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THE OCCURRENCE OF PESTICIDES IN BERRY FRUITS FROM ORGANIC AND CONVENTIONAL CULTIVATION

WYSTĘPOWANIE ŚRODKÓW OCHRONY ROŚLIN W OWOCACH JAGODOWYCH Z UPRAW KONWENCJONALNYCH I EKOLOGICZNYCH

Abstract: Food from organic and conventional crops should retain sufficient nutritional value as well as a low content of substances which may pose a risk to health such as pesticide residues. The aim of the study was to determine and evaluate the residues of pesticides in raw berry fruits from organic and conventional crops from Podlasie region in Poland. The 141 samples of berry fruits from conventional crops and 61 samples of berry fruits from organic crops were collected in 2011: blackcurrant (57), redcurrant (26) and strawberry (119). The study included 160 pesticides, among which 28 were detected in the products of conventional crops, and 11 were found in the products from organic crops. During the study one detected the presence of substances whose use in plant protection is prohibited. Procymidone was found in 1 sample of blackcurrant. On the basis of conducted study a share of samples with multi-residues detected in the products was estimated: 21 % of the samples of organic crops contained from 2 to 5 residues, and 53 % of the samples of conventional crops contained from 2 to 9 residues. Because of the presence of residues of plant protection products in the organic products it is recommended to monitor food produced from these crops.

Keywords: pesticide residues, berry fruits, organic and conventional crops

The use of pesticides in conventional agriculture resulted in a significant increase in agricultural production and reduction of crop losses. However, the wide use of plant protection products has also disadvantages – there is the risk of residues in food and different elements of the natural environment, which can cause a variety of health effects. The risk arising from the use of pesticides affects mainly persons engaged in the distribution and production of these compounds, agricultural workers and those living in rural areas or eating contaminated food [1].

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In the recent years, organic farming has been promoted in Poland by governmental financial support which has been reflected in rural areas development plans. Polish farmers may apply for the European Union surcharges which are targeted at those who by the implementation of organic production not only produce high quality food, but also help to maintain biodiversity and protect natural resources [2]. According to Tomalak et al [3], organic production is considered to be the best system of farm management and food production that combines the best environmental practices, a high level of biodiversity, preservation of natural resources, application of high animal welfare standards and a production method corresponding to needs of certain consumers preferring products made from natural ingredients and as a result of natural processes. The main assumption of plant protection in organic farming is not to fight the diseases and pests, but creation the right conditions for plant growth, so that these factors could not develop in the crop or their impact on yield should be minimal. Organic products should not contain residues of other plant protection products, apart from those approved for use. The Maximum Residue Levels (MRLs) of plant protection products in organic farming are not standardized either in Poland or in the European Union, and even some countries believe that there is no need to normalize them [4]. Generally, residues should not be higher than the limit of detection [5].

The aim of this study was to evaluate and determine the residues of pesticides in raw berry fruits from organic and conventional crops from Podlasie region in Poland.

Materials and methods

The 141 samples of berry fruits from conventional crops and 61 samples of berry fruits from organic crops were collected in 2011: blackcurrant (57), redcurrant (26) and strawberry (119) from the Podlasie region in Poland. Pesticides (160 active substances) from various chemical and biological groups were investigated.

Berry fruits samples were obtained according the Polish norm [6] from the north-eastern Poland. The berry fruits samples were put into polyethylene bags and stored at –20 °C. Before the analysis they were thoroughly shredded and homogenized, except the analysis of dithiocarbamate residues where whole fruits were left.

The samples were analyzed by multi-residue method (MRM) by matrix solid phase dispersion method (MSPD), which is one of the most promising techniques to reduce matrix interferences. It involves dispersion of the sample over a solid support and subsequent elution with a relatively small volume of solvent [7, 8, 9].

The Pesticide Residues Laboratory (Białystok, Poland) is accredited according to PN-EN ISO/IEC 17025 by the Polish Centre for Accreditation and takes part in official food control every year [10]. The scope of accreditation covers different numbers of matrix/pesticide combinations. All the methods were validated. The quality of analytical methods is in compliance with the requirements of Document SANCO/10684/2009 [11].

An indispensable precondition for setting MRL is a risk assessment demonstrating consumer safety (consumer intake not exceeding the toxicological reference values).
The results under the limit of detection (LOD) of analytical methods used for intake calculations were taken as LOD values.

**Results and discussion**

Unlike most other chemical products, pesticides are deliberately released into the environment for controlling undesired organisms such as weeds, fungi and insects. Pesticides are biologically active compounds with a toxic component. They are regarded as significant sources of diffuse pollution that might cause long-term health implications in humans [12]. Among 141 samples from conventional farms, the remains of plant protection products were found in 78 samples. In 8 of them MRLs was exceeded, which constituted 5.7%. In the 78 samples analyzed 28 active substances were detected. Table 1 presents the results of the analyzed samples according to assortment. Six pesticides exceeding MRL were observed: carbendazim and fenazaquin (in 2 samples), procymidone, cypermethrin, acetamiprid and propargite (each in 1 sample). During the study one detected the presence of substances whose use in plant protection is prohibited. It was procymidone, which was found in 1 sample of blackcurrant. According to Slowik-Borowiec et al [13], the presence of procymidone in the analyzed samples is associated with the widespread use of the preparations containing this substance in the recent years to effectively combat among others grey mould (*Botrytis cinerea*) in a wide range of fruit plants, vegetables and ornamentals. However, in the samples obtained from organic farms, plant protection products were found in 51 samples and 16 active substances were detected (Table 1, Fig. 1).

<table>
<thead>
<tr>
<th>Crop</th>
<th>Samples without residues</th>
<th>Fungicide</th>
<th>Insecticide</th>
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<tr>
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<td>&lt; MRLs</td>
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<tr>
<td>Organic crop</td>
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<td>Blackcurrant</td>
<td>2</td>
<td>2</td>
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<tr>
<td>Redcurrant</td>
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<tr>
<td>Strawberry</td>
<td>40</td>
<td>11</td>
<td>0</td>
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<tr>
<td>Conventional crop</td>
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<tr>
<td>Blackcurrant</td>
<td>27</td>
<td>14</td>
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<tr>
<td>Redcurrant</td>
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<td>13</td>
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<tr>
<td>Strawberry</td>
<td>54</td>
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According to Fernandes [14], although synthetic pesticides are not allowed for use in organic crops production, their sporadic presence of their residues can be readily explained. Organic and conventional agriculture usually takes place on adjoining farms, as a result of which the risk of cross-contamination cannot be excluded. Sometimes, the
presence of pesticide residues in organic crops can also occur due to unlawful use of synthetic pesticides.

Pesticide residues were appraised according to the European Union Regulations [15] and compared with MRL. Maximum Residue Levels are the upper legal levels of concentration for pesticide residues in or on food or feed based on good agricultural practices, ensuring the lowest possible consumer exposure. Regulation (EC) No 396/2005 [16] establishes the MRLs of pesticides permitted in products of plant or animal origin intended for human or animal consumption. MRLs are derived after a comprehensive assessment of the properties of the active substance and residue levels resulting from the good agricultural practices defined for the treated crops. In Poland the year 2008 was very important for the harmonization of pesticide MRL legislation at the European level. Before September 1, 2008, a mixed system, with harmonized Community MRLs for about 250 active substances and national MRLs for the remaining substances, was applicable. When Regulation (EC) No 396/2005 [16] was introduced, it harmonized MRLs for all active substances used in plant protection products. According to Niewiadomska et al [17], one of the important measures to ensure food safety is constant control of pollutants. Such research is done not only to protect the health of consumers, but also to meet the quality requirements of food production both for the domestic market and the international.

Figure 1 illustrates all the detected active substances in the samples from organic crops. There were eight insecticides such as dimethoate, chloropyrifos, atrazine

![Diagram of detected active substances](https://example.com/diagram.png)

**Fig. 1.** Detected active substances of plant protection products in berry fruits from ecological crops
cyflutrin, acetamipryd, lambda-cyhalothrin, bifenthrin and cypermethrin, which were detected more than once. Moreover, eight fungicides such as dithiocarbamates, tetraconazole, boscalid, pyrimethanil, pyraclostrobin, cyprodinil, carbendazim and fenexamid were detected in the analysed samples. The highest concentration of fungicide, 3.05 mg · kg⁻¹, was observed for dithiocarbamates in a sample of strawberry. According to Claeys et al [17], dithiocarbamates have been widely used in the agricultural industry for 80 years. These compounds have shown wide applications as pesticides, fungicides in agriculture. Tetraconazole (fungicide) was detected at concentrations ranging from 0.01 to 1.07 mg · kg⁻¹ (MRL = 0.2 mg · kg⁻¹), boscalid was found in 1 sample at concentration 1.9 mg · kg⁻¹ (MRL = 0.05 to 10.00 mg · kg⁻¹). The highest concentration of insecticide 0.14 mg · kg⁻¹ (MRL = 0.5 mg · kg⁻¹) was observed for bifenthrin in a sample of strawberry. Cypermethrin, the most commonly used insecticide in crops of berry fruits, was found in 5 samples at concentrations ranging from 0.002 to 0.02 mg · kg⁻¹ (MRL = 0.02 mg · kg⁻¹) (Fig. 1).

Cypermethrin is important synthetic pyrethroid insecticide, extensively used in cotton, fruit and vegetable crops as well as in animal health, home and garden pest control worldwide [18]. As stated by Weston et al [19], the use of cypermethrin has increased sharply, especially over the recent years, with the restrictions or eliminations of highly toxic organophosphate pesticides, and it has become one of the dominant insecticides among retail sales to consumers.

In the tested samples from conventional farms captan, dithiocarbamates and boscalid were the most active substances detected among fungicide, while propigate and chlorpyrifos-ethyl among – insecticides. The highest concentration of fungicide, 3.42 mg · kg⁻¹, was observed for captan in a sample of blackcurrant. According to Barreda et al [20], captan is used to control fungal disease on a wide variety of crops. It acts through inhibition of a fungal process of respiration and metabolism through a non-specific thiol reactant. Although it is not a systemic fungicide, adjuvants can enhance transport of captan through a plant cuticle [21]. Teixeira et al [22] have found that levels of captan and procymidone residues were reduced by the pre-harvest intervals and/or culinary application, such as washing, peeling and storage. Boscalid is the second active substance which was detected at concentrations ranging from 0.02 to 0.99 mg · kg⁻¹ (MRL = 0.05 to 10.00 mg · kg⁻¹). Dithiocarbamates was found in 18 sample at concentrations ranging from 0.05 to 1.49 mg · kg⁻¹ (MRL = 5.00 mg · kg⁻¹) (Fig. 2).

Many authors [23–25] report that berry fruits have high levels of nutrients that are beneficial for health, a high water activity and low pH value, which makes blueberries particularly susceptible to fungal spoilage. To avoid it, the application of fungicides, as eg boscalid, is recommended for the prevention and treatment of grey mold (Botrytis cinerea) in fruit plants and vines.

Fungicides are considered to be non-selective and are used commonly to control a broad spectrum of plant diseases; hence, they have the potential to cause critical changes in soil microbial populations. It has been concluded by some authors that even a single application of fungicide at field rates may cause lasting changes in nitrogen transformations and availability in soils [26].
Another problem is multi-residue samples in plants. Although these effects are clearly observed in animal study for some substances, human epidemiological study have inherent limitations in identifying causes and effects of chronic exposures. A causal link between chronic exposure to pesticides and their possible health effects is difficult to establish because consequences appear years after a generally intense exposure or after repeated low-intensity exposures over many years [27].

During this period, 14.8 % (9 samples) of all samples were detected with one residue and 13.2 % (8 samples) contained more than one residue (from 2 to 5 active substances). Most samples contained two compounds, which constituted approximately
6.6% (4 samples) of all samples, while four and five – 1.6% (1 sample). Dithiocarbamates (F), tetraconazole (F) and cypermethrin (I) were the most often found combinations in the multi-residue samples from organic crops. Multi-residues were found most frequently in strawberry samples, which is in accordance with study conducted by Gnusowski et al [5]. The multi-residue samples are presented in Fig. 3.

According to Grosicka-Maciag [28], the occurrence of multiple residues in single crop samples can be the results many different factors, including the usage of pesticide formulations which contain more than one pesticide agent, the presence of certain persistent compounds in the environment, the application of various pesticides at different stages of growth and the mixture of different lots.

The results (Fig. 4) showed that the concentration of pesticide multi-residues in berry fruits amounted to 25.5% (36 samples) of all samples were detected with one residue and 53.0% (74 samples) contained more than one residue (from 2 to 9 active substances). Most samples contained two or three compounds, approximately 14.9%
(21) and 10.6 % (15), while eight and nine – 0.7 % (1) and 1.4 % (2), respectively. Captan (F), boscalid (F), dithiocarbamates (F) and propargite (I) were the most often found in combinations in multi-residue samples from conventional crops.

Conventionally grown crops are expected to contain some pesticide residues because pesticides are used to control pests on these crops. The MRL values should be set at levels that are high enough to prevent chance of contravention if pesticides are used in compliance with good agricultural practice (GAP), but at the same time not so high that misuse will not be detected. In contrast, in the case of organically grown crops synthetic pesticides are not allowed, but as aforementioned, the presence of pesticides cannot be totally avoided due to circumstances that are beyond the control of the organic operator such as cross-contamination, especially from the earlier period, when pesticides were used on the fields. Nevertheless, samples of organic crops have apparently a much lower rate of pesticide residue findings compared with conventionally grown crops [29].

Conclusions

1. High percentage of berry fruits samples with residue below and above the allowed level (MRL) was observed in those samples taken from conventional crops.

2. High percentage of multi-residue samples was observed in the samples from organic crops. In terms of quality and food safety, multi-residues in berry fruits samples may carry increased risks to health of consumers, due to the overlapping various effects of the compounds characterized by different modes of action.

3. Due to the common occurrence of pesticide residue above MRL, prohibited pesticide and samples with multi-residues, berry fruits should be systematically monitored. Nevertheless, the results emphasize the need for continuous monitoring of pesticide residues in samples from organic crops for the purpose of authentication.

4. Due to the short growing season of berries and their instability, this study confirm the necessity of monitoring the correct performance of chemical treatments by farmers, in particular in conventional crops compliance with grace periods and manufacturers’ instructions of plant protection products use.

References

Abstrakt: Celem badań było określenie pozostałości pestycydów w świeżych owocach jagodowych z upraw ekologicznych i konwencjonalnych w województwie Podlaskim, Polska. Materiał do badań w 2011 r. stanowiło 141 próbek owoców jagodowych z upraw konwencjonalnych oraz 61 próbek z upraw ekologicznych, w tym: czarnej porzeczki (60), czerwonej porzeczki (25) i truskawek (119). Badaniami objęto 160 substancji aktywnych, z których 28 wykryto w produktach z upraw konwencjonalnych i 16 stwierdzono w produktach
z upraw ekologicznych. Podczas badania wykryto obecność substancji, których stosowanie jako środków ochrony roślin jest zabronione. Do nich należy procymidon stwierdzony w 1 próbie porzeczki czarnej. Na podstawie przeprowadzonych badań oceniono udział próbek zawierających multipozostałości: od 2 do 5 pozostałości s.a. wykryto w 21,0 % produktów z upraw ekologicznych, a 53,0 % produktów z upraw konwencjonalnych zawierało od 2 do 9 pozostałości s.a. Ze względu na obecność pozostałości środków ochrony roślin w produktach ekologicznych zaleca się systematyczny monitoring żywności z tych upraw.

Słowa kluczowe: pozostałości pestycydów, owoce jagodowe, uprawy ekologiczne i konwencjonalne