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Pesticide residues in raspberries and their risk assessment

[1*]Łozowicka, B., [1]Kaczyński, P., [1]Jankowska, M., [1]Rutkowska, E., [1]Hrynko, I. and [2]Paritowa, A.

[1]*Plant Protection Institute – National Research Institute, Regional Experimental Station, Pesticide Residue Laboratory, 22 Chełmońskiego St., 15-195 Bialystok, Poland*
[2]*Kazakh Agrarian National University, Abay Ave. 8, Almaty 050010, Kazakhstan*

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Abstract

Raspberry is one of the oldest fruits, used for millennia in the nutritional and medicinal purposes. Cultivation of this fruit in Poland is quite common because of its complex flavor and pharmacological effectiveness. The objective of this study was to investigate the residue levels of 130 pesticides on raspberries from north-eastern Poland producers during seven years (2005–2011). A risk assessment of the pesticides in raspberries was conducted by calculating acceptable daily intakes (ADI) and acute reference dose (ARfD). Pesticide residues exceeding maximum residue levels (MRLs) were found in 29.3% of samples. Among the detected compounds, the most frequently detected pesticide was pyrimethanil (34.8%). Fenhexamid was the fungicide with the highest concentration (5.53 mg/kg). The ADIs ranged from 0.003% to 3.183% for adults and 0.008% to 9.739% for toddlers. The chronic dietary intakes of 18 pesticides for adults and toddlers didn't overcome the toxicologically acceptable levels. The most critical case was procymidone with 180.9% of ARfD for toddlers and 83% of ARfD for adults. The results of this research show that raspberries are safe in long and short term nutrition of human beings.

Introduction

Raspberry (*Rubus idaeus* L.) is very healthy, tasty fruit and the ultimate source of major health elements. These fruits contain high levels of beneficial physiochemicals including anthocyanins, hydrolyzable tannins and phenolic acids. They are a particularly rich source of cyanidin and are unique among the berries for their high ellagitannin content, which can be hydrolyzed to yield ellagic acid (Aiyer *et al.*, 2008). Listed among these health benefits are their potential role in the prevention of cancer, cardiovascular diseases, diabetes, obesity, neurodegenerative diseases and aging. Raspberries are potentially a very high-value crop, but they are also one of the most difficult small fruit crops to grow because the plant and fruit are susceptible to many disease and insect pests.

Recently, raspberry cultivation increased rapidly due to relatively high export of fresh fruits. Poland is the most important producer of raspberries in the world. The total area of raspberry cultivation in Poland in orchards have an upward trend from 20 600 ha in 2007, amounted to 28 3000 ha in 2010 (GUS, 2012). Currently a number of new generation pesticides have been used in raspberry protection. Many insects and plant pathogens (i.e. *Botrytis cinerea*, *Didymella aplanata*, *Aphididae*, *Neotetranychus rubi*, *Anthonomus rubi*, *Thomasiniana theobaldi*) affect the aforementioned raspberry cultivations and their occurrence demands the use of pesticides in order to eliminate economic losses. The key issues during crop protection planning are to use the pesticides at the right stage of crop (i.e. flowering) and to keep the levels of pesticide residues below the MRLs at harvest stage.

New groups such as anilinopyrimidines (i.e. cyprodinil and pyrimethanil), carboxamides (i.e. boscalid), hydroxyanilides (i.e. fenhexamid), phenylpyrrole (i.e. fludioxonil) and strobilurins (i.e. pyraclostrobin) are tested for plant protection. Today's insecticides and fungicides are manufactured from literally hundreds of chemical compounds – both organic and inorganic. These chemical compounds, in turn, can be grouped into several dozen chemical groups. Each group of insecticides and fungicides has associated with it a particular mode of activity or mode of action (MOA). These MOAs serve to describe how a particular chemical or chemical group acts to kill or disable insects or fungi (FRAC, 2010).

The use of pesticides is often necessary in raspberry cultivation because they are very sensitive and that is why plant protection products may be a potential risk to human health. Pesticide residues may translocate, accumulate or deposit into fruit tissues. Many reports have been published about

*Corresponding author.
Email: *B.Lozowicka@iorpib.poznan.pl*

pesticide residues in various agricultural crops in Poland (Nowacka *et al.*, 2006, 2007, 2008, 2009, 2010, 2011, 2012; Łozowicka *et al.*, 2013). However, only few researches have performed analyses and risk assessment study of pesticides on raspberries.

A risk assessment is carried out when residues are found in foods to determine whether, at the levels found, they present a concern for consumer health or not. Consumer risk assessments are routinely assessed as part of the approval process for pesticides and are based on residue trials. Approval of a pesticide is only recommended when the consumer risk is acceptable.

Before permitting any use of a pesticide, a detailed assessment is made to ensure that residues in foods derived from commodities comply with maximum residue levels (MRLs) and will not give rise to unacceptable risks to consumers. MRLs do take account of consumer safety aspects and, in effect, are set at levels below safety limits. However, MRLs must not be confused with safety limits, which are expressed in terms of the acceptable daily intakes (ADI) (expressed as mg/kg body weight/day) of a particular pesticide residue from all sources.

The consumer intake assessments focus on short-term (acute) dietary exposure as being of most relevance and most critical in assessing the risk to consumers. Consumer exposure estimates have been compared to the most appropriate acute reference dose (ARfD) where available and relevant. Where a specific ARfD has not been readily available, short-term exposure estimates have been compared to the ADI. Established independently peer reviewed toxicological end points have been used wherever possible. However, some reference doses used have been determined by PSD (PSD, 2006) and have not been independently peer reviewed and should be regarded as provisional.

The objective of this study was to analyze residue levels of 130 pesticides on raspberry samples produced in Poland. Also a risk assessment was conducted by calculating ADI and ARfD of pesticides in raspberries. The reason why raspberries were selected for pesticide residue risk assessment is that the large amounts of fresh fruits are consumed daily in Poland, especially during the summer period. Thus the aim of the study was not only to confirm that consumption of these products was safe for adults, but also for more sensitive population groups such as toddlers.

Material and Methods

Standards

Pesticide reference standards were purchased from Dr. Ehrenstorfer (Ausberg, Germany). Pesticide standard stock solutions (purity for all standards >95%) of various concentrations were prepared in acetone and stored in dark below 4°C. Standard working solutions were prepared by dissolving appropriate amounts of stock solution with a mixture hexane/acetone (9:1).

Reagents and chemicals

All reagents used were analytical reagent grade. Acetone, acetonitrile, dichloromethane, n-hexane, diethyl ether and methanol for pesticide residue analysis were provided by J.T. Baker (Deventer, Holland), as well as florisil (60-100 mesh) and phosphate buffer pH = 8. Silica gel (230 – 400 mesh) and N,N-Dimethyl-1,4-phenylenediammonium dichloride were obtained from Merck (Darmstadt, Germany). The anhydrous sodium sulfate was purchased from Fluka (Seelze-Hannover, Germany). Before use florisil, anhydrous sodium sulfate and silica gel were activated at 600°C. Hydrochloric acid, sodium hydroxide, potassium hydroxide, zinc acetate dehydrate grade ($Zn(CH_3COO)_2 \cdot 2H_2O$), anhydrous sodium acetate, anhydrous tin (II) chloride, ammonium iron (III) sulfate were purchased form POCH (Gliwice, Poland). Sodium sulfide nonahydrate and celite were supplied by Sigma-Aldrich (St. Louis, USA).

Samples

A total of 184 raspberry samples were purchased from north-eastern Poland during the period 2005 – 2011. The fresh raspberry samples were put into polyethylene bags and stored at -20°C. Before analysis they were thoroughly shredded and homogenized except dithiocarbamate residues analysis where whole fruits were left.

From 130 pesticides analyzed 30 was or is authorized for protection raspberries in the period studied (acetamiprid, α-cypermethrin, bifenthrin, boscalid, chlorpyrifos, cypermethrin, cyprodinil, deltamethrin, diazinon, dichlofluanid, dimethoate, esfenvalerate, fenazaquin, fenhexamid, fenitrothion, fenpropathrin, fludioxonil, hexythiazox, iprodione, λ-cyhalothrin, malathion, phosalone, pirimicarb, procymidone, pyraclostrobin, pyridaben, pyrimethanil, thiuram, tolylfluanid, vinclozolin).

Extraction and clean-up

Sample preparation was done using three methods (by matrix solid phase dispersion method (MSPD) (extract 1), for determination of carbendazim residues (extract 2) and for determination of dithiocarbamates (extract 3). Figure 1 presents all preparation

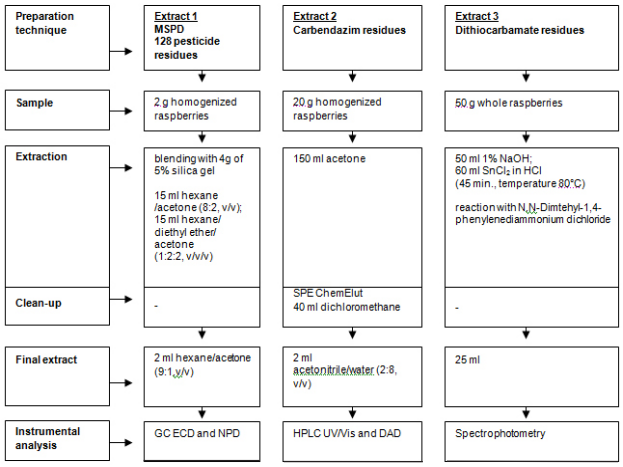

Figure 1. Scheme of sample preparation procedures

Legend:
MSPD – matrix solid phase dispersion
GC – gas chromatography
HPLC – high-performance liquid chromatography
ECD – electron capture detection
NPD – nitrogen phosphorus detection
DAD – diode array detection
UV/Vis –ultraviolet-visible

techniques used for pesticide residue analysis in raspberry samples.

MSPD extraction (extract 1)

The samples were analyzed by multi-residue method (MRM) by MSPD. 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 (Fernandez *et al.*, 2000; Barker *et al.*, 2000). 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). 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.

Extraction of carbendazim residues (extract 2)

20 g of representative sample was homogenized for 5 min with 150 ml acetone. Then 5 g of celite was added to the extract and filtered above solution with 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 HPLC vessel and placed to the rack of the autosampler.

Extraction of dithiocarbamate residues (extract 3)

50 g of sample was heated for 45 minutes (temperature about 80°C) with 60 ml of hydrochloric acid and tin (II) chloride to release carbon disulphide from dithiocarbamates in an alkaline environment. Ditiocarbamates decomposed with emission of carbon disulphide. Carbon disulphide was separated and collected in a methanolic solution of potassium hydroxide. Under these conditions carbon disulphide 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 spectrophotometer.

Quality check

In addition of the in-house quality assurance programs, in 2005 – 2011 the laboratory successfully participated in twelve rounds of proficiency testing schemes organized and run by the Food Analysis Performance Assessment Scheme (FAPAS; Central Science Laboratory in York) and by the European Commission (in the beginning by the University of Uppsala and then by the University of Almeria). Described above own methods for determination of pesticides in raspberry were accredited by standard ISO IEC 17 025 by the Polish Accreditation Centre (PCA) (PKN, 2005).

Instrumental analysis

Gas chromatography (GC)

The final extract number 1 (Figure 1) was analyzed by an Agillent 7890 gas chromatograph (GC) equipped with two selective detectors: 63Ni electron capture (ECD) and nitrogen-phosphors (NPD) (Łozowicka, 2010) and HP 6890 autosampler and split/splitless injector. A capillary column HP-5 (5%-phenylmethylpolysiloxane) (30 m x 0.32 mm, 0.5 μm film thickness) was used. The injector and detectors temperature were set at 210°C and 300°C, respectively. The oven temperature was programmed as follows: 120°C 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 carrier gas at a flow rate of 3.0 ml/min. Nitrogen was used as make up 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.

High performance liquid chromatography (HPLC)

Benomyl and thiophanate-methyl determined as carbendazim (extract number 2) were analyzed by high-performance liquid chromatography (HPLC) (Łozowicka and Kaczyński, 2009) in the dual detection system equipped with selective detectors: diode array (DAD) and fluorescence (Sharma *et al*., 2010). The extracts obtained were analyzed with liquid chromatography (Waters Alliance 2695 chromatograph) with 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 mm x 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.

Spectrophotometry

Dithiocarbamate residues (extract number 3) were determined by a modified colorimetric method (Chmiel, 1979). This method allows determination of dithiocarbamate fungicides (mancozeb, maneb, methiram, propineb, thiram, ziram), express as carbon disulphide, 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) (Łozowicka and Kaczyński, 2009a). The absorbance was calculated into concentartion and results were expressed in mg CS_2/kg.

Method validation

The validation of these analytical methods was carried out according to the EU regulations (SANCO, 2009). The validation studies were performed using pesticide-free raspberry samples (previously analyzed). The sensitivity was evaluated by determining the limit of detection (LOD) and the limit of quantification (LOQ) of the assay. The limits of detection and quantitation were calculated using the signal-to-noise ratio (S/N) criteria in all cases (LOD = 3 S/N, LOQ = 10 S/N).

The influence of matrix co-extractive on the detection response of analytes is a well-known phenomenon (matrix-effect) in pesticide residue analysis (Hajslova *et al*., 1998). This can produce an enhanced or decreased analyte signal in matrix extract compared to a matrix-free solution. In order to eliminate the matrix-effect, the linearity of the analytical procedure was tested using a matrix-matched standard in three concentration levels; first level ranged from 0.001 to 0.05 mg/kg, second: 0.1 – 0.5 mg/kg and third 0.5 – 2.5 mg/kg. Matrix-matched standards were prepared by adding appropriate amounts of standards to the blank matrix of raspberries. Each point was obtained as the average of three injections of the analyzed samples, and the integrated peak high data were used for quantification purposes.

In order to check the accuracy of the proposed method, a recovery study was carried out by fortifying a raspberry sample with known amounts of pesticide standards. The sample was mixed homogenously and left for one hour to allow the solvent to evaporate and the pesticide to get in contact with the raspberry samples. Each sample was prepared in three replicates.

Risk assessment

The data concerning residues were received in 2005 – 2011 and used for estimation of risk according to the methodology described in our previous publication (Łozowicka *et al.*, 2012). Values of ADI and ARfD are elaborated by European Food Safety Authority (EFSA) of European Union (EU) (EFSA, 2008). The risk assessment was based on Estimated Daily Intake (EDI) which was compared to ADI and expressed as a percentage ADI (chronic dietary exposure). The calculation of EDI was expressed in mg/kg body weight/day. Residue levels used were those derived from the mean of detected samples. The average daily intake of raspberry was 34.5 g for toddlers and 59.1 g for adults. Moreover the effects of processing factors were not taken into account in any case (PF = 1). The body weight used for all calculations was 14.5 and 60 kg. The ADI values for pesticides were taken from official EU Pesticides

Database (DG SANCO, 2008).The risk assessment for chronic exposure was calculated only with the positive samples.

Estimated Short Term Intake (ESTI) was used to estimate acute dietary exposure. For the calculation of intake the maximum reported values of residues for each pesticide (in mg/kg) were multiplied by previously reported food consumption for raspberry and was divided by body weight for the same group used for calculation chronic risk (14.5 and 60 kg).

Results

Method validation

The LODs and LOQs for 130 pesticides ranged from 0.001 to 0.01 and 0.003 to 0.03 mg/kg, respectively. The limit of quantification was sufficiently below the MRLs for all pesticides established by European Union (EU) (EC Reg., 2005). The calibration graphs obtained by plotting concentration against average peak high (each samples injected in triply) were linear over the range 0.001 – 2.5 mg/kg. All linearity values (calculated as determination coefficients (R^2)) were above 0.994.

Recoveries for most of pesticides were between 70.1 and 119.6% and relative standard deviations (RSDs) ranged from 0.6 to 16.2%. The exceptions were captan, coumphos, deltamethrin, fenarimol, folpet, nitrofen, phosalone, tecnazen, thriazophos which resulted in recoveries <70% (43.8 – 66.4%) and dicloran, fenpropimorph, iprodione, lenacil (125.1 – 127.4%) in recoveries >120% but with the RSDs below 20%. The results of the recovery study and RSDs are also given in Table 1. These results indicate that the recoveries and accuracy of pesticides were good. Consequently, the pesticides were satisfactorily determined using this method. Those results suggest that the analytical methods including extraction and instrumental analysis is suitable for use in the analysis of the target pesticide residues in the raspberry.

Pesticide levels in raspberry

During seven years (2005 – 2011), 184 samples of raspberry produced in the north-eastern Poland were analyzed. Pesticide residue levels were compared to Polish legislation (Reg. Minister of Health, 2004, 2007) for samples collected between 2005 and 2007 and European MRLs (EC Reg., 2008) for samples surveyed in 2008 – 2011. Pesticide residues were detected in 57.6% of samples. Residues exceeding MRLs in 29.3% of samples were found among them the biggest percentage accounted dithiocarbamates (15.8%). Procymidone, fenazaquin and chlorothalonil above MRLs were found in 10.6%, 1.6% and 0.5% of

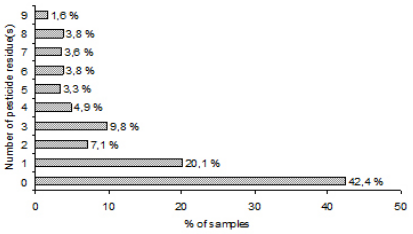

Figure 2. Number of pesticide residues in an individual samples

samples, respectively. In the case of procymidone, all exceedances of MRLs were noted after June 7, 2010 when the value of the MRL has changed from 10 to 0.02 mg/kg (EC Reg., 2008).

Also residues of the active substances which were not recommended for the protection of raspberry in Poland were found: cyprodinil, fludioxonil, folpet in 2009; chlorothalonil, folpet, procymidone in 2010 and carbendazim, folpet, procymidone in 2011. Irregularities connected both with non-authorized pesticides and residues above the MRLs in 12% of samples were observed. During the period, 20.1% (40) of samples with one residue and 37.5% (69) with two or more were detected (Figure 2). The largest number of residues (nine pesticides) in three samples was recorded. The highest concentration in multiresidue sample was 6.07 mg/kg. The most often occurring pesticide combination was two fungicides: fenhexamid and pyrimethanil (in 48 samples). In terms of food safety, multiresidue samples carry a higher risk of exposure to consumer health.

Among 130 analyzed pesticides (49 fungicides, 14 herbicides and 67 insecticides) 18 active substances (13.8%) were found. Pyrimethalin, fenhexamid, cyprodinil, boscalid and procymidone were the most frequently detected pesticides in 64 (34.8%), 61 (33.2%), 42 (22.8%), 36 (19.6%) and 36 (19.6%) samples, respectively (Table 2). The most often fungicides were detected. Fenhexamid was the fungicide with the highest concentration of 5.53 mg/kg, followed by another fungicide: procymidone with concentration 5.37 mg/kg. Among insecticides the most frequently chlorpyrifos and fenazaquin were found. A more details overview of levels of pesticide residues in raspberry presents Table 2.

Risk assessment

The pesticide residue concentrations were used for the assessment of human consumers' risk. The risk assessment was performed for all detected chemical. Based on the reported calculations, Table 2 presents the cumulative chronic risk assessment of the intake for raspberry samples monitored in 2005 – 2011. As can been seen in Table 2 consumers exposure to pesticides do not exceeded the ADI in

Table 1. Parameters of validation MRM for 130 pesticides

Mode of action	Pesticide	R^2	1st fort. level (mg/kg)	Mean recovery ± RSD (n=3) (%)	2nd fort. level (mg/kg)	Mean recovery ± RSD (n=3) (%)	3rd fort. level (mg/kg)	Mean recovery ± RSD (n=3) (%)	LOD (mg/kg)	LOQ (mg/kg)
	azoxystrobin	0.99794	0.020	109.6 ± 2.7	0.200	89.2 +/- 5.6	1.000	95.1 +/- 13.5	0.005	0.010
	benalaxyl	0.99990	0.030	100.2 ± 0.6	0.300	87.5 +/- 9.7	1.500	94.2 +/- 5.5	0.010	0.020
	bitertanol	0.99997	0.020	107.9 ± 2.8	0.200	87.6 +/- 5.2	1.000	100.4 +/- 3.9	0.006	0.010
	boscalid[1]	0.99923	0.005	107.5 ± 1.8	0.100	102.0 +/- 9.8	0.500	107.0 +/- 6.5	0.002	0.010
	bromuconazole	0.99994	0.010	108.0 ± 2.6	0.100	92.8 +/- 6.2	0.500	108.5 +/- 8.5	0.004	0.010
	bupirimate	0.99698	0.010	96.6 ± 0.2	0.100	93.8 +/- 9.0	0.500	114.2 +/- 7.2	0.004	0.005
	captan[2]	0.99938	0.010	78.0 ± 2.8	0.100	73.5 +/- 7.7	0.500	*65.5 +/- 2.5*	0.005	0.010
	carbendazim[1]	0.99991	0.020	114.5 ± 2.4	0.200	74.5 +/- 6.8	2.000	99.4 +/- 8.7	0.005	0.020
	chlorothalonil[1]	0.99968	0.005	98.7 ± 1.2	0.100	89.3 +/- 8.9	0.500	99.0 +/- 6.0	0.001	0.005
	cyprodinil[1]	1.00000	0.010	103.8 ± 1.1	0.100	71.0 +/- 9.9	0.500	87.0 +/- 7.2	0.004	0.010
	cyproconazole	0.99995	0.010	87.5 ± 2.5	0.100	92.5 +/- 6.8	0.500	105.2 +/- 5.1	0.005	0.010
	dichlofluanid	0.99559	0.010	73.6 ± 2.2	0.100	89.5 +/- 3.8	0.500	100.5 +/- 8.0	0.004	0.005
	dicloran[2]	0.99932	0.010	108.1 ± 2.5	0.100	*125.1 ± 4.1*	0.500	119.8 +/- 8.0	0.003	0.005
	difenoconazole	0.99463	0.050	103.1 ± 1.4	0.500	87.5 +/- 9.8	2.500	103.3 +/- 3.7 15.5	0.006	0.010
	diphenylamine	0.99771	0.010	103.4 ± 3.1	0.100	85.2 +/- 4.5	0.500	103.0 +/- 9.1	0.005	0.010
	ditiocarbamates[1]	0.99922	0.030	85.3 ± 2.9	0.300	75.0 +/- 5.8	1.500	105.6 +/- 9.5	0.010	0.030
	epoxiconazole	0.99424	0.010	102.5 ± 3.3	0.100	96.5 +/- 2.4	0.500	107.2 +/- 9.2	0.005	0.010
	fenarimol[2]	0.99906	0.010	74.0 ± 2.4	0.100	95.7 +/- 3.8	0.500	*59.6 +/- 8.9*	0.004	0.010
	fenbuconazole	0.99975	0.010	103.0 ± 2.6	0.100	89.9 +/- 2.5	0.500	103.9 +/- 6.2	0.004	0.010
	fenhexamid[1]	0.99992	0.005	101.4 ± 0.8	0.100	94.8 +/- 13.6	0.500	102.4 +/- 8.0	0.005	0.010
	fenpropimorph[2]	0.99752	0.020	*125.4 +/- 9.4*	0.200	79.7 +/- 12.8	1.000	105.0 +/- 7.1	0.010	0.020
	fluquinconazole	0.99969	0.010	106.0 ± 1.4	0.100	82.6 +/- 9.5	0.500	107.5 +/- 6.0	0.005	0.010
	fludioxonil[1]	0.99834	0.010	109.3 ± 4.8	0.100	88.5 +/- 5.6	0.500	106.1 +/- 4.4	0.005	0.010
	flusilazole	1.00000	0.010	104.6 ± 1.6	0.100	77.7 +/- 2.4	0.500	104.8 +/- 5.8	0.005	0.010
F	**folpet**[1,2]	1.00000	0.010	70.1 ± 1.4	0.100	70.8 +/- 3.8	0.500	*67.3 +/- 4.1*	0.005	0.010
	hexaconazole	0.99975	0.010	104.8 ± 1.5	0.100	89.6 +/- 4.9	0.500	107.4 +/- 6.4	0.005	0.010
	imazalil	0.99475	0.010	72.8 ± 0.8	0.100	73.7 +/- 6.0	0.500	78. 5 +/- 8.3	0.008	0.010
	iprodione[1,2]	0.99923	0.020	*127.4 ± 2.1*	0.200	93.0 +/- 4.5	1.000	106.6 +/- 6.4	0.005	0.010
	kresoxim-methyl	0.99989	0.010	106.7 ± 3.3	0.100	96.7 +/- 3.6	0.500	106.8 +/- 7.1	0.005	0.010
	mepanipyrim	0.99697	0.020	104.9 ± 4.6	0.200	92.3 +/- 5.9	1.000	104.2 +/- 8.2 810.0	0.005	0.020
	metalaxyl	0.99991	0.010	104.7 ± 1.7	0.100	85.8 +/- 2.4	0.500	104.8 +/- 7.2	0.005	0.010
	oxadixyl	0.99958	0.030	99.7 ± 3.3	0.300	95.4 +/- 8.2	1.500	106.3 +/- 9.9	0.010	0.030
	penconazole	0.99997	0.010	98.8 ± 2.4	0.100	95.2 +/- 5.6	0.500	109.8 +/- 9.2	0.004	0.005
	pyrimethanil[1]	0.99962	0.010	94.5 ± 1.1	0.100	100.9 +/- 8.9	0.500	106.3 +/- 4.5 16.2	0.005	0.010
	procymidone[1]	0.99466	0.010	101.3 ± 0.6	0.100	96.8 +/- 7.9	0.500	108.7 +/- 8.7	0.005	0.010
	propiconazole	0.99950	0.010	104.8 ± 3.7	0.100	82.0 +/- 9.5	0.500	85.4 +/- 3.4	0.005	0.010
	pyraclostrobin[1]	0.99995	0.050	95.1 ± 3.3	0.500	79.7 +/- 6.4	2.500	98.5 +/- 4.0	0.010	0.020
	pyrazophos	0.99986	0.010	114.5 ± 0.3	0.100	89.6 +/- 11.9	0.500	106.5 +/- 9.1	0.004	0.005
	quinoxyfen	0.99740	0.010	83.7 ± 3.5	0.100	78.7 +/- 4.3	0.500	98.3 +/- 7.5	0.008	0.010
	quintozene	0.99900	0.005	101.0 ± 3.5	0.050	93.3 +/- 6.0	0.250	101.3 +/- 6.5	0.002	0.005
	tebuconazole	0.99594	0.010	76.5 ± 2.5	0.100	77.4 +/- 3.2	0.500	94.6 +/- 7.2	0.005	0.010
	tecnazene[2]	0.99693	0.005	78.0 ± 0.1	0.050	*59.1 +/- 8.9*	0.250	98.3 +/- 6.1	0.003	0.005
	tetraconazole[1]	0.99893	0.010	104.1 ± 4.1	0.100	78.7 +/- 1.9	0.500	95.2 +/- 8.3	0.004	0.005
	tolclofos-methyl	0.99997	0.010	106.6 ± 2.9	0.100	105.5 +/- 3.5	0.500	107.3 +/- 9.1	0.002	0.005
	tolylfluanid[1]	0.99798	0.010	106.8 ± 3.0	0.100	71.4 +/- 8.9	0.500	77.3 +/- 6.0	0.005	0.008
	triadimefon	0.99998	0.010	99.8 ± 4.8	0.100	88.4 +/- 11.3	0.500	108.3 +/- 9.7	0.005	0.010
	triadimenol	0.99894	0.050	101.1 ± 1.2	0.500	95.4 +/- 0.98	2.500	113.0 +/- 5.1	0.010	0.020
	trifloxystrobin	0.99990	0.010	94.7 ± 2.5	0.100	100.2 +/- 5.9	0.500	103.2 +/- 9.0	0.003	0.005
	vinclozolin	0.99723	0.010	94.7 ± 3.3	0.100	85.6 +/- 2.8	0.500	116.2 +/- 2.4 16.2	0.003	0.005
	atrazine	0.99990	0.010	85.3 ± 3.9	0.100	95.6 +/- 6.6	0.500	104.2 +/- 6.5	0.002	0.005
	chlorpropham	0.99958	0.010	93.0 ± 1.7	0.100	95.3 +/- 14.2	0.500	113.7 +/- 5.1	0.005	0.010
	lenacil[2]	0.99988	0.020	104.0 ± 0.4	0.200	*126.8 ± 5.1*	1.000	118.9 +/- 5.8	0.010	0.020
	metribuzin	0.99995	0.010	94.5 ± 2.2	0.100	95.6 +/- 1.8	0.500	106.5 +/- 5.2	0.003	0.005
	myclobutanyl	0.99894	0.010	107.8 ± 2.2	0.100	94.9 +/- 5.7	0.500	104.6 +/- 6.8 10.0	0.005	0.010
	napropamide	0.99910	0.020	105.3 ± 2.7	0.200	94.8 +/- 5.6	1.000	100.2 +/- 6.2	0.010	0.020
H	nitrofen[2]	0.99991	0.005	83.6 ± 2.9	0.050	*66.4 ± 5.8*	0.250	99.6 +/- 9.0	0.001	0.003
	pendimethalin	0.99894	0.010	104.6 ± 2.4	0.100	97.3 +/- 4.4	0.500	105.2 +/- 3.8 15.0	0.005	0.010
	propham	0.99990	0.020	107.4 ± 3.3	0.200	91.6 +/- 3.7	1.000	103.8 +/- 6.9	0.004	0.005
	prometrine	0.99956	0.005	97.5 ± 0.8	0.050	89.4 +/- 5.6	0.250	98.2 +/- 8.0	0.005	0.010
	propachlor	0.99811	0.010	105.3 ± 4.0	0.100	82.3 +/- 4.6	0.500	96.2 +/- 6.3	0.010	0.020
	propyzamide	0.99930	0.020	104.0 ± 0.2	0.200	94.4 +/- 7.7	1.000	118.2 +/- 6.4	0.005	0.010
	simazine	0.99283	0.010	106.3 ± 5.1	0.100	97.5 +/- 5.4	0.500	100.6 +/- 5.3	0.003	0.005
	trifluralin	0.99783	0.010	89.4 ± 2.5	0.100	98.4 +/- 4.5	0.500	115.4 +/- 1.2 4.2	0.005	0.010

Table 1 continued

	acetamiprid	0.99994	0.010	90.3 ± 3.1	0.100	80.3 +/- 3.6	0.500	105.8 +/- 6.4	0.008	0.010
	aldrine	0.99990	0.005	103.9 ± 1.5	0.050	85.6 +/- 1.2	0.250	95.2 +/- 8.2	0.001	0.003
	α-cypermethrin	0.99864	0.010	98.5 ± 5.3	0.100	97.4 +/- 3.4	0.500	103.9 +/- 8.4 15.5	0.001	0.005
	α-endosulfan	0.99984	0.005	109.1 ± 5.0	0.050	90.6 +/- 2.5	0.250	95.8 +/- 6.2	0.002	0.004
	α-HCH	0.99999	0.005	106.7 ± 2.0	0.050	90.5 +/- 3.5	0.250	101.6 +/- 5.0	0.005	0.010
	azinphos-ethyl	0.99730	0.010	96.1 ± 6.5	0.100	92.6 +/- 4.8	0.500	104.6 +/- 0.5 0.50.44	0.003	0.005
	azinphos-methyl	0.99969	0.010	106.6 ± 0.8	0.100	97.4 +/- 7.6	0.500	94.6 +/- 16.2	0.003	0.005
	β-cyfluthrin	0.99940	0.010	105.2 ± 3.3	0.100	82.1 +/- 3.8	0.500	105.9 +/- 8.6	0.004	0.005
	β-endosulfan	0.99745	0.005	91.2 ± 3.9	0.050	83.5 +/- 1.1	0.250	92.8 +/- 4.9	0.003	0.020
	β-HCH	0.99995	0.010	93.7 ± 2.2	0.100	79.8 +/- 9.8	0.500	119.6 +/- 6.7	0.002	0.005
	bifenthrin	0.99695	0.010	100.6 ± 2.4	0.100	98.6 +/- 2.5	0.500	96.5 +/- 8.3	0.003	0.005
	bromopropylate	0.99948	0.010	96.5 ± 2.9	0.100	89.4 +/- 5.2	0.500	106.8 +/- 8.1	0.004	0.005
	buprofezin	0.99903	0.010	78.0 ± 0.9	0.100	100.6 +/- 5.8	0.500	106.7 +/- 4.3	0.004	0.005
	chlorfenvinphos	0.99984	0.010	93.7 ± 3.1	0.100	104.5 +/- 9.8	0.500	103.1 +/- 9.2	0.008	0.010
	chlorpyrifos[1]	0.99997	0.005	93.1 ± 6.2	0.050	101.0 +/- 5.3	0.250	107.2 +/- 5.3	0.003	0.005
	chlorpyrifos-methyl	0.99592	0.005	105.5 ± 2.7	0.050	96.1 +/- 1.5	0.250	104.2 +/- 6.4	0.005	0.010
	coumphos[2]	0.99490	0.020	79.6 ± 2.4	0.200	*65.8 +/- 3.9*	1.000	105.8 +/- 7.3	0.005	0.010
	cyfluthrin	0.99970	0.010	108.0 ± 0.8	0.100	80.3 +/- 8.8	0.500	91.5 +/- 9.5	0.003	0.005
	cypermethrin[1]	0.99976	0.030	90.9 ± 4.1	0.300	101.6 +/- 1.1	1.500	109.8 +/- 6.5	0.002	0.005
	deltamethrin[2]	0.99989	0.010	103.3 ± 2.8	0.100	*59.6 +/- 5.6*	0.500	115.9 +/- 3.1	0.002	0.005
	diazinon	0.99968	0.010	99.0 ± 4.5	0.100	87.4 +/- 4.5	0.500	122.1 +/- 5.5	0.001	0.002
	dicofol	0.99847	0.020	94.8 ± 3.8	0.200	90.3 +/- 2.3	1.000	103.8 +/- 8.0	0.001	0.003
	dieldrin	0.99807	0.003	94.5 ± 4.4	0.030	76.3 +/- 8.5	0.150	108.6 +/- 9.6	0.001	0.005
	dimethoate	0.99726	0.005	84.8 ± 2.2	0.050	95.0 +/- 2.4	0.250	106.8 +/- 6.1	0.005	0.010
	endosulfan-sulfate	0.99989	0.010	97.4 ± 1.2	0.100	90.7 +/- 1.9	0.500	101.9 +/- 4.2	0.001	0.002
	endrin	0.99919	0.004	95.9 ± 2.1	0.040	84.3 +/- 2.4	0.200	99.8 +/- 5.4	0.003	0.005
	esfenvalerate	0.99995	0.010	86.6 ± 5.0	0.200	83.4 +/- 11.3	1.000	103.5 +/- 3.1	0.005	0.010
	etion	0.99967	0.005	94.8 ± 1.3	0.050	77.3 +/- 0.5	0.250	105.9 +/- 6.3	0.005	0.008
	ethoprophos	0.99920	0.005	115.1 ± 0.6	0.050	74.8 +/- 5.5	0.250	99.8 +/- 4.5	0.005	0.006
	fenazaquin[1]	0.99983	0.020	90.7 ± 3.5	0.200	77.0 +/- 2.0	1.000	108.5 +/- 2.5 14.0	0.010	0.020
	fenitrothion	0.99840	0.008	93.9 ± 2.1	0.080	95.2 +/- 6.5	0.400	98.7 +/- 5.3	0.002	0.004
	fenpropathrin	0.99970	0.006	96.6 ± 5.4	0.060	95.1 +/- 3.4	0.300	105.8 +/- 6.2	0.002	0.005
	fenvalerate	0.99528	0.020	92.8 ± 2.5	0.200	92.6 +/- 7.8	1.000	99.5 +/- 5.1	0.001	0.003
I	fipronil	0.99996	0.004	92.4 ± 2.1	0.040	78.3 +/- 7.1	0.200	98.6 +/- 8.3	0.001	0.003
	formothion	0.99795	0.005	107.2 ± 1.3	0.050	81.9 +/- 8.3	0.250	100.9 +/- 7.2	0.001	0.002
	g-HCH (lindane)	0.99987	0.003	96.5 ± 0.5	0.300	91.2 +/- 8.2	1.500	104.6 +/- 5.3	0.005	0.010
	HCB	0.99893	0.003	97.2 ± 1.5	0.300	85.2 +/- 2.9	1.500	91.6 +/- 6.2	0.001	0.003
	heptachlor	0.99960	0.002	112.2 ± 4.5	0.020	93.1 +/- 5.4	0.100	106.6 +/- 8.0	0.002	0.010
	heptachlor-epoxide	0.99850	0.003	93.1 ± 3.6	0.300	79.4 +/- 6.7	1.500	108.6 +/- 5.6	0.003	0.005
	heptenophos	0.99852	0.010	101.7 ± 1.5	0.100	76.1 +/- 0.5	0.500	105.7 +/- 8.3	0.003	0.005
	isofenphos	0.99994	0.010	113.0 ± 6.7	0.100	93.1 +/- 9.4	0.500	103.8 +/- 8.2 16.1	0.005	0.010
	l-cyhalothrin[1]	0.99978	0.010	97.4 ± 1.6	0.100	94.1 +/- 10.4	0.500	109.8 +/- 5.3	0.005	0.010
	malathion	0.99972	0.010	102.7 ± 1.6	0.100	96.6 +/- 7.6	0.500	96.8 +/- 8.0	0.003	0.006
	mecarbam	0.99673	0.010	108.5 ± 2.3	0.100	92.1 +/- 8.3	0.500	104.2 +/- 8.4	0.003	0.006
	methidathion	0.99995	0.010	92.4 ± 2.5	0.100	92.5 +/- 1.0	0.500	94.6 +/- 9.4	0.003	0.007
	methoxychlor (DMDT)	0.99865	0.010	91.7 ± 1.0	0.100	82.1 +/- 3.8	0.500	97.6 +/- 9.6	0.002	0.004
	p.p'-DDD	0.99700	0.006	95.6 ± 3.4	0.060	92.5 +/- 8.3	0.300	105.8 +/- 7.4	0.010	0.020
	p.p'-DDE	0.99964	0.004	93.4 ± 4.5	0.040	93.4 +/- 10.2	0.200	94.6 +/- 7.3	0.008	0.010
	o.p'-DDT	0.99995	0.006	98.9 ± 1.6	0.060	78.9. +/- 7.2	0.300	107.1 +/- 8.3	0.005	0.010
	p.p'-DDT	0.99769	0.007	98.5 ± 3.3	0.070	85.9 +/- 9.4	0.350	105.9 +/- 6.2	0.002	0.010
	parathion-ethyl	0.99711	0.010	90.0 ± 2.2	0.100	95.1 +/- 3.6	0.500	106.5 +/- 9.3	0.003	0.005
	parathion-methyl	1.00000	0.010	106.8 ± 2.9	0.100	97.1 +/- 5.9	0.500	115.9 +/- 8.0	0.003	0.005
	permethrin	0.99971	0.040	88.7 ± 2.4	0.040	90.1 +/- 8.2	0.200	108.9 +/- 4.7	0.010	0.020
	phorate	0.99991	0.010	103.7 ± 4.0	0.100	70.7 +/- 4.5	0.500	87.2 +/- 6.8	0.003	0.005
	phosmet	0.99750	0.010	88.4 ± 0.7	0.100	94.5 +/- 5.3	0.500	95.3 +/- 8.9	0.003	0.005
	phosalone[2]	0.99991	0.010	*54.6 ± 3.5*	0.100	*43.8 +/- 8.6*	0.500	*55.2 +/- 9.7*	0.005	0.010
	pirimiphos-methyl	0.99997	0.010	88.4 ± 0.6	0.100	88.3 +/- 8.5	0.500	107.6 +/- 7.6	0.002	0.005
	pirimicarb	0.99997	0.010	90.9 ± 3.3	0.100	90.1 +/- 8.4	0.500	108.6 +/- 5.3	0.002	0.005
	profenofos	0.99580	0.010	95.0 ± 3.0	0.100	93.4 +/- 0.9	0.500	104.6 +/- 6.2	0.005	0.080
	propoxur	0.99597	0.010	90.1 ± 3.2	0.100	92.6 +/- 10.3	0.500	106.9 +/- 5.0	0.005	0.010
	pyridaben	0.99963	0.020	106.5 ± 0.8	0.200	98.5 +/- 4.2	1.000	105.9 +/- 4.5 4.813.1	0.010	0.020
	pyriproxyfen	0.99922	0.030	104.4 ± 2.1	0.300	85.6 +/- 4.7	1.500	106.6 +/- 8.2	0.010	0.020
	quinalphos	0.99984	0.010	96.9 ± 2.3	0.100	76.5 +/- 6.7	0.500	110.9 +/- 7.3	0.005	0.010
	tebufenpyrad	1.00000	0.030	85.4 ± 4.0	0.300	89.1 +/- 3.4	1.500	109.9 +/-2.8	0.004	0.010
	tetradifon	0.99975	0.010	106.1 ± 3.8	0.100	97.9 +/- 0.9	0.500	99.3 +/- 6.1	0.003	0.005
	triazophos[2]	0.99739	0.010	*52.8 ± 2.4*	0.100	104.2 +/- 6.8	0.500	109.3 +/- 7.0	0.003	0.005
	ζ-cypermethrin	0.99839	0.020	113.5 ± 2.0	0.200	97.0 +/- 3.1	1.000	102.9 +/- 5.1	0.005	0.010

R^2 – correlation coefficient; a – alpha, b – beta, g – gamma, l – lambda, ζ –zeta
bolded – detected pesticide [1], italics – pesticides with recovery <70% and >120% [2],
fort. – fortification, F – fungicides (49), H – herbicides (14), I – insecticides (67)

Table 2. Pesticide residues in raspberry samples from north-eastern Poland (2005–2011) and their chronic and acute dietary exposure

Active substance	Samples with residues		Samples with residues exceeding MRLs		Range of residues min. – max.	Average residue level	National*/ EU** MRLs	Acceptable Daily Intake (ADI)	Acute Reference Dose (ARfD)	Regulation year/source	Toddlers consumption [34.5 g/p./d.]				Adults consumption [59.1 g/p./d.]			
	N	%	N	%	[mg/kg]	[mg/kg]	[mg/kg]	[mg/kg b.w.]	[mg/kg b.w.]		Intake [µg/kg b.w.]	% ADI	Intake [µg/kg b.w.]	% ArfD	Intake [µg/kg b.w.]	% ADI	Intake [µg/kg b.w.]	% ARfD
Boscalid (F)	36	19.6	–	–	0.01–0.28	0.018750	5.0/10.0	0.04	0.40[1]	2006/JMPR	0.045	0.112	1.13	2.83	0.015	0.036	0.52	1.30
Carbendazim (F)	1	0,5	-	-	0.02	0.020000	0.10/0.10	0.02	0.02	2007/EFSA	0.048	0.238	0.04	0.08	0.016	0.078	0.04	0.19
Chlorpyrifos (I)	5	2.7	–	–	0.005–0.012	0.005086	0.05/0.50	0.01	0.1	2005/COM	0.012	0.121	0.04	0.04	0.004	0.040	0.02	0.02
Chlorothalonil (F)	1	0.5	1	0.5	0.01	0.010000	10.0/0.01	0.015	0.6	2006/COM	0.024	0.159	0.04	0.007	0.008	0.052	0.02	0.003
Cypermethrin (I)	1	0.5	–	–	0.03	0.030000	0.5/0.5	0.05	0.2	2005/COM	0.071	0.143	0.12	0.10	0.023	0.047	0.06	0.05
Cyprodinil (F)	42	22.8	–	–	0.01–0.51	0.019922	2.0/10.0	0.03	0.03[1]	2003/JMPR	0.047	0.158	2.06	6.87	0.015	0.052	0.95	3.15
Dithiocarbamates (F)	29	15.8	29	15.8	0.08–0.85	0.063750	0.05/0.05	0.05	0.6[2]	2005/COM	0.152	0.303	3.44	0.57	0.050	0.099	1.58	0.26
Fenazaquin (I)	4	2.2	3	1.6	0.01–0.04	0.010234	0.10/0.01	0.005	0.1	2006/BfR	0.024	0.487	0.16	0.20	0.008	0.159	0.07	0.10
Fenhexamid (F)	61	33.2	–	–	0.02–5.53	0.093359	10.0/10.0	0.2	0.2[1]	1998/COM	0.222	0.111	22.35	11.17	0.073	0.036	10.25	5.13
Fludioxonil (F)	20	10.9	–	–	0.01–0.09	0.012266	2.0/5.0	0.37	0.37[1]	2007/EFSA	0.029	0.008	0.36	0.10	0.010	0.003	0.17	0.05
Folpet (F)	20	10.9	–	–	0.02–0.68	0.024063	3.0/3.0	0.1	0.2	1995/JMPR	0.057	0.057	2.75	1.37	0.019	0.019	1.26	0.63
Iprodione (F)	20	10.9	–	–	0.02–0.47	0.024219	10.0/10.0	0.06	0.06[1]	1995/JMPR	0.058	0.096	1.90	3.17	0.019	0.031	0.87	1.45
λ-cyhalothrin (I)	1	0.5	–	–	0.07	0.010469	0.2/0.2	0.005	0.075	2001/COM	0.025	0.498	0.28	0.40	0.008	0.163	0.13	0.20
Procymidone (F)	36	19.6	21	10.6	0.02–5.37	0.114609	10.0/0.02	0.0028	0.012	2006/EFSA	0.273	9.739	21.7	180.9	0.089	3.183	9.96	83.0
Pyrimethanil (F)	64	34.8	–	–	0.01–0.51	0.038359	5.0/10.0	0.17	0.17[1]	2007/JMPR	0.091	0.054	2.06	1.21	0.030	0.018	0.95	0.56
Pyraclostrobin (F)	3	1.6	–	–	0.02–0.08	0.040313	0.02/2.0	0.03	0.03	2003/JMPR	0.096	0.320	0.32	1.10	0.031	0.104	0.15	0.50
Tetraconazole (F)	1	0.5	–	–	0.06	0.010391	0.2/0.2	0.004	0.03	2004/BfR	0.025	0.618	0.24	0.80	0.008	0.202	0.25	0.40
Tolylfluanid (F)	4	2.2	–	–	0.04–0.72	0.029141	5.0/5.0	0.1	0.25	2005/EFSA	0.069	0.069	2.91	1.20	0.023	0.023	1.33	0.50

MRLs – maximum residue limits; *MRLs according to EC standards; **MRLs according to Polish regulations; b.w. – body weight; p. – person; d. – day; JMPR - Joint FAO/WHO Meeting on Pesticide Residues; COM – European Commission; EFSA - European Food Safety Authority; BfR -Bundesinstitut für Risikobewertung; Acute dietary exposure based on the highest pesticide residue: [1] – in the absence of the ARfD for the calculations was used ADI; [2] – ARfD for mancozeb; If below the ARfD, therefore no concern for consumer health.

any of the reported cases. The data show the chronic dietary exposure is pretty low. For adults it does not exceed 4.5%, and for toddlers slightly above 13%. The risk of exposure was considered as insignificant in the cases where the estimated exposure was equal or lower than to ARfD. Table 2 presents the estimated short-term intake of pesticides residues by adults and toddlers in Poland. The ARfD values for pesticides were taken from official EU Pesticides Database (DG SANCO, 2008).

In raspberry samples from the values of ESTI as a percentage of ARfD ranged from for toddlers (0.007 – 11.2% of ARfD) and for adults (0.003 – 5.1% of ARfD) (Table 2), indicating a minimum acute risk from the detected pesticides, except in the case of procymidone in toddlers population, with the ARfD estimated as the 97.5th percentile value of pesticides residues levels exceeded 180% of ARfD allowed value and for adults is 83%. The exposure of toddlers' population is higher in comparison with the general population.

The dietary intakes estimated from all individual pesticide levels detected in the raspberry samples, do not represent a health risk to consumers, but the intake estimated from the highest procymidone level (5.37 mg/kg) is uncomfortably over the short-term health standards for the pesticide (180.9 for toddlers and 83 for adults % of ARfD) and exceeds the short-term standard using the EFSA high consumption diets (EFSA, 2008). Procymidone may have an effect in humans that is similar to endocrine effects. Procymidone is known to interfere with the endocrine system related to its anti-androgenic activity ultimately resulting. Intake estimated from the highest fenhexamid concentration (5.53 mg/kg) didn't over the short-term health standards for the pesticide (11.17 for toddlers and 5.13 for adults % of ARfD).

The risk assessment process for multiple residues is not standing still. Currently there is no compliance at the international level regarding the methodology for estimating the cumulative risk for exposure to pesticide residues in food. Human exposure to mixtures of toxic chemicals is probably more common

than exposure to single compound (Gordon *et al.*, 2006). Therefore, for estimating the acute exposure for samples containing of more than one pesticide residue is recommended.

The additive effect of two or more pesticides is also unlikely because the polish raspberry contribution to the intakes estimated from all pesticides detected in the study does not add up to 4% for adults and 13% for toddlers. Interactive effects between two or more pesticides are also unlikely when residue levels are below the ADIs (EFSA, 2008). However, it should be noted that ADIs do not account for intakes from non-food sources (EFSA, 2008) and cumulative and synergistic effects from chemical exposures are likely in farming communities and also in the general public (for example from the use of organophosphate pesticides). Estimated combined acute risk assessment of samples containing more than one residue did not exceed 8% for adults and for toddlers 17% of the ARfD.

Discussion

Results from north-eastern Poland were compared with residues found in raspberry samples produced in other parts of Poland. The percentage of raspberry samples with residues from Polish monitoring (62.2%) is comparable with samples from north-eastern Poland (Nowacka *et al*., 2006, 2007, 2008, 2009, 2010, 2011, 2012) and the pesticides most frequently found were procymidone (35.6%) and pyrimethanil (23.9%). However, the percentage of sample with residues above the MRLs is much lower for the Polish monitoring program (9.4%) than those in this study. In this case, it seems that the growers used pesticides that have no been permitted to application on raspberry.

The available data suggest that the risk from combined exposures to residues of pesticides with different modes of action is not appreciably greater than the risk from residues of the individual pesticides, when exposure is below the respective ADIs or ARfDs. In the almost cases risk assessment was carried out for residues of more than one pesticide with the same toxicological mode of action: systemic – curative, except of: chlorpyrifos – AchE inhibitors, cypermethrin – sodium channel modulators and mitochondrial complex I electron transport inhibitors – fenazaquin.

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