>
<td>fenitrothion</td>
<td>0.09±0.027</td>
<td>0.05*</td>
</tr>
<tr>
<td></td>
<td>black currant</td>
<td>IF</td>
<td>conven.</td>
<td>fenitrothion</td>
<td>0.02±0.006</td>
<td>0.01*</td>
</tr>
<tr>
<td></td>
<td>black currant</td>
<td>F</td>
<td>conven.</td>
<td>fenitrothion</td>
<td>0.11±0.058</td>
<td>0.10*</td>
</tr>
<tr>
<td></td>
<td>black currant</td>
<td>I</td>
<td>conven.</td>
<td>fenazaquin</td>
<td>0.13±0.039</td>
<td>0.10*</td>
</tr>
<tr>
<td></td>
<td>red currant</td>
<td>IF</td>
<td>integr.</td>
<td>fenitrothion</td>
<td>0.02±0.006</td>
<td>0.01*</td>
</tr>
<tr>
<td></td>
<td>strawberry</td>
<td>F</td>
<td>conven.</td>
<td>tolylfluanid</td>
<td>0.10±0.030</td>
<td>5.00*</td>
</tr>
<tr>
<td></td>
<td>strawberry</td>
<td>F</td>
<td>conven.</td>
<td>tolylfluanid</td>
<td>0.49±0.147</td>
<td>5.00*</td>
</tr>
<tr>
<td>2008</td>
<td>black currant</td>
<td>IP</td>
<td>conven.</td>
<td>esfenvalerate</td>
<td>0.10±0.030</td>
<td>0.02**</td>
</tr>
<tr>
<td></td>
<td>black currant</td>
<td>IP</td>
<td>conven.</td>
<td>esfenvalerate</td>
<td>0.15±0.045</td>
<td>0.02**</td>
</tr>
<tr>
<td></td>
<td>black currant</td>
<td>F</td>
<td>conven.</td>
<td>flusilazole</td>
<td>0.03±0.009</td>
<td>5.00**</td>
</tr>
<tr>
<td></td>
<td>red currant</td>
<td>I</td>
<td>conven.</td>
<td>fenazaquin</td>
<td>0.09±0.027</td>
<td>0.01**</td>
</tr>
<tr>
<td>2009</td>
<td>black currant</td>
<td>I</td>
<td>conven.</td>
<td>fenazaquin</td>
<td>0.05±0.015</td>
<td>0.01**</td>
</tr>
<tr>
<td></td>
<td>black currant</td>
<td>F</td>
<td>conven.</td>
<td>cypermethrin</td>
<td>0.10±0.030</td>
<td>0.05**</td>
</tr>
<tr>
<td></td>
<td>black currant</td>
<td>F</td>
<td>conven.</td>
<td>azoxystrobin</td>
<td>0.06±0.018</td>
<td>5.00**</td>
</tr>
<tr>
<td></td>
<td>strawberry</td>
<td>F</td>
<td>conven.</td>
<td>procymidone</td>
<td>0.22±0.066</td>
<td>0.02**</td>
</tr>
</tbody>
</table>

*maximum residue levels (MRLs) according to European Commission (EC) regulations

**maximum residue levels (MRLs) according to Polish (PL) regulations

**bolded** – active substance of forbidden p.p.p. with residues > MRLs

*italics* – active substance of forbidden p.p.p. with residues < MRLs


Conven. – conventional, Integr. – integrated
In the study period of 2005-2010, the highest number of notifications was prepared in 2008 (46%). This is due to the harmonization of Polish standards with the EU on the maximum levels of pesticides. The EU directive has introduced strict limits for certain active substances, often setting MRLs on the detection level of the analytical method. An example might be fenazaquin for which the national MRL is ten times lower than the European (MRL = 0.01 mg/kg UE).

The analyzed data shows the most often identified pesticides exceeding the MRLs were: fenazaquin (I) and fenitrothion (IF), which were present in black currant and red currant samples. The frequency of the detected compounds in non-complying samples is shown in Figure 2.

Taking into account the concentration levels detected in berry fruit samples from the three production systems, non-compliances were found in 3% of samples from the integrated production and 15% from the conventional. Therefore it can be concluded, that integrated agriculture clearly produces less contaminated food compared with the conventional. In samples from organic production, as planned, no pesticide residues were detected.

The study adopted a rather critical assessment of consumer exposure criteria for having a high level of consumption combined with the highest level of pesticide residues found in berry fruit samples. Cases where the risk assessment indicates the possibility of exceeding the limits, the ARfD or ADI are transferred to the RASFF national focal point.

The estimated surveyed population with a chronic dietary health exposure from the consumption of all the pesticide residues detected in 2005-2010 in berry fruit, is shown in Figure 3. The estimated ADI values ranged from 0.1% to 17.1% for young children and from 0.1% to 17.4% for adults. Long-term exposure is quite low, and only in the case of procymidone for adults was it about 32%.

One of the most important elements of risk assessment is a reference to the estimated consumption of a product containing high levels of pesticide residues in the acute reference dose (ARfD) designated for this pesticide. This approach enables quantitative assessment of risk, providing the grounds for further decisions concerning this product (Ludwicki and Kostka, 2008).

Short-term exposure (acute) was estimated only for compounds having a specific value ARfD, with regard to their highest detected level. Total % ARfD for all pesticides for the individual berries is low, and for adults did not exceed 3%. For young children was slightly above 7.5% (Fig. 4.). For the highest recorded pesticide residue level – procymidone in the black currant sample (0.57 mg/kg), the estimated short-term exposure was only 0.6% for adults and less than 2% for children.

All RASFF notifications were considered as information which was provided, and following a risk assessment, none of them went to the EC database CIRCA.
Health risk analysis of pesticide residues in berry fruit…

Figure 2. Frequency of detected compounds with non-compliances related to exceeding the MRLs and related to the presence of active substance/s of forbidden plant protection product/s

Figure 3. Chronic dietary exposure to pesticides in berry fruit for adults and young children

ADI – Acceptable Daily Intake
According to the European Commission, one of the reasons for the increase in the number of RASFF notifications in recent years may be the more active involvement of Member States in reporting on the identified risks (Łozowicka, 2010). This may be explained by the improvement of the analytical performance of the laboratories (increased number of pesticides searched for, and higher sensitivity of detection) methods. For example in the Pesticide Residue Laboratory in Bialystok only 25 active substances were determined in 1975. Nowadays, after broadening the scope of the active substances and lowering the limit of quantification, approximately 130 compounds are analyzed.

The present study shows a high incidence rate of pesticides (mostly insecticides) in the analyzed samples. The most critical commodity was black currant samples (the highest number of samples with MRLs violations). The results also emphasize the need for regular monitoring of a greater number of berry fruit samples for pesticide residues.

**CONCLUSIONS**

1. As a result of authorized control methods carried out in 2005-2010, twenty-three incompliances of the analyzed berry fruit samples were found.
2. Results from a six-year period showed that producers did not
comply with the recommendations of the use of preparations according to the label (15 notifications) and also used p.p.p. which were unauthorized on the market (8 notifications).

3. The largest number of incompliances was noted for black currant samples – 17, which were mostly associated with insecticides, such as fenazaquin and fenitrothion.

4. Despite the fact that residues in conventional fruits were in 61.5% of the samples and 78.2% of the integrated group, the vast majority of incompliances were related to conventional production, only 1 case was related to integrated production. There were no incompliances for organic samples.

5. The largest number of RASFF was reported in 2008 (11 notifications) as a result of more stringent EU values of MRLs (than national).

6. Risk assessment has shown that consumer exposure to pesticide residues in berry fruit samples is relative low. No products were found in which consumption could have negative health effects.

7. The estimated risks to the health of children and adults based on the level of pesticide residues detected in the analyzed samples, indicates that intake of pesticides did not exceed the “safe” values of ADI and ARfD.

8. Pesticide residue monitoring is an important element of consumer health protection. The monitoring allows for the rapid elimination of a health threat (particularly for children) at the stage before the product would appear on the market.

9. Data justify the extension of authorized control procedures for the detection of pesticide residues, especially when it comes to currants, because they may be a potential source of food contamination from chemicals.

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The rapid alert system for food and feed of the European Union. 30 years of keeping consumers safe. Luxembourg, 2009.
OCENA NARAŻENIA KONSUMENTA NA POZOSTAŁOŚCI PESTYCYDÓW W OWOCACH JAGODOWYCH Z PÓŁNOCNO-WSCHODNIEJ POLSKI

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S T R E S Z C Z E N I E


Procedurę RASFF (Rapid Alert System for Food and Feed) w trakcie sześciolatnich badań wszczęto w dwudziestu trzech przypadkach, tylko raz dla próbek z produkcji integrowanej (flusilazol), w pozostałych przypadkach dotyczyły owoców wyprodukowanych w sadach konwencjonalnych. Nie stwierdzono niezgodności dla owoców ekologicznych. Powiadomienia przesłano ze względu na przekroczenia najwyższego dopuszczalnego poziomu pozostałości (NDP) (15 zgłoszeń) oraz stosowania niedozwolonych środków ochrony roślin (8 zgłoszeń). Największą liczbę powiadomień odnotowano w 2008 roku, w większości dla próbek porzeczki czarnej – 17 powiadomień (74% wszystkich zgłoszeń RASFF). Najczęściej zgłoszenia RASFF dotyczyły insektycydów (70%), to jest fenazachin i fenitrotionu.

Oszacowane ryzyko narażenia dla populacji generalnej (dorośli) i populacji krzyżowej tzn. małych dzieci na pozostałości środków ochrony roślin wykazało, że jest ono stosunkowo niskie. W omawianym okresie nie stwierdzono produktów z owocami jagód, których spożycie mogło mieć negatywne skutki zdrowotne.

Słowa kluczowe: owoce jagodowe, pozostałości pestycydów, powiadomienia RASFF, ocena ryzyka, najwyższe dopuszczalne poziomy