Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.883793

52 (2014) 3804–3818
May

Pesticide residues in berries fruits and juices and the potential risk for consumers

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Received 2 March 2013; Accepted 10 September 2013

ABSTRACT

The aim of this study was to determine the residues of pesticides in raw and processed berries from Poland and to propose the estimation of risk assessment for two populations: of adults and children as the most critical group. The 170 samples of berry fruits and their products were collected in 2011: gooseberry (11), blackcurrant (25) and redcurrant (35), raspberry (27), strawberry (62), and the concentrated juice of blackcurrant (3), redcurrant (1), raspberry (2), and strawberry (4). The study included 160 pesticides, among which 29 were detected. Pesticide residues were noted in 44.7% samples, 14.7% samples above the maximum residue level were found. During the study, the prohibited substances for protection of crops were found such as procymidone, flusilazole, tetraconazole, and trifloxystrobin. Procymidone was found in 10 samples of raspberry and blackcurrant, while flusilazole, tetraconazole, and trifloxystrobin were detected in gooseberry. About 34.1% of the samples contained more than one residue (from 2 to 9). Based on the results of the occurrence of pesticide residues in berry fruits, long- and short-term health risk was estimated. The acute and chronic exposures were minimal and did not exceed a safe value of 100% safety value acute reference dose and acceptable daily intake.

Keywords: Pesticide residues; Berries fruits; ADI; ARfD

1. Introduction

Food is necessary for people and should be "safe." Over the last few years, one has observed an increase in various types of chemical contaminants in food [1]. Residuals are one of the most important chemical contaminants in food of plant origin, found in small concentrations, but they may affect the health of consumers [2–5]. These residues are mainly a consequence of agricultural chemicals use and application of pesticides to protect crops from unwanted agrophages. Attention is focused on pesticide contamination due to their high toxicity and persistence in the environment. Organochlorine compounds (OCs), such as polychlori-

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Presented at the 11th Scientific Conference on Microcontaminants in Human Environment. 25–27 September 2013, Wisla, Poland Organized by Department of Chemistry, Water and Wastewater Technology, Faculty of Environmental Engineering and Biotechnology, Czestochowa University of Technology

nated biphenyls and organochlorine pesticides (OCPs), are ubiquitous pollutants in the environment, and have been of great concern owing to their persistence, chronic toxicity, and bioaccumulation. Moreover, the use of OCPs, was restricted or forbidden by legislation many years ago, but nowadays these compounds are still detected. Pesticide contaminants may be related to the origins of these plants if they are grown in the contaminated environment, e.g. banned pesticides such as DDT was deposited in soil many years ago [6]. During growing and post harvest times, plants can be protected by controlled use of plant protection products (insecticides, fungicides, and herbicides) against agrophages. It is the main source of pesticide residues. The term "residue" of plant protection products means the sum of chemical compounds, and thus both the sum of the unchanged active substance and its metabolites, degradation products (e.g. 1,1,1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl) ethane; 1,1-dichloro-2-(o-chlorophenyl)-2-(p-echlorophenyl) ethane; 1,1-bis(4-chlorophenyl)-2,2-dichloroethane; dichlorodiphenyldichloroethane; 1,1-dichloro2,2-bis(p-chlorophenyl) ethylene; 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene; 1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane), or isomers (e.g. α-, β-endosulfan), which are "in" or "on" plants or plant products. Toxic effects of pesticides are dependent on biological activity of substances, the way of applications and forms, persistence, and bioaccumulation [7,8]. Therefore, increased awareness about the negative effects of residues of plant protection products in food makes it extremely important to monitor their presence, quality evaluation, and consumers' health risks of exposure to these residues [9].

This is especially important in the case of berries such as strawberries, blueberries, and currants, which very intensively chemically protected and which are an important part of the human diet. The implemented programs of chemical plant protection are often dictated by the prevailing climatic conditions. For example, an increase in humidity is an important cause of fungal attack (*Botrytis cinerea*), and as a consequence plantation use a lot of fungicides [8].

Nutritionists recommend a daily intake of fruit at about 250–400 g. This amount covers optimal conditions of the metabolism in the body since fruit is a source of vitamins, minerals, biologically active substances, and dietary fiber [10]. Good taste, nutritional values, and antioxidant properties of berries [11] cause the increase of the number of consumers in Poland and worldwide.

The raw or processed berries are eaten seasonally as well as throughout the year. They ensure proper functioning of the body and stimulate a number of biochemical processes occurring in it. Their nutritional, medicinal, and health properties are effective when these fruits do not contain residues of pesticides used extensively in the cultivation of raspberries [12].

A mathematical analysis was carried out in order to estimate chronic and acute risk health of consumers to pesticide residues. The information concerning consumption of berry fruits and the level of detected pesticide residues are combined to estimate both terms residues intake of pesticides by the diet. Estimating intake residues in the diet is then set against accepted safe levels (Acceptable daily intake (ADI) and Acute reference dose (ARfD)) [8]. ADI is the amount of residue which can be eaten every day in life without the slightest harm to health, while the ARfD is the amount that can be eaten in one meal or on one day without harmful effects on our health. The estimated intake residues in the diet are then compared with the "acceptable safe levels" (that is ADI and ARfD).

In order to assess the risk of exposure of human health to the pesticide residues, first of all, the individual components of dietary intakes must be known [13], taking into account different age groups (e.g. infants, toddlers, school children, adults, etc.), as it relates to body weight and nutritional prevention. Accordingly, 13 GEMS/Food Consumption Cluster Diets were developed based on FAO Food Balance Sheet data from 183 countries. The average intake for each food item at the cluster level was weighed by the population size of the reporting country. The western and central parts of Europe, such as the United Kingdom, Poland, Germany, etc., have been classified into the same Consumption Cluster Diets E [14].

The first aim of this study was to determine the residues of plant protection products in raw and processed berries from the northeastern Poland (Podlasie). The second aim was to estimate the risk of consumers' health and to detect pesticide residues for the two subpopulations: critical population composed of adults and toddlers, who are the most sensitive to the effects of exposure.

2. Materials and methods

This study was conducted in 2011 on 170 samples: gooseberry (11), blackcurrant (25) and redcurrant (35), raspberry (27), strawberry (62), and the processed concentrated juice of blackcurrant (3), redcurrant (1), raspberry (2), and strawberry (4) from Podlasie region in Poland. Pesticides (160 active substances) from various chemical and biological groups were investigated (Table 1).

2.1. Samples

Berry samples were purchased according to the Polish norm [15] from northeastern Poland. The berry samples were put into polyethylene bags and stored at −20˚C. Before the analysis they were thoroughly shredded and homogenized except dithiocarbamate residues analysis where the whole fruits were left.

2.2. Gas chromatography multiresidue method

The samples were analyzed by multiresidue method by matrix solid phase dispersion method. This 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 [16,17].

First, 2 g of a homogenized sample was put in a mortar with 4 g of solid support (5% silica gel, prepared by adding 5 mL of distilled water to 95 g of activated silica gel). The solid support and sample were manually blended together using a pestle to produce a homogeneous mixture. The mixed materials were transferred to the glass column with 5 g anhydrous sodium sulfate and 2.5 g silica gel. Adsorbed analytes were eluted using 15 mL of a mixture of hexane/acetone (8:2, v/v) and 15 mL of a mixture of hexane/diethyl ether/acetone (1:2:2, v/v/v). The extract was evaporated to dryness in a rotary vacuum evaporator at temperature about 40˚C. The residue was dissolved in 2 mL volume of a mixture of hexane/acetone (9:1, v/v). The final solution was put into a GC vessel and placed to the rack of the autosampler. The final extract was analyzed by an Agillent 7890 gas chromatograph (GC) equipped with two selective detectors: ^{63}Ni electron capture (ECD) and nitrogen–phosphorus (NPD) [18] and HP 6890 autosampler and split/splitless injector. A capillary column HP-5 (5%-phenylmethylpolysiloxane) (30 m × 0.32 mm, 0.5 µm film thickness) was used. The injector and detectors temperature were set at 210 and 300˚C, respectively. The oven temperature was programmed as follows: 120 to 190˚C at a rate of 16˚C/min, increased to 230˚C at 8˚C/min and then to 285˚C at 18˚C/min, and remain there for 18 min. Helium was used as a carrier gas at a flow rate of 3.0 mL/min. Nitrogen was used as a makeup gas: EC detector and NP detector were set at 57 and 8 mL/min, respectively. The air and hydrogen (for NPD) gas flows were set at 60 and 3 mL/min, respectively. The injection volume was 2 µL. The GC was controlled by a personal computer system using Chemstation software (Hewlett-Packard). Identification of the unknown peaks in the samples was managed by comparing the retention time of the unknown peaks to the retention time of the reference standards.

2.3. Carbendazim residues

The measurement of carbendazim residues was conducted, taking 20 g of representative sample. Then it was homogenized for 5 min with 150 mL acetone. Then 5 g of Celite was added to the extract and filtered above the solution through a Buchner funnel. Final filtrate was evaporated in a rotary evaporator leaving about 20 mL. The sample was clean-up on ChemElut cartridge using two 20 mL portions of dichloromethane as a solvent. The organic solvent was evaporated to dryness using rotary vacuum evaporator at 40˚C. The dry extract was dissolved in 2 mL volume of a mixture of acetonitrile/water (2:8, v/v). The final solution was put into a high-performance liquid chromatography (HPLC) vessel and placed to the rack of the autosampler.

Benomyl and thiophanate-methyl determined as carbendazim (extract number 2) were analyzed by HPLC [19] in the dual detection system equipped with selective detectors: diode array (DAD) and fluorescence [20].

The extracts obtained were analyzed with liquid chromatography (Waters Alliance 2695 chromatograph) with the simultaneous use of a diode array detector (Waters 2996) at 285 nm and a fluorescence detector (Waters 2475) (λ_{ex} = 285 nm, λ_{em} = 315 nm). The external standard method was used, by applying of 100 µL standard solution on the column (Supelcosil LC-18, 5 µm, 250 × 4.6 mm). The mobile phase was acetonitrile-phosphate buffer pH = 8, delivered at a flow rate of 0.8 mL/min with a gradient composition, consisting of 20% (v/v) acetonitrile for 2 min, a linear increase over 13 min to 50% acetonitrile, then an increase to 80% acetonitrile over 5 min and finally a decrease at 20% acetonitrile over 5 min. All solvents and mobile phases were firstly filtered under vacuum trough 0.45 µm nylon filters.

The measurement of dithiocarbamate residues was conducted, taking 50 g of sample. Then it was heated for 45 min (temperature about 80˚C) with 60 mL of hydrochloric acid and tin(II) chloride to release carbon disulfide from dithiocarbamates in an alkaline environment. Ditiocarbamates decomposed with emission of carbon disulfide. Carbon disulfide was separated and collected in a methanolic solution of potassium

Table 1
Analyzed 160 active substances sorted by a chemical group

Active substance	Substance group	Active substance	Substance group	Active substance	Substance group	Active substance	Substance group
Benalaxyl (F)	Acylalanine	Fenhexamid (F)	Hydroxyanilide	Malaoxon (I, A)	Organophosphate	Bupirimate (F)	Pyrimidinol
Napropamide (H)	Alkanamide	Dimethomorph (F)	Morpholine	Malathion (I, A)		Quinoxyfen (F)	Quinoline
Diphenylamine (F, I)	Amine	Fenpropimorph (F)		Mecarbam (I, A)		Azoxystrobin (F)	Strobilurin
Cyprodinil (F)	Anilinopyrimidine	Acetamiprid (I)	Neonicotinoid	Phorate (I, A)		Dimoxystrobin (F)	
Mepanipyrim (F)		Endrin (I)	Organochlorine (and isomer mix)	Phosalone (I, A)		Kresoxim-methyl (F)	
Pyrimethanil (F)		α-HCH (I)		Phosmet (I, A)		Pyraclostrobin (F)	
Fluazifop-p-butyl (H)	Aryloxyphenoxypropionate	β-HCH (I)		Pirimiphos-ethyl (I, A)		Trifloxystrobin (F)	
Propyzamide (H)	Benzamide	Heptachlor (I)		Pirimiphos-methyl (I, A)		Picoxystrobin (F)	
Bromopropylate (A)	Benzilate	Heptachlor-epoxide (I)		Profenofos (I, A)		Dichlofluanid (F)	Sulphamide
Dichlobenil (H)	Benzonitrile	Methoxychlor (DMDT) (I)		Quinalphos (I, A)		Tolylfluanid (F)	
Tetradifon (A)	Bridged diphenyl	op′ DDT (I)		Bromophos-ethyl (I)	Organothiophosphate	Prometrine (H)	Triazine
Iprovalicarb (F)	Carbamate	pp′ DDD (I)		Bromophos-methyl (I)		Simazine (H)	
Carbaryl (I)		pp′ DDE (I)		Fenchlorphos (I)		Metribuzin (H)	Triazinone
Pirimicarb (I)		pp′ DDT (I)		Formothion (I, A)		Azaconazole (F)	Triazole (and isomer mix)
Chlorpropham (H)		γ-HCH (I, A)		Methacrifos (I, A)		Bitertanol (F)	
Propham (H)		α-endosulfan (I, A)		Indoxacarb (I)	Oxadiazine	Cyproconazole (F)	
Carbofuran (I, A)		β-endosulfan (I, A)		Vinclozolin (F)	Oxazole	Difenoconazole (F)	
Propoxur (I, A)		Dicofol (A)		Metalaxyl (F)	Phenylamide	Diniconazole (F)	
Boscalid (F)	Carboxamide	Endosulfan-sulfate (I, A)		Oxadixyl (F)		Epoxiconazole (F)	
Hexythiazox (A)		Coumaphos (I)	Organophosphate	Fipronil (I)	Phenylpyrrole	Fenbuconazole (F)	
HCB (F)	Chlorinated hydrocarbon	Paraoxon-ethyl (I)		Fludioxonil (F)		Fluquinconazole (F)	
Dieldrin (I)		Paraoxon-methyl (I)		Pyrazophos (F)	Phosphorothiolate	Flusilazole (F)	
Acetochlor (H)	Chloroacetamide	Parathion-methyl (I)		Captan (F)	Phthalimide	Flutriafol (F)	
Metazachlor (H)		Chlorpyrifos (I)		Folpet (F)		Hexaconazole (F)	
Propachlor (H)	Chloroacetamide	Ethoprophos (I)		Tebufenpyrad (A)	Pyrazole	Imibenconazole (F)	
Chlorothalonil (F)	Chloronitrile	Fenitrothion (I)		Cypermethrin (I)	Pyrethroid (and isomer mix)	Metconazole (F)	
Dichloran (F)	Chlorophenyl	Fenthion (I)		Esfenvalerate (I)		Myclobutanyl (F)	
Quintozene (F)		Heptenophos (I)		α-cypermethrin (I)		Paclobutrazol (F)	
Tecnazene (F)		Isofenphos (I)		Cyfluthrin (I)		Penconazole (F)	
Tolclofos-methyl (F)		Izofenphos methyl (I)		Deltamethrin (I)		Propiconazole (F)	
Tetrachlorvinphos (I, A)		Azinphos-ethyl (I, A)		λ-cyhalothrin (I)		Tebuconazole (F)	
Aldrin (I)	Cyclodiene	Azinphos-methyl (I, A)		Permethrin (I)		Tetraconazole (F)	
Iprodione (F)	Dicarboximide	Chlorfenvinphos (I, A)		ζ-cypermethrin (I)		Triadimefon (F)	
Procymidone (F)	Dicarboximide	Methidathion (I, A)		Acrinathrin (I, A)		Bromuconazole (F)	

(*Continued*)

Table 1 (*Continued*)

Active substance	Substance group	Active substance	Substance group	Active substance	Substance group	Active substance	Substance group
Pendimethalin (H)	Dinitroaniline	Parathion (I, A)		Bifenthrin (I, A)		Triadimenol (F)	
Trifluralin (H)		Triazophos (I, A)		Fenpropathrin (I, A)		DEET (I)	Unclassified
Nitrofen (H)	Diphenyl ether	Chlorpyrifos-methyl (I, A)		Fenvalerate (I, A)		Pyriproxyfen (I)	
Fenamidone (F)	Imidazole	Diazinon (I, A)		beta-cyfluthrin (I)		Buprofezin (I, A)	
Imazalil (F)		Dimethoate (I, A)		Pyridaben (I, A)	Pyridazinone	Fenazaquin (A, I)	
Prochloraz (F)		Ethion (I, A)		Fenarimol (F)	Pyrimidine	Lenacil (H)	Uracil

A—acaricides, F—fungicides, H—herbicides, I—insecticides.

hydroxide. Under these conditions carbon disulfide forms potassium xantogenate which was next heated with zinc acetate to obtain zinc sulfide. This compound in an acidic medium released hydrogen sulfide which formed with N,N-dimethyl-1,4-phenylenediammonium dichloride and in presence of iron ions Fe(III) (from ferrous ammonium sulfate solution) methylene blue. Finally, the quantity of formed complex (final volume 25 mL) was estimated by measure of absorbance on the spectrophotometer.

2.4. *Dithiocarbamate residues*

Dithiocarbamate residues were determined by a modified colorimetric method [21]. This method allows for determination of dithiocarbamate fungicides (mancozeb, maneb, methiram, propineb, thiram, and ziram), expressed as carbon disulfide, as a group. The solution of the complex formed was put into cuvettes and absorbance was measured at 662 nm wavelength using a spectrophotometer (Helios Delta VIS) [22]. The absorbance was calculated into concentration and results were expressed in mg CS_2/kg.

2.5. *Quality check*

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 [23]. 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 [24].

2.6. *Risk assessment*

An indispensable precondition for setting maximum residue levels (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.

The values of ADI and ARfD are elaborated by the European food safety authority (EFSA) of EU [3] or the federal institute for risk assessment (BfR), Berlin, Germany [25].

The risk assessment of exposure to consumer health associated with consumption of berry fruits, which contains residues of pesticide, was based on the available epidemiological studies conducted for the

British taking into account a high degree of consumption (97.5 percentile). There are a lot of such studies on Polish consumers [26], however, they include only the general population and consumption at the average level, which had no practical application in this study.

For the estimation of consumer residue intake a new model from the Pesticides Safety Directorate (PSD) of the Department for Environment, British Food and Rural Affairs (London, United Kingdom) was applied. Calculations were performed using the Chronic and Acute Consumer ver 1.1. (The Food and Agricultural Organization of the United Nations, Rome, Italy) with built-in consumption database for 10 groups of consumers [27]. This paper contains the results for two most vulnerable subgroups: children and adults.

The long-term risk was calculated by means of using Eq. (1):

$$\mathrm{NEDI} = \sum \frac{F_i \times RL_i}{\mathrm{mean\_body\_weight}} \quad (1)$$

where NEDI—National Estimated Daily Intake, F_i—food consumption data, and RL_i—average residue level in the commodity.

Short-term risk was calculated by means of using Eq. (2) [28]:

$$\mathrm{NESTI} = \sum \frac{F \times HR.P}{\mathrm{mean\_body\_weight}} \quad (2)$$

where NESTI—National estimates of short-term intake, F—full portion consumption data for the commodity unit, and $HR.P$—the highest residue level detected after correction for processing or removal of non-edible portions.

3. Results and discussion

One of the important measures to ensure food safety is a constant control of the pollutants [4]. Such research is done not only to protect consumers' health, but also to fulfill the requirements concerning the quality of food production for domestic and international markets. Due to widespread consumption of berries, often raw, the quality of the fruit from the northeastern Poland was analyzed for the presence of pesticide residues.

The list of active substances was designed based on the information obtained from agricultural producers declaring the use of plant protection products. In addition, most studies included compounds most commonly used in agriculture and long persistent in the environment.

Pesticide residues were appraised according to the European Union Regulations [29] and compared with MRL. MRL are the upper legal levels of a concentration of pesticide residues in or on food or feed based on good agricultural practices, ensuring the lowest possible consumer exposure. The Regulation (EC) No 396/2005 establishes the MRL of pesticides permitted in products of plant or animal origin intended for human or animal consumption. MRL are derived after a comprehensive assessment of the properties of the active substance and residue levels resulting from the good agricultural practices defined for treated crops. In Poland, the year 2008 was very important because of harmonization of pesticide MRL legislation at the European level. Whereas, before 1 September 2008, a mixed system, with harmonized Community MRL for about 250 active substances and national MRL for the remaining substances, was applicable, when Regulation (EC) No 396/2005 was introduced, it harmonized MRL for all active substances used in plant protection products.

In the present study during the one year testing period, 55.3% (94 samples) of berry samples and their concentrate juices were found free of residues above the detection limits of analytical methods, 44.7% (76 from 170 samples) contained residues, of which 30.0% (51) had residues below MRL and 14.7% (25) above MRL. The results of the samples analyzed divided by particular assortment are presented in Fig. 1. Nine pesticides exceeding MRL were observed: procymidone (in 8 samples); dithiocarbamates (in 5 samples); carbendazim (in 3 samples); difenoconazole, cypermethrin, and fenazaquin (in 2 samples); and acetamiprid, flusilazole, and esfenvalerate (1 sample each).

The samples of concentrate juices had less pesticide residues in comparison with the fresh berry fruits. For example, blackcurrant juice samples had only one active substance and in fresh blackcurrant 14

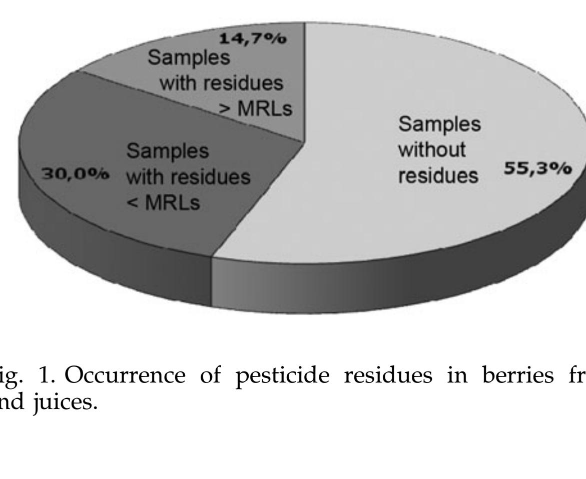

Fig. 1. Occurrence of pesticide residues in berries fruits and juices.

pesticides were detected. It may be the effect of technological processing, such as: washing berries and boiling them at high temperature [30].

Research revealed the presence of pesticides at use in prohibited plant protection or not recommended for a given crop. Fungicide as procymidone belongs to this group. This pesticide was detected in 11 samples (6.5%), one sample of blackcurrant and ten of raspberry (Table 2). According to Słowik-Borowiec et al. [31], the presence of procymidone in the analyzed samples is associated with widespread use of the preparations containing this substance in the recent years to effectively combat among others gray mould (*B. cinerea*) in a wide range of fruit plants, vegetables, and ornamentals. It was also found that there were substances not recommended for growing gooseberry. They belong to the group of fungicides: flusilazole, tetraconazole, and trifloxystrobin (Table 2). Gooseberry is a minor crop in Poland and therefore the phytopharmaceuticals company for purely economic reasons is not interested in the registration of pesticides on the fruit. In order to avoid affecting crops, the growers take preparations available on the market, but not registered for a given crop.

Out of 160 analyzed pesticides, 19 belong to fungicides and 10 belong to insecticides were detected. The residues of herbicides were not detected in the analyzed samples. Fig. 2 illustrates the frequency of all detected active substances. The highest concentration 1.49 mg/kg was observed for dithiocarbamates (fungicide) in a sample of gooseberry. Boscalid was detected at concentrations ranging from 0.01 to 1.00 mg/kg (MRL = 10.0 mg/kg), dithiocarbamates were found in 28 samples at concentrations ranging from 0.05 to 1.49 mg/kg (MRL = 0.05 to 10.00 mg/kg) and λ-cyhalothrin was found in 10 samples at concentrations ranging from 0.01 to 0.04 mg/kg (MRL = 0.20 mg/kg). The detailed data on levels of residues of plant protection products detected in the berries samples and their products from the northeastern Poland are given in Table 2.

The previous studies on agricultural samples carried out by Łozowicka [8] showed that fungicides were the most frequently detected group of compounds (80.0%). They are recognized as carcinogens, mutagens that can weaken the immune system (cancer-causing, reproductive disorders, endocrine disorders, and neurotoxic), which play an important role in protecting plants against diseases caused by several species of fungi [32–38]. This fact is confirmed by the present analysis of samples of berry fruits. Fungicides accounted for 65.5% of all detection, where boscalid was the most often detected active substances (19.4%).

In the case of insecticides, out of 35.5% of the detection λ-cyhalotryna (5.9%) was detected most commonly (Fig. 2). Although the residues of fungicides widely occur in berry fruit samples, in contrast to insecticides, they have a less harmful effect on humans and the environment. This is due to rapid decomposition and the low dose used in plant protection. In addition, modern pesticides are often not active outside the living cell and do not interfere with basic physiological processes of plants [8,39]. According to Nowacka et al. [40], on the basis of monitoring samples study of the Polish fruit and vegetables, it was observed that the samples from the region of Podlasie are less charged with pesticide residues in comparison to the rest of Poland. The most common compounds in the berries and juice are shown in Fig. 2.

During this period, 10.6% (18 samples) of all samples were detected with one residue and 34.1% (58 samples) contained more than one residue (from 2 to 9 active substances). Most samples contained two and five compounds, approximately 8.2 (14) and 10.6% (18), while eight and nine of 0.6% (1) and 1.2% (2), respectively. Boscalid (F), dithiocarbamates (F), and λ-cyhalothrin (I) were the most often found combinations in multiresidue samples. Multiresidue samples are presented in Fig. 3.

In comparison to the results of the EU monitoring [2,4,5], the percentage of samples of fruits, vegetables, and cereals with multiple residues (i.e. single samples which contain residues of more than one pesticide) has increased over the time, from 15.0% in 1997 to 26.0% in 2007. In 2008, the residues of two or more pesticides were found in 27.0% of the analyzed samples of fruits, vegetables, and cereals. The highest number of different pesticides in a single sample was 26 in 2008 and it was recorded for a table grape sample. In Poland 2.3% multiresidue samples were noted.

The occurrence of multiple residues in one sample can result from the application of different types of pesticides (e.g. insecticides, fungicides, and herbicides) to protect the crop against different pests, diseases, or other threats having an impact on the quality or yield of crops, from mixing of lots with different treatments, contaminations, but also from practices which do not respect the principles of good plant protection practice [5].

Human exposure to mixtures of toxic chemicals is probably more common than exposure to a single compound [41], it is therefore recommended in order to estimate the acute exposure for samples containing of more than one pesticide residues. As noted by Faustman et al. [42], children may be more susceptible to the effects of these exposures, as they have higher

Table 2
Occurrence of pesticide residues in berry fruits

Crop	Number of analyzed samples	Active substance (pesticide group)	Samples with residues		Determined residue [mg/kg]	MRL [mg/kg]
			Number of samples	[%] of samples		
Gooseberry	11	Azoxystrobin (F)	5	45.5	0.04–0.12	5.00
		Bupirimate (F)	10	90.9	0.04–0.58	5.00
		Chlorothalonil (F)	4	36.4	0.04–0.47	10.00
		Cyprodinil (F)	6	54.5	0.01–0.15	5.00
		Difenoconazole (F)*	4	36.4	0.06–0.24	0.10
		Dithiocarbamates (F)	8	27.7	0.09–1.49	5.00
		Flusilazole (F)*	1	9.1	0.03	0.02
		Tetraconazole (F)	2	18.2	0.01–0.04	0.20
		Trifloxystrobin (F)	2	18.2	0.02–0.13	1.00
Blackcurrant	28	Acetamipryd (I)*	1	3.6	0.02	0.01
		Alfa-cypermethrin (I)	1	3.6	0.02	0.05
		Boscalid (F)	4	14.3	0.67–1.00	10.00
		Bupirimate (F)	1	3.6	0.02	5.00
		Carbendazim(F)*	11	39.3	0.02–0.11	0.10
		Chlorpyrifos-ethyl (I)	3	10.7	0.018–0.126	1.00
		Difenoconazole (F)	5	17.9	0.04–0.07	0.20
		Dithiocarbamates (F)	8	28.6	0.08–0.58	5.00
		Esfenvalerate (I)*	1	3.6	0.09	0.02
		Fenazaquin (I)	1	3.6	0.31	0.01
		λ-cyhalothrin (I)	4	14.3	0.02–0.04	0.20
		Pirimicarb (I)	1	3.6	0.01	1.00
		Procymidone (F)*	1	3.6	0.02	0.02
		Pyraclostrobin (F)	4	14.3	0.35–0.52	3.00
Redcurrant	36	Boscalid (F)	6	16.7	0.31–0.82	10.00
		Captan (F)	1	2.8	0.02	3.00
		Carbendazim (F)*	6	16.7	0.02–0.17	0.10
		Cypermethrin (I)*	2	5.6	0.05–0.09	0.05
		Difenoconazole (F)	5	13.9	0.03–0.10	0.20
		Dithiocarbamates (F)	3	8.3	0.09–0.24	5.00
		Fozalon (I)	1	2.8	0.01	0.05
		λ-cyhalothrin (I)	6	16.7	0.01–0.03	0.20
		Pyraclostrobin (F)	6	16.7	0.12–0.35	3.00
Raspberry	29	Boscalid (F)	7	24.1	0.01–0.04	10.00
		Carbendazim (F)	1	3.4	0.02	0.10
		Chlorpyrifos-ethyl (I)	1	3.4	0.012	0.50
		Cyprodinil (F)	10	34.5	0.01–0.12	10.00
		Dithiocarbamates (F)*	5	17.2	0.06–0.28	0.05
		Fenazaquin (I)*	1	3.4	0.02	0.01
		Fenhexamid (F)	12	41.4	0.06–0.29	10.00
		Fludioxonil (F)	4	13.8	0.01–0.04	5.00
		Folpet (F)	8	27.6	0.025–0.59	3.00
		Iprodione (F)	9	31.0	0.02–0.47	10.00
		Procymidone (F)*	10	34.5	0.02–0.14	0.02
		Pyraclostrobin (F)	1	3.4	0.02	2.00
		Pyrimethanil (F)	14	48.3	0.02–0.38	10.00
Strawberry	66	Bifenthrin (I)	4	6.1	0.02–0.03	0.50
		Boscalid (F)	10	15.2	0.01–0.42	10.00
		Carbendazim (F)	2	3.0	0.02–0.03	0.10
		Chlorpyrifos-ethyl (I)	1	1.5	0.007	0.20
		Cyprodinil (F)	8	12.1	0.01–0.05	5.00

(*Continued*)

Table 2 (*Continued*)

Crop	Number of analyzed samples	Active substance (pesticide group)	Samples with residues: Number of samples	Samples with residues: [%] of samples	Determined residue [mg/kg]	MRL [mg/kg]
		Dithiocarbamates (F)	4	6.1	0.05–0.1	10.00
		Fenhexamid (F)	2	3.0	0.02	5.00
		Fludioxonil (F)	6	9.1	0.01–0.06	3.00
		Folpet (F)	1	1.5	0.05	3.00
		Iprodione (F)	5	7.6	0.07–0.22	15.00
		Pyraclostrobin (F)	4	6.1	0.10–0.17	1.00
		Pyrimethanil (F)	1	1.5	0.03	5.00
Blackcurrant juice conc.	3	Boscalid (F)	1	33.3	0.01	10.00
Redcurrant juice conc.	1	Boscalid (F)	1	100	0.05	10.00
		Cyprodinil (F)	1	100	0.01	5.00
Raspberry juice conc.	2	Boscalid (F)	1	50.0	0.01–0.05	10.00
		Cyprodinil (F)	1	50.0	0.04	10.00
		Fenhexamid (F)	1	50.0	0.14	10.00
		Iprodione (F)	1	50.0	0.04	10.00
		Pyrimethanil (F)	1	50.0	0.09–0.33	10.00
Strawberry juice conc.	4	Boscalid (F)	3	75.0	0.03–0.13	10.00
		Fenhexamid (F)	1	25.0	0.02	3.00
		Fludioxonil (F)	1	25.0	0.02	3.00
		Trifloxystrobin (F)	1	25.0	0.03	0.50

*The substance of which residue level exceeded maximum residue levels (MRL).
I—insecticide, F—fungicide, conc.—concentrate.

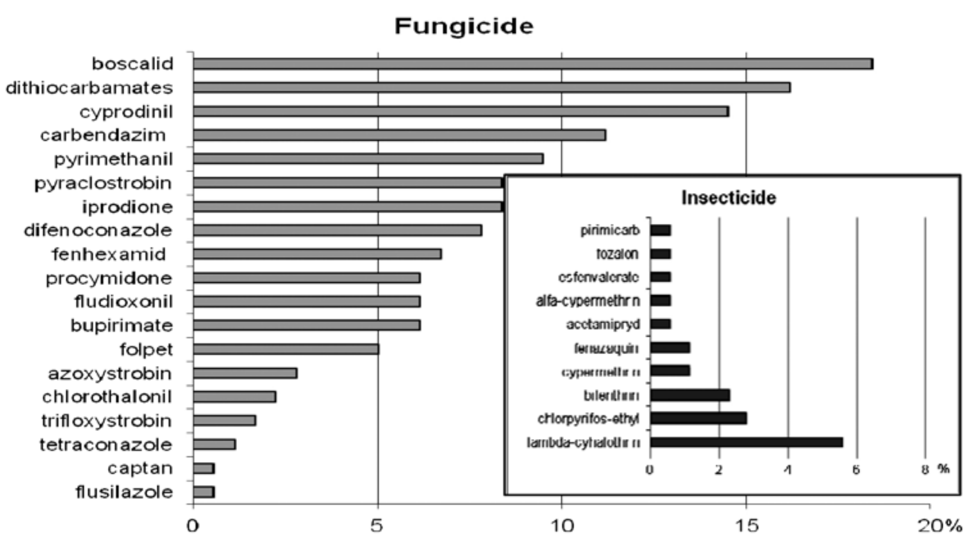

Fig. 2. Detected active substances of plant protection products in berries fruits and juices.

rates of metabolism, less mature immune systems, and different patterns of activity and behavior than adults.

According to Łozowicka et al. [43], children and adults eating fruit from the intensive agriculture may be exposed to overlapping effects of organophosphorus compounds and N-methyl carbamates, which in turn may lead to various diseases caused by toxins. Organophosphate and organochloride insecticides are particularly hazardous [44].

The results of the survey study were used to perform exposure assessments. The evaluation of the health risks of exposure of children and the elderly

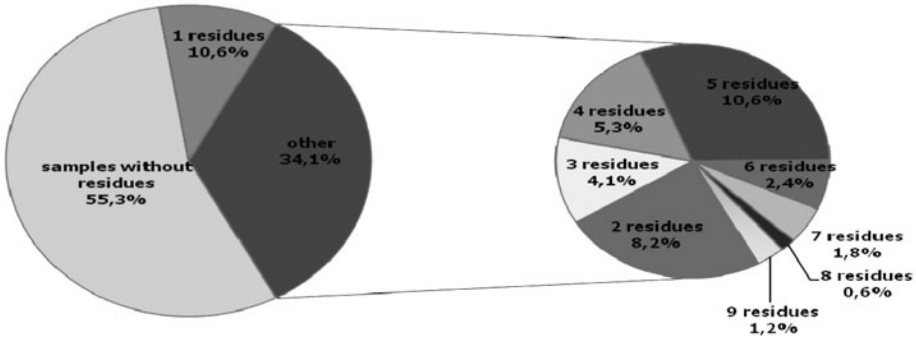

Fig. 3. Frequency of occurrence samples without residues, with one residue, and with multiresidue in berries fruits and juices.

related to the consumption of berries from the northeastern Poland containing the residues of plant protection products was based on the available epidemiological studies conducted on British children aged 1.5–4 years and adults, taking into account the high level of consumption (97.5%). There are no complete studies for Polish consumers, Szponar et al. [26] conducted a study taking into account only the general population and consumption on the average level. The values of ADI and ARfD included in the risk assessment are set independently, both at the FAO/WHO [45,46], as well as at the stage of registration of active substances in the EU. According to the EU recommendations, ADI and ARfD value should be determined for each pesticide [3,4].

Consumer risk assessments are routinely evaluated as a part of the approval process for pesticides and are based on residue trials. The approval of a pesticide is only recommended when the consumer risk is acceptable [4,47].

The assessment of the acute (short-term) consumers' exposure was performed for the four fruits: blackcurrant and redcurrant, gooseberry, and raspberry, which were analyzed in this study. Acute exposure was calculated only for a compound exceeding the MRL and shown in Table 3. The assessment was based on the worst-case scenarios: the consumption data for consumers (two groups of British children aged 1.5–4 years and adults) who eat a large size portion of the berry fruit item under consideration were combined with the highest residue found in berry samples from the agricultural northeastern Poland in 2011. It seems that these critical cases of consumption, however, have no reasonable possibility of occurring. Assuming that by coincidence these events did occur (high food consumption and high residue concentration), potential consumer risk is

Table 3
Estimation of acute dietary exposure of pesticide residues based on their highest residues detected in berries fruits and juices

				Toddlers (14.5 kg)		Adults (70 kg)	
Active substance	Crop	The highest residue level [mg/kg]	ARfD [mg/kg b.w.]	Intake [μg/kg b.w.]	% ARfD	Intake [μg/kg b.w.]	% ARfD
Acetamipryd	Blackcurrant	0.02	0.100	0.00010	0.1	0.00003	0.0
Carbendazim	Redcurrant	0.17	0.020	0.00037	1.8	0.00017	0.9
Cypermethrin	Redcurrant	0.09	0.200	0.00002	0.0	0.00004	0.1
Difenoconazole	Gooseberry	0.24	0.250	0.00038	0.1	0.00025	0.1
Dithiocarbamates	Raspberry	1.49	0.600	0.00440	0.2	0.00283	0.2
Esfenvalerate	Blackcurrant	0.09	0.050	0.00030	0.6	0.00014	0.3
Fenazaquin	Blackcurrant	0.31	0.100	0.00109	0.1	0.00050	0.5
Flusilazole	Gooseberry	0.03	0.005	0.00003	0.7	0.00003	0.6
Procymidone	Gooseberry	0.11	0.035	0.00072	2.2	0.00028	0.8

Table 4
Estimation of chronic dietary exposure to pesticide residue based on average residues detected in berry fruits

Active substance	Average residues level [mg/kg]	ADI [mg/kg b.w.]	Consumption* (g/person/day)		Intake			
					Toddlers (14.5 kg)		Adults (70 kg)	
			Toddlers	Adults	μg/kg b.w.	% ADI	μg/kg b.w.	% ADI
Gooseberry								
Azoxystrobin	0.18182	0.050	0.14	1.32	0.002	0.004	0.003	0.007
Bupirimate	0.04182	0.100			0.000	0.0001	0.001	0.001
Chlorothalonil	0.08727	0.015			0.001	0.006	0.002	0.011
Cyprodinil	0.05000	0.030			0.000	0.002	0.001	0.003
Difenoconazole	0.07273	0.010			0.001	0.007	0.001	0.014
Dithiocarbamates	0.46455	0.050			0.004	0.009	0.009	0.017
Flusilazole	0.02091	0.002			0.000	0.010	0.000	0.020
Tetraconazole	0.01273	0.004			0.000	0.003	0.000	0.006
Trifloxystrobin	0.02182	0.100			0.000	0.0001	0.000	0.0001
Blackcurrant								
Acetamipryd	0.02000	0.015	26.0	38.1	0.036	0.239	0.011	0.072
Alfa-cypermethrin	0.01033	0.070			0.019	0.026	0.006	0.008
Boscalid	0.12567	0.040			0.225	0.563	0.068	0.171
Bupirimate	0.01033	0.050			0.019	0.037	0.006	0.011
Chlorpyrifos-ethyl	0.01083	0.010			0.019	0.194	0.006	0.059
Difenoconazole	0.04267	0.010			0.077	0.765	0.023	0.232
Dithiocarbamates	0.09100	0.050			0.163	0.326	0.049	0.099
Esfenvalerate	0.02233	0.020			0.040	0.200	0.012	0.061
Fenazaquin	0.02000	0.005			0.036	0.717	0.011	0.217
Carbendazim	0.03033	0.020			0.054	0.272	0.016	0.082
λ-cyhalothrin	0.01233	0.005			0.022	0.442	0.007	0.134
Pirimicarb	0.02933	0.035			0.053	0.150	0.016	0.046
Procymidone	0.02000	0.003			0.036	1.281	0.011	0.388
Pyraclostrobin	0.07867	0.030			0.141	0.470	0.043	0.143
Redcurrant								
Boscalid	0.28583	0.040	11.4	23.9	0.225	0.562	0.097	0.244
Cypermethrin	0.03667	0.050			0.029	0.058	0.013	0.025
Cyprodinil	0.01000	0.030			0.008	0.026	0.003	0.011
Difenoconazole	0.04333	0.010			0.034	0.341	0.015	0.148
Dithiocarbamates	0.08333	0.050			0.066	0.131	0.028	0.057
Phosalone	0.01000	0.010			0.008	0.079	0.003	0.034
Captan	0.05250	0.020			0.041	0.206	0.018	0.089
Carbendazim	0.02000	0.100			0.016	0.016	0.007	0.007
λ-cyhalothrin	0.01167	0.005			0.009	0.183	0.004	0.080
Pyraclostrobin	0.11667	0.030			0.092	0.306	0.040	0.133
Raspberry								
Boscalid	0.02873	0.040	34.5	59.1	0.049	0.123	0.017	0.044
Chlorpyrifos-ethyl	0.02028	0.015			0.028	0.189	0.010	0.067
Cyprodinil	0.00503	0.010			0.049	0.164	0.017	0.058
Dithiocarbamates	0.01239	0.030			0.158	0.316	0.056	0.112
Fenazaquin	0.05141	0.050			0.025	0.491	0.009	0.174
Fenhexamid	0.02000	0.200			0.145	0.073	0.051	0.026
Fludioxonil	0.01197	0.370			0.026	0.007	0.009	0.002
Folpet	0.02042	0.100			0.158	0.158	0.056	0.056
Iprodione	0.02592	0.060			0.140	0.233	0.049	0.082

(*Continued*)

Table 4 (*Continued*)

Active substance	Average residues level [mg/kg]	ADI [mg/kg b.w.]	Consumption* (g/person/day)		Intake			
					Toddlers (14.5 kg)		Adults (70 kg)	
			Toddlers	Adults	μg/kg b.w.	% ADI	μg/kg b.w.	% ADI
Carbendazim	0.02014	0.020			0.048	0.238	0.017	0.084
Pyrimethanil	0.01028	0.170			0.177	0.104	0.063	0.037
Procymidone	0.05423	0.030			0.081	2.878	0.029	1.020
Pyraclostrobin	0.01028	0.10			0.094	0.312	0.033	0.111
Strawberry								
Bifenthrin	0.02028	0.015	28.9	72.6	0.040	0.269	0.021	0.140
Boscalid	0.02065	0.040			0.057	0.143	0.030	0.074
Chlorpyrifos-ethyl	0.00523	0.010			0.010	0.100	0.005	0.052
Cyprodinil	0.01194	0.015			0.025	0.082	0.013	0.043
Dithiocarbamates	0.02065	0.030			0.102	0.205	0.053	0.106
Fenhexamid	0.06645	0.050			0.040	0.020	0.021	0.010
Fludioxonil	0.01032	0.005			0.024	0.006	0.012	0.003
Folpet	0.06097	0.200			0.041	0.041	0.021	0.021
Iprodione	0.01097	0.370			0.052	0.086	0.027	0.045
Carbendazim	0.06661	0.100			0.040	0.201	0.021	0.104
Pyrimethanil	0.05871	0.060			0.020	0.012	0.011	0.006
Pyraclostrobin	0.02000	0.020			0.108	0.360	0.056	0.187
Trifloxystrobin	0.07419	0.170			0.020	0.020	0.011	0.011

*High level (97.5 %) of long term consumption. b.w.—body weight.

small. The highest potential level exceeding the toxicological reference value was indicated for procymidone (0.11 mg/kg) and carbendazime (0.17 mg/kg) on black and redcurrant and gooseberry (2.2% for toddlers and 0.8% for adults and 1.8 and 0.9% of ARfD, respectively), flusilazole (0.03 mg/kg) on raspberry and blackcurrant (0.7%; 0.6%). However, the critical intake events identified in the acute risk assessment calculations were considered very unlikely to occur, taking into account the frequency of critical residues and the frequency of extreme consumption events.

Table 4 shows the estimated long-term (chronic) exposure for the same consumer groups (toddlers and adults) on the basis of calculated average concentrations of all detected residues in the tested samples. In the present study, in most cases, the exposure was within the range from 0.0001% of ADI to 1,3% of ADI. Among the substances analyzed, the highest estimated long-term (chronic) exposure of the consumer groups participating in the research study is observed for procymidone. It is one of the most frequently used fungicides, which may be absorbed through the roots, with translocation to leaves, flowers, and fruits in order to prevent gray mold [48]. As noted by Hass et al. [48], procymidone may also have an influence on the endocrine system and the reproductive development in males. Procymidone for toddlers amounted to about 2.9% of ADI for raspberries and had a slightly lower value of ADI, i.e. 1.3% in blackcurrant was observed. Moreover, for adults it amounted to about 1.0% of ADI for raspberries and 0.4% of ADI for blackcurrant.

According to Hass et al. [49], when considering the cumulative risk assessment, it is recommended that one should include all kinds of chemicals e.g. pesticides, industrial chemicals, and environmental contaminants, as endocrine disrupters exist within all of these chemicals classes and humans may be exposed to several of them simultaneously. The risk assessments for single chemicals is likely to underestimate the risk and that there is a need for modification of risk assessment procedures for pesticides, in order to take account of mixture effects and the potentially serious impact of mixed exposure on development. The highest cumulative exposure associated with the presence of 14 compounds in blackcurrant samples was observed in the case of toddlers (5.7% of ADI), slightly lower in raspberries (5.3% of ADI). For adults, it amounted to less than 2.0% of ADI for all assortments of berries. Moreover, the dietary intakes estimated from all pesticide level detected in berry fruit and juices do not represent a health risk to local consumers, the intake estimated from the highest pesticide residues level is low and did not exceed the short-term health standards. The obtained results lead to the conclusion that the berries from the northeastern Poland are "safe" in both long and short term for both adults and toddlers and do not exceed a safe value of 100.0% ADI and ARfD.

According to EFSA reports and the EU Commission, studies on pesticide residues should still be developed and should include more and more active substance and various species of vegetables, fruits, cereals, and processed goods of plant origin. Imported vegetables and fruits should also be controlled because of their consumption increase. This will create a possibility of estimating the entire diet pesticide residues health hazard for human in Poland, not only for Polish crops.

4. Conclusions

(1) High percentage of berries and juices samples with residue below and above permission level (MRL) was observed. This is due to big sensitivity of this fruit to fungal diseases, so fungicides were the most commonly detected group. However, insecticides were frequently detected above MRL (mainly in the samples of blackcurrant, redcurrant and raspberry).

(2) High percentage of multiresidue samples was observed in this study, which means that the berry crops were intensively chemically protected. Multiresidues in berry and juices samples, in terms of quality and food safety, may carry increased risks to health of consumers, due to the overlapping various effects of the compounds characterized by a different mode of action.

(3) Due to the common occurrence of pesticide residue, above MRL, prohibited pesticide and samples with multiresidues in the berry fruits should be systematically monitored.

(4) Estimated long-term and short-term exposures associated with the consumption of fruit were small and the risk of adverse health effects was negligible. These fruits can be eaten by small children and adult consumers in both the short and the long time.

(5) Due to the short growing season of berries and their instability, these studies confirm the necessity of monitoring the correct performance of chemical treatments by farmers, in particular, compliance with waiting periods and the use of the manufacturers' instructions of plant protection products.

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