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Estimation of Pesticide Residues in Selected Products of Plant Origin from Poland with the Use of the HPLC-MS/MS Technique

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Abstract: The purpose of this work was to compare the content of pesticide residues (250) in unprocessed plant products from farms situated in the eastern part of Poland. The content of pesticide residues in the analysed samples was assayed with the use of the QuEChERS (Quick Easy Cheap Effective Rugged Safe) method combined with HPLC-MS/MS (high performance liquid chromatography with tandem mass spectrometry) analysis. The analyses revealed that among 160 analysed samples, pesticide residues were detected in 83 samples (approximately 52%), while in 77 samples (approximately 48%), no presence of those substances was noted. In all the samples in which the presence of the sought compounds was identified, their levels did not exceed the Maximum Residue Levels (MRL). The most often identified ones were azoxystrobin—detected in 36 samples (22.5%), linuron—assayed in 33 samples (20.6%), chlorpyrifos and carbendazim—each detected in 13 samples (8.1%), metalaxyl and metalaxyl M—in 11 samples (6.9%), and acetamiprid—in 7 samples (4.4%).

Keywords: pesticide residues; QuEChERS; LC-MS/MS; vegetables; fruits; herbs; spices

1. Introduction

The estimation of contaminants and chemical residues in food of plant origin assumes a significant importance, which is related with the progress of science and results from the critical attitude of consumers towards the applied methods of agricultural production and to the environmental pollution [1]. Accumulation of pesticide residues in food may cause toxic and allergic effects for human health and life as a result of the consumption of contaminated products [2]. For the protection of public health, the European Union introduced the highest permissible levels of pesticide residues in food and feed of plant and animal origin, regulated by the Regulation (EC) No. 396/2005 of the European Parliament and Council on 23 February 2005. Quantitative assays of pesticide residues in food allow the estimation of the exposure of consumers to the presence of those compounds and to perform risk assessment. The results of such analyses also provide important information on actual levels of pesticide residues and may cause a modification of the scope of their application in agriculture for the purpose of reduction of excessive levels relative to the Maximum Residue Levels (MRL). A highly important aspect in the estimation of the presence of pesticide residues is the application of a suitable analytical procedure that should meet the assumed requirements and guarantee the obtainment of results which can constitute the basis for making correct administrative decisions. Current studies in the field of estimation of pesticide residues indicate the universal character of the technique of liquid

chromatography with mass spectrometry (LC/MS/MS) in the analysis of that group of substances in samples of plant raw materials and in ready food products. Literature data confirm that the LC/MS/MS technique is characterised by adequate selectivity and specificity and allows to acquire, in the course of the analytical process, the required values of parameters confirming the quality of the result [3–10].

The quality requirements relating to food impose on the producers the necessity of controlling the quality of market products. Such a control results in an improvement of the quality of the food produced. One can also observe a trend towards minimisation of the number of plant protection treatments, but in spite of the existing legal regulations in this area, there are instances of breaking the regulations, resulting in the risk of products with exceeded limit levels for pesticide residues finding their way onto the market. In view of the above, the objective of this study was to compare the content of pesticide residues in 6 kinds of food products, i.e., vegetables, fruits, herbs, spices, and fruit and vegetable juices, as well as industrial plants originating from production farms in the eastern part of Poland.

2. Materials and Methods

2.1. Experimental Material

The research material consisted of samples of unprocessed plant products collected at random from farms situated in the eastern part of Poland, in the period of 2015–2016. Imported spices and juices were purchased in Lublin supermarkets. Minimum weight of a sample was 3 kg. The total number of samples was 160, classified into 6 groups:

1. Vegetables (20)—carrot (2), cabbage (1), beetroot (2), root celery (1), parsley (2), green pea (1), cucumber (1), broccoli (1), pumpkin (3), beans (1), radish (1), chive (1), dill (1), peppers (1), field pea (1).
2. Fruits (26)—blackcurrant (9), cherry (2), strawberry (4), blueberry (1), aronia berry (1), apple (3), pear (2), raspberry (2), elderberry (2).
3. Herbs (85)—root of valerian (2), herbage of thyme (39), leaf of mint (3), root of common dandelion (4), leaf of lemon balm (3), herbage of common origanum (1), herbage of marjoram (1), fruit of coriander (3), linseed (17), leaf of small plantain (3), leaf of sage (1), herbage of rock rose (1), leaf of nettle (1) root of liquorice (1), flower of marigold (1), flower of elderberry (1), leaf of blackcurrant (2), leaf of purple coneflower (1).
4. Spices (22)—black pepper (4), bay leaf (1), orange skin (1), fruit of caraway (3), curcuma (1), nutmeg (1), allspice (1), ginger (1), herbal spice (4), herbal pepper substitute (3), Herbes de Provence (2).
5. Fruit and vegetable juices (4)—multifruit juice (1), pear juice (1), apple juice (1), beetroot juice (1).
6. Industrial plants (3)—wheat (2), rape (1).

2.2. Chemicals

High-purity pesticide standards (250) were used for testing (98–99%, Dr. Ehrenstorfer GmbH, Augsburg, Niemcy; ChemService, West Chester, PA, USA): 2,4,5-T, 2,4-D, 2,4-DB, 3,5-Dichloroaniline, 3-hydroxycarbofuran, Abamectin, Acephate, Acetamiprid, Acrinathrin, Alachlor, Aldicarb, Aldicarb Sulfoxide, Aldicarb Sulphone, Ametryn, Amitraz, Atrazine, Azinophos-Ethyl, Azinophos-Methyl, Azoxystrobin, Benfuracarb, Bentazon, Benzoylprop ethyl, Bifenazate, Bromacil, Bromoxynil, Bromuconazole, Buprofezine, Butoxycarboxin, CAP (Captan), Carbaryl, Carbendazim, Carbetamide, Carbofuran, Carbosulfan, Carboxin, Chlorantraniliprole, Chloridazon, Chlorotoluron, Chlorpyrifos, Chlorsulfuron, Clofentezine, Clomazone, Clothianidin, Coumaphos, Cyanazine, Cyanofenphos, Cycloate, Cymoxanil, Cyphenothrin, Cyprofuram, DEF (Decafentin), Demeton-S-methyl, Demeton-S-methylsulphon, Desethyl atrazin, Desisopropyl atrazin, Desmedipham, Desmetryn, Diafenthiuron, Dialifos, Diazinon, Dicamba, Dichlofluanid, Dichloprop

(2.4-DP), Diclorvos, Dicrotophos, Diflubenzuron, Dimefuron, Dimethachlor, Dimethenamide, Dimethoate, Dimethomorph, Diniconazole, Diphenamide, Diphenylamine, Disulfoton, Ditalimfos, Diuron, DMF (2,4-Dimethyl-phenyl-formamidine), Dodine, Epoxiconazole, Etaconazole, Ethiofencarb, Ethirimol, Ethofenprox, Etoxazole, Etrimphos, Fenamidon, Fenamiphos, Fenazaquin, Fenbuconazole, Fenhexamid, Fenoxap-p-ethyl, Fenoxycarb, Fenpropimorph, Fenpyroximate, Fenthion, Fenthion sulfon, Fenuron, Fipronil, Flazasulfuron, Florosulam, Fluazifop, Fluazifop-p-butyl, Fluazinam, Fludioxonil, Flufenacet, Flufenoxuron, Fluometuron, Fluroxypyr, Flurtamon, Fluthiacet methyl, Flutriafol, Fonofos, Fosthiazate, Fuberidazol, Furathiocarb, Halfenprox, Haloxyfop, Haloxyfop methyl, Haloxyfop-2-ethoxyethyl, Heptenophos, Hexaflumuron, Hexazinone, Hexythiazox, Imazalil, Imazamox, Imazapyr, Imidacloprid, Indoxacarb, Ioxynil, Iprodione, Iprovalicarb, Isazofos, Isocarbamide, Isomethiozin, Isoproturon, Isoxaflutole, Lenacil, Linuron, Lufenuron, Malaoxon, Malathion, MCPA (2-Methyl-4-chlorophenoxyacetic acid), MCPB (4-(2-Methyl-4-chlorophenoxy) butyric acid), MCPP (Mecoprop), Mecarbam, Mepanipyrim, Metalaxyl, Metalaxyl-M, Metamitron, Metazachlor, Metconazol, Methabenzthiazuron, Methacrifos, Methamidophos, Methidathion, Methiocarb, Methoprotryne, Methoxyfenozide, Metobromuron, Metolachlor, Metolachlor S, Metosulam, Metoxuron, Metrafenon, Monocrotophos, Monolinuron, Monuron, Myclobutanil, Nicosulfuron, Nitenpyram, Norflurazon, Novaluron, Omethoate, Oxamyl, Oxycarboxin, Oxydemethon methyl, Paraoxon ethyl, Paraoxon methyl, Parathion ethyl, Pebulat, Penconazole, Pencycuron, Phenkapton, Phenmedipham, Phenothrin, Phenthoate, Phorate, Phosalone, Phosmet, Phosphamidon, Phoxim, Picoxystrobin, Pirimicarb, Pirimiphos methyl, Prochloraz, Profenofos, Prometryn, Propamocarb, Propanil, Propaquizafop, Prophos, Prosulfuron, Pyraclostrobin, Pyraflufen ethyl, Pyridaphenthion, Pyridate, Pyrimiphos ethyl, Pyriproxyfen, Quinmerac, Quizalofop-p-ethyl, Resmethrine, Rimsulfuron, Sebuthylazin, Sethoxydim, Siltiopham, Simazine, Simetryn, Spinosad A, Spinosad D, Spirotetramat, Spiroxamin, Sulfotep, Sulprofos, Tebuconazole, Tebufenozide, Tebufenpyrad, Tebutam, Teflubenzuron, Tepraloxydim, Terbucarb, Terbumeton, Terbuthialzine desethyl, Terbuthylazine, Tetramethrin, Thiabendazole, Thiacloprid, Thiamethoxam, Thiodicarb, Thiophanate methyl, Tolclofos methyl, Tolylfluanid, Triadimefon, Tri-allate, Triamiphos, Triazophos, Trichlorofon, Triclopyr, Trifloxystrobin, Triflumuron, Triforine. Standard solutions of pesticide in acetonitrile, with concentration of approximately 1000 mg L^{-1}, were prepared. Next, standard solutions of a mixture of pesticides in acetonitrile, with concentration of about 35 mg L^{-1}, were prepared for each of the compounds. Working standard solutions were prepared by diluting the standard mixtures of pesticide solutions with acetonitrile. All standard solutions were stored at temperatures lower than −20 °C. The choice of analysed pesticides resulted from the demand of herb producers' customers for analyses in line with the laboratory services market in the region. In addition, only pesticides for which the criteria for analytical quality were met were included in the analysis.

2.3. Preparation of Samples

The analytical procedure was described in earlier work [11]. Portions of about 3 kg of plant material were suitably mixed to obtained uniform material, and then samples of approximately 100 g were collected and homogenised. The obtained homogenisate was transferred in suitable amounts to 50 mL test tubes. In the case of dry matrices, the samples were moistened to the level of about 95%.

The next step was the addition, to the homogenisate, of 10 mL of acetonitrile (Merck, Darmstadt, Germany) and 100 µL of internal standard of triphenylphosphate (Merck, Darmstadt, Germany) (10 µg mL^{-1}) assayed in the mode of positive ionisation and 100 µL of internal standard of bis-nitrophenyl urea (Merck) (10 µg mL^{-1}) assayed in the mode of negative ionisation as an internal standard. The test tube was shaken vigorously for 1 min. Next, a mixture of salts QuECheRS Mix I (Agilent Technologies, Santa Clara, CA, USA) was added, and the tube was shaken again for 1 min and centrifuged for 5 min (1361 rcf). The obtained extract was purified by adding the mixture of salts QuEChERS Mix II (Agilent Technologies, Santa Clara, CA, USA), while in the case of samples containing chlorophyll, the mixture QuEChERS Mix III (Agilent Technologies, Santa Clara, CA, USA)

was additionally added, and the tube was shaken again for 1 min, and then centrifuged for 5 min (1361 rcf). The extract prepared in this manner was transferred to the autosampler vial and subjected to chromatographic analysis.

2.4. Pesticides Analysis

The content of pesticide residues in the analysed samples was assayed following a modified procedure developed in accordance with the standard PN-EN 15662:2008 [12], with the use of the method QuEChERS combined with LC-MS/MS analysis. The procedure applied in the study has been approved by the Polish Centre of Accreditation (PCA 1375).

HPLC MS/MS Analysis

A Shimadzu Prominence/20 series HPLC system (Shimadzu, Tokyo, Japan) and AB SCIEX 4000 QTRAP®LC-MS/MS system with Turbo V source (Foster City, California, USA) were used for LC-MS/MS analysis. The HPLC system was equipped with a LC-20 AD binary pump, a SIL-20 AC autosampler, a DGU-20A5 online degasser and a CTO-20A column oven. Nitrogen with a purity of at least 99% generated from a Peak Scientific nitro en generator (Billerica, MA, USA) was used in the ESI source and the collision cell. Analysis was performed using a 4.6 × 100 mm × 5 µm Agilent ZORBAX Eclipse XDB C18 column with a 10 µL injection. The column temperature was constant at 40 °C. A mobile phase gradient of water with 5 mM ammonium acetate and methanol with 5 mM ammonium formate and flow rate of 0.5 mL min^{-1} were used. Mobile phase was composed of HPLC-grade water containing 5 mM ammonium acetate (eluent A) and HPLC-grade methanol containing 5 mM ammonium acetate (eluent B). The gradient elution was performed as follows: 0–0.1 min: 20% B; 0.1–1 min: 20–45% B; 1–9 min: 45–80% B; 9–19 min: 80–100% B, 19–20 min: 100% B; 20–21 min: 100–20% B; 21–24 min: 20% B. A flow rate of 0.5 mL min^{-1} and an injection volume of 15 mL were used in the LC-MS/MS system.

The mass spectrometer was operated using an ESI source in the positive and negative mode. ESI parameters were as follows: ion spray voltage 5.5 kV (ESI+) and −4.5 kV (ESI−), source temperature 600 °C, curtain gas (nitrogen) 35 psi, ion source gas "1" 50 psi, ion source gas "2" 65 psi, and collision gas (nitrogen) 5 psi. ESI-MS/MS was operated in scheduled multiple reaction monitoring mode (MRM), in both positive and negative polarities, by scanning two precursor/products ion transitions for each target analyte. Both transitions were used for quantification and confirmation purposes (see the Supplementary Material: Tables S1 and S2).

The recovery for pesticides in the matrices tested ranged from 70% to 120%. The limit criterion for linearity was the range above $r \geq 0.995$ (values from 0.9950 to 0.9998 were obtained).

3. Results

The analyses revealed that among 160 analysed samples, pesticide residues were detected in 83 samples (approximately 52%), while in 77 samples (approximately 48%), no presence of those substances was noted. In all the samples in which the presence of the sought compounds was identified, their levels did not exceed the Maximum Residue Levels (MRL). The occurrence of the analysed contaminants in the particular kinds of analysed samples is presented in Table 1. Residues of plant protection agents were found most often in samples of fruits—approximately 70%, while in herbs and fruit juices, pesticides were noted in approximately 53% and 50% of the samples, respectively. The lowest share of samples containing that group of analysed contaminants was noted in the case of vegetables—40%, and spices—approximately 43% (Table 1). Among the food samples subjected to analysis, pesticide residues were most frequently detected: in the group of herbs—in thyme (80%), in the group of fruits—in blackcurrant (44.4%), and in the group of spices—in black pepper (44.4%) (Table 2). Residues of two or more pesticides were hound in 54 samples (65.1%). In total, the presence of two pesticides was found in 25 samples (30.12%), the presence of three pesticides was noted in 11 samples (13.3%), and the presence of four and five pesticides, in 8 and 6 samples, respectively

(9.6% and 7.2%). One each of the analysed samples contained combinations of 7, 8, 9, and 12 of the identified compounds (Table 2). Co-occurrence of pesticide residues was noted in 44 herbal samples (91.8%), in 4 fruit samples (14.8%), in 2 vegetable samples (10%), and in 2 spice samples (9.5%). In the case of the herbal samples, the most often detected combination was that of a fungicide and a herbicide (azoxystrobin and linuron)—28 samples (32.9%), a combination of 2 fungicides with a herbicide (azoxystrobin, carbendazim and linuron) was assayed in 8 samples (9.4%), and combinations of 2 fungicides with 2 herbicides (azoxystrobin, linuron, metalaxyl, and metalaxyl M) were found in 8 samples (9.4%).

The presence of residues of an insecticide (acetamiprid) and a fungicide (trifloxysrobin) was found in 4 samples of fruits, in 2 samples of vegetables, a combination of a fungicide (azoxystrobin) and a herbicide (linuron) was detected, and the occurrence of a fungicide (azoxystrobin) and a herbicide (linuron) was noted in 2 samples of spices. In individual samples of herbs, the most often detected pesticide residues were linuron and azoxysrobin, in fruit samples—thiacloprid and trifloxystrobin, in spice samples—metalaxyl, metalaxyl M, and chloropyrifos, while in vegetable samples—azoxystrobin and chlorpyrifos (Table 2).

In the analysed samples, a total of residues of 40 pesticides were identified. The most often identified ones were azoxystrobin—detected in 36 samples (22.5%), linuron—assayed in 33 samples (20.6%), chlorpyrifos and carbendazim—each detected in 13 samples (8.1%), metalaxyl and metalaxyl M—in 11 samples (6.9%), and acetamiprid—in 7 samples (4.4%). The frequency of occurrence of all identified pesticides is presented in Figure 1. From among the 250 compounds sought in the presented experiment, in the analysed samples, the presence of 40 pesticides was found, which means that no presence of 210 pesticides from the estimated group of plant protection agents was detected. In terms of the use of the marked substances, they were classified into groups: fungicides (47.5%), insecticides (32.5%), herbicides (15%), carbamates (2.5%), and organophosphorus pesticides (2.5%). In the presented research, all identified pesticide residues are authorised in Poland. All pesticides found in individual products of plant origin are dedicated to the protection of a given plant species.

Table 1. Number of samples with and without detected pesticides residues for each analysed food product.

	Food Product													
	Vegetables		**Fruits**		**Herbs**		**Spices**		**Fruit and Vegetable Juices**		**Cereals**		**Total**	
	Number of Sumples	**%**	**Number of Sumples**	**%**	**Number of Sumples**	**%**	**Number of Sumples**	**%**	**Number of Sumples**	**%**	**Number of Sumples**	**%**	**Number of Sumples**	**%**
Samples analysed	20	-	27	-	85	-	21	-	4	-	3	-	160	-
No residues found	12	60	8	29.6	40	47.1	12	57.1	2	50	3	100	77	48.1
Residues found < MRL	8	40	19	70.4	45	52.9	9	42.9	2	50	0	0	83	51.9
Residues found > MRL	0	0	0	0	0	0	0	0	0	0	0	0	0	0

MRL—Maximum Residue Levels.

Table 2. Pesticide residues concentration in examined food samples.

No.	Food Product	Pesticide Residue	MRL (mg kg^{-1})	LOQ (mg kg^{-1})	Concentration (mg kg^{-1})	Uncertainty (mg kg^{-1})
			Herbs			
1	Thyme herb	Acetamiprid	3.0	0.0001	0.026	±0.005
		Azoxystrobin	70.0	0.0001	0.073	±0.026
		Carbendazim	0.1	0.0001	0.052	±0.016
		Chlorpyriphos	0.05	0.0001	0.012	±0.003
		Dimethoate	0.02	0.0001	0.010	±0.003
		Linuron	1.0	0.0002	0.014	±0.005
		Metalaxyl	2.0	0.0001	0.046	±0.009
2	Thyme herb	Azoxystrobin	70	0.005	0.023	±0.008
3	Thyme herb	Acetamiprid	3.0	0.0001	0.018	±0.004
		Azoxystrobin	70.0	0.0001	0.052	±0.018
		Carbendazim	0.1	0.0001	0.027	±0.008
		Linuron	1.0	0.0002	0.015	±0.005
4	Thyme herb	Azoxystrobin	70	0.0001	0.035	±0.012
		Carbendazim	0.1	0.0001	0.042	±0.013
		Linuron	1.0	0.0002	0.009	±0.012
		Metalaxyl	2.0	0.0001	0.013	±0.003
		Metazachlor	0.3	0.0001	0.024	±0.006
5	Thyme herb	Azoxystrobin	70.0	0.005	0.069	±0.024
		Linuron	1.0	0.005	0.026	±0.008
6	Thyme herb	Linuron	1.0	0.005	0.057	±0.018
7	Thyme herb	Azoxystrobin	70.0	0.005	0.036	±0.017
		Linuron	1.0	0.005	0.031	±0.012
8	Thyme herb	Azoxystrobin	70.0	0.005	0.098	±0.034
		Linuron	1.0	0.005	0.022	±0.009
		Metalaxyl	2.0 *	0.002	0.028	±0.006
		Metalaksyl M		0.002	0.027	±0.005
9	Thyme herb	Azoxystrobin	70.0	0.005	0.013	±0.005
		Carbendazim	0.1	0.002	0.08	±0.034
		Linuron	1.0	0.005	0.032	±0.012
10	Thyme herb	Azoxystrobin	70.0	0.005	0.028	±0.010
		Carbendazim	0.1	0.002	0.093	±0.035
		Linuron	1.0	0.005	0.019	±0.007
11	Thyme herb	Azoxystrobin	70.0	0.005	0.042	±0.02
		Carbendazim	0.1	0.002	0.022	±0.007
		Linuron	1.0	0.005	0.027	±0.01
		Pyraclostrobin	2.0	0.002	0.022	±0.007
12	Thyme herb	Azoxystrobin	70.0	0.005	0.009	±0.002
		Chlorantraniliprole	20.0	0.005	0.270	±0.130
		Dimethoate	0.02	0.002	0.140	±0.040
		Linuron	1.0	0.005	0.012	±0.004
13	Thyme herb	Azoxystrobin	70.0	0.005	0.007	±0.001
		Linuron	1.0	0.005	0.03	±0.010
14	Thyme herb	Azoxystrobin	70.0	0.005	0.053	±0.018
		Carbendazim	0.1	0.002	0.021	±0.007
15	Thyme herb	Metalaxyl	2.0 *	0.002	0.073	±0.015
		Metalaxyl-M		0.002	0.073	±0.015
16	Thyme herb	Azoxystrobin	70.0	0.005	0.031	±0.015
		Carbendazim	0.1	0.002	0.086	±0.033
		Linuron	1.0	0.005	0.029	±0.009
		Metalaxyl	2.0 *	0.002	0.018	±0.004
		Metalaxyl-M		0.002	0.018	±0.004

Table 2. *Cont.*

No.	Food Product	Pesticide Residue	MRL (mg kg^{-1})	LOQ (mg kg^{-1})	Concentration (mg kg^{-1})	Uncertainty (mg kg^{-1})
17	Thyme herb	Chlorantraniliprole	20.0	0.005	0.17	±0.080
		Linuron	1.0	0.005	0.061	±0.019
18	Thyme herb	Carbendazim	0.1	0.002	0.062	±0.019
		Chlorantraniliprole	20.0	0.005	0.160	±0.07
19	Thyme herb	Carbendazim	0.1	0.002	1.29	±0.005
		Linuron	1.0	0.005	0.016	±0.005
		Metalaxyl	2.0 *	0.002	0.008	±0.002
		Metalaxyl-M		0.002	0.006	±0.002
20	Thyme herb	Azoxystrobin	70.0	0.005	0.067	±0.013
		Linuron	1.0	0.005	0.110	±0.030
21	Thyme herb	Azoxystrobin	70.0	0.005	0.035	±0.007
		Linuron	1.0	0.005	0.120	±0.040
22	Thyme herb	Azoxystrobin	70.0	0.005	0.013	±0.003
		Linuron	1.0	0.005	0.021	±0.006
		Metalaxyl	2.0 *	0.002	0.058	±0.017
		Metalaxyl-M		0.002	0.060	±0.019
23	Thyme herb	Azoxystrobin	70.0	0.005	0.041	±0.008
		Carbendazim	0.1	0.002	0.022	±0.007
		Chlorantraniliprole	20.0	0.005	0.094	±0.043
		Chlorotoluron	0.02	0.002	0.009	±0.002
		Linuron	1.0	0.005	0.062	±0.019
		Metalaxyl	2.0 *	0.002	0.015	±0.004
		Metalaxyl-M		0.002	0.013	±0.004
		Metolachlor	0.05 *	0.005	0.012	±0.003
		Metolachlor S		0.002	<LOQ = 0.002	±0.002
24	Thyme herb	Azoxystrobin	70.0	0.005	0.020	±0.004
		Linuron	1.0	0.005	0.016	±0.005
25	Thyme herb	Azoxystrobin	70.0	0.005	0.050	±0.01
		Linuron	1.0	0.005	0.100	±0.003
26	Thyme herb	Azoxystrobin	70.0	0.005	0.210	±0.040
		Linuron	1.0	0.005	0.026	±0.008
27	Thyme herb	Linuron	1.0	0.005	0.110	±0.030
28	Thyme herb	Azoxystrobin	70.0	0.005	0.009	±0.002
		Linuron	1.0	0.005	0.014	±0.004
29	Thyme herb	Azoxystrobin	70.0	0.005	0.290	±0.060
		Linuron	1.0	0.005	0.015	±0.005
30	Thyme herb	Linuron	1.0	0.005	0.085	±0.026
31	Thyme herb	Azoxystrobin	70.0	0.005	0.059	±0.012
		Linuron	1.0	0.005	0.008	±0.002
		Metalaxyl	2.0 *	0.002	0.018	±0.005
		Metalaxyl-M		0.002	0.015	±0.005
32	Thyme herb	Azoxystrobin	70.0	0.005	0.330	±0.110
		Linuron	1.0	0.005	0.015	±0.005
33	Thyme herb	Azoxystrobin	70.0	0.005	0.044	±0.009
		Linuron	1.0	0.005	0.013	±0.004
34	Thyme herb	Azoxystrobin	70.0	0.005	0.230	±0.080
		Linuron	1.0	0.005	0.018	±0.006
35	Thyme herb	Azoxystrobin	70.0	0.005	0.290	±0.099
		Linuron	1.0	0.005	0.048	±0.015
		Metalaxyl	2.0 *	0.002	0.11	±0.030
		Metalaxyl-M		0.002	0.12	±0.040
		Trifloxystrobin	15.0	0.002	0.015	±0.003

Table 2. *Cont.*

No.	Food Product	Pesticide Residue	MRL (mg kg^{-1})	LOQ (mg kg^{-1})	Concentration (mg kg^{-1})	Uncertainty (mg kg^{-1})
36	Thyme herb	Azoxystrobin	70.0	0.005	0.27	±0.092
		Linuron	1.0	0.005	0.029	±0.009
37	Blackcurrant leaf	Azoxystrobin	5.0	0.005	1.530	±0.520
		Linuron	0.05	0.005	0.160	±0.050
		Tebuconazole	1.5	0.005	0.015	±0.004
38	Blackcurrant leaf	Azoxystrobin	5.0	0.005	1.620	±0.550
		Clomazone	0.01	0.005	0.038	±0.010
		Linuron	0.05	0.005	0.290	±0.090
		Tebuconazole	1.5	0.005	0.051	±0.013
39	Valerian root	Azoxystrobin	50.0	0.005	0.210	±0.070
40	Coriander fruit	Azoxystrobin	70.0	0.005	0.009	±0.002
41	Elderbery flower	Picoxystrobin	0.01	0.005	0.009	±0.002
42	Purple coneflower leaf	Chlorpyrifos	0.05	0.002	0.043	±0.010
43	Sage leaf	Linuron	1.0	0.005	0.012	±0.004
44	Linseed	Epoxiconazole	0.05	0.005	0.010	±0.003
45	Linseed	Chlorpyrifos	0.05	0.005	0.050	±0.012
			Fruits			
46	Blackcurrant	Thiacloprid	1.0	0.002	0.060	±0.022
47	Blackcurrant	Thiacloprid	1.0	0.002	0.050	±0.019
48	Blackcurrant	Fenpyroximate	1.0	0.002	0.027	±0.009
		Thiacloprid	1.0	0.002	0.022	±0.004
		Trifloxystrobin	1.0	0.002	0.021	±0.006
49	Blackcurrant	Thiacloprid	1.0	0.002	0.016	±0.006
50	Blackcurrant	Acetamiprid	2.0	0.002	0.016	±0.003
		Trifloxystrobin	1.0	0.002	0.070	±0.030
51	Blackcurrant	Acetamiprid	2.0	0.002	0.023	±0.005
52	Blackcurrant	Acetamiprid	2.0	0.002	0.011	±0.002
		Thiacloprid	1.0	0.002	0.066	±0.024
53	Blackcurrant	Fenpyroximate	1.0	0.002	0.040	±0.013
54	Cherry	Dodine	5.0	0.002	0.087	±0.018
		Thiacloprid	0.02	0.002	0.003	±0.001
55	Cherry	Dodine	5.0	0.002	0.037	±0.008
56	Strawberry	Acetamiprid	0.5	0.001	0.005	±0.001
		Azoxystrobin	10.0	0.0001	0.100	±0.034
		Chlorotoluron	0.01	0.0005	0.009	±0.002
		Cyprodinil	5.0	0.001	0.150	±0.038
		Difenoconazole	0.4	0.0002	0.063	±0.016
		Fludioxonil	4.0	0.0001	0.200	±0.068
		Mepanipyrim	1.5	0.0001	0.080	±0.026
		Trifloxystrobin	1.0	0.0001	0.330	±0.092
57	Apple	Diflubenzuron	0.05	0.01	0.042	±0.011
		Fenpyroximate	0.05	0.002	0.013	±0.004
		Fenpropimorph	0.05	0.002	0.011	±0.003
		Teflubenzuron	2.0	0.01	0.046	±0.012
		Triflumuron	2.0	0.002	0.063	±0.016

Table 2. *Cont.*

No.	Food Product	Pesticide Residue	MRL (mg kg^{-1})	LOQ (mg kg^{-1})	Concentration (mg kg^{-1})	Uncertainty (mg kg^{-1})
58	Apple	Acetamiprid	0.8	0.002	0.024	±0.005
		Carbendazim	0.2	0.002	0.098	±0.030
		Chlorpyrifos	0.5	0.002	0.085	±0.020
		Diflubenzuron	5.0	0.01	0.014	±0.004
		Fenpyroximate	0.3	0.002	0.018	±0.006
		Fludioxonil	5.0	0.002	0.013	±0.004
		Methoxyfenozide	2.0	0.002	0.064	±0.016
		Pirimicarb	2.0	0.002	0.020	±0.005
		Pyraclostrobin	0.5	0.002	0.039	±0.012
		Thiacloprid	0.3	0.005	0.023	±0.009
		Tebuconazole	0.3	0.002	0.025	±0.006
		Trifloxystrobin	0.5		0.025	±0.007
59	Apple	Carbendazim	0.2	0.002	0.062	±0.019
60	Strawberry	Azoxystrobin	60.0	0.005	0.009	±0.003
61	Strawberry	Fludioxonil	4.0	0.002	0.043	±0.015
62	Raspberry	Imidacloprid	5.0	0.005	0.009	±0.003
		Thiamethoxam	0.05	0.002	0.009	±0.003
63	Elderberry	Chlorpyrifos	0.05	0.002	0.015	±0.003
			Spices			
64	Black pepper	Metalaxyl	0.1 *	0.002	0.016	±0.003
		Metalaxyl-M		0.002	0.015	±0.003
65	Black pepper	Acetamiprid	0.05	0.002	0.012	±0.002
		Azoxystrobin	0.3	0.005	0.022	±0.007
		Carbofuran	0.05	0.002	0.015	±0.004
		Metalaxyl	0.1 *	0.002	0.019	±0.004
		Metalaxyl-M		0.002	0.018	±0.004
66	Black pepper	Metalaxyl	0.1 *	0.002	0.041	±0.008
		Metalaxyl-M		0.002	0.039	±0.008
67	Black pepper	Metalaxyl	0.1 *	0.002	0.011	±0.002
		Metalaxyl-M		0.002	0.010	±0.002
68	Orange skin	Imazalil	5.0	0.002	3.090	±0.772
		Prochloraz	10.0	0.002	0.071	±0.018
		Thiabendazole	5.0	0.005	2.020	±0.505
70	Curcuma	Chlorpyrifos	1.0	0.002	0.042	±0.010
69	Caraway fruit	Chlorpyrifos	1.0	0.002	0.051	±0.012
71	Caraway fruit	Acetamiprid	0.05	0.002	0.99	±0.200
		Azoxystrobin	0.3	0.005	0.014	±0.003
		Carbendazim	0.1	0.002	1.50	±0.450
		Chlorpyrifos	1.0	0.002	0.095	±0.022
		Thiamethoxam	0.05	0.002	0.100	±0.030
72	Caraway fruit	Carbendazim	0.1	0.002	0.048	±0.014
		Chlorpyrifos	1.0	0.002	0.028	±0.006
		Fenpropimorph	0.1	0.002	0.011	±0.003
			Vegetables			
73	Carrot	Chlorpyrifos	0.1	0.002	0.013	±0.006
74	Beetroot	Tebuconazole	0.02	0.005	0.008	±0.002
75	Celery root	Azoxystrobin	1.0	0.005	0.007	±0.003
		Linuron	0.5	0.005	0.027	±0.010
		Tebuconazole	0.5	0.005	0.013	±0.004
76	Parsley root	Linuron	0.2	0.005	0.038	±0.013
77	Broccoli	Chlorpyrifos	0.05	0.002	0.200	±0.048

Table 2. *Cont.*

No.	Food Product	Pesticide Residue	MRL (mg kg^{-1})	LOQ (mg kg^{-1})	Concentration (mg kg^{-1})	Uncertainty (mg kg^{-1})
78	Radish	Metalaxyl	0.1 *	0.002	0.011	±0.004
		Metalaxyl-M		0.002	0.011	±0.003
		Pyraclostrobin	0.5	0.002	0.016	±0.005
79	Chive	Azoxystrobin	70.0	0.005	0.051	±0.024
		Imidacloprid	2.0	0.005	0.009	±0.003
		Linuron	1.0	0.005	0.007	±0.002
80	Dill	Azoxystrobin	0.3	0.005	0.028	±0.013
		Chlorpyrifos	5.0	0.002	0.019	±0.006
		Mepanipyrim	0.05	0.002	0.012	±0.004
81	Parsley root	Azoxystrobin	70.0	0.005	0.050	±0.024
		Chlorpyrifos	0.05	0.002	0.220	±0.090
Fruit and vegetable juices						
82	Pear juice	Acetamiprid	0.8	0.0001	0.010	±0.004
		Bosacalid	2.0	0.0005	0.015	±0.004
		Clothianidin	0.4	0.0005	0.008	±0.003
83	Beetroot juice	Tebuconazole	0.02	0.0001	0.068	±0.017

LOQ—The Limit of Quantification, MRL—Maximum Residue Levels, * sum of Metalaxyl and Metalaxyl-M.

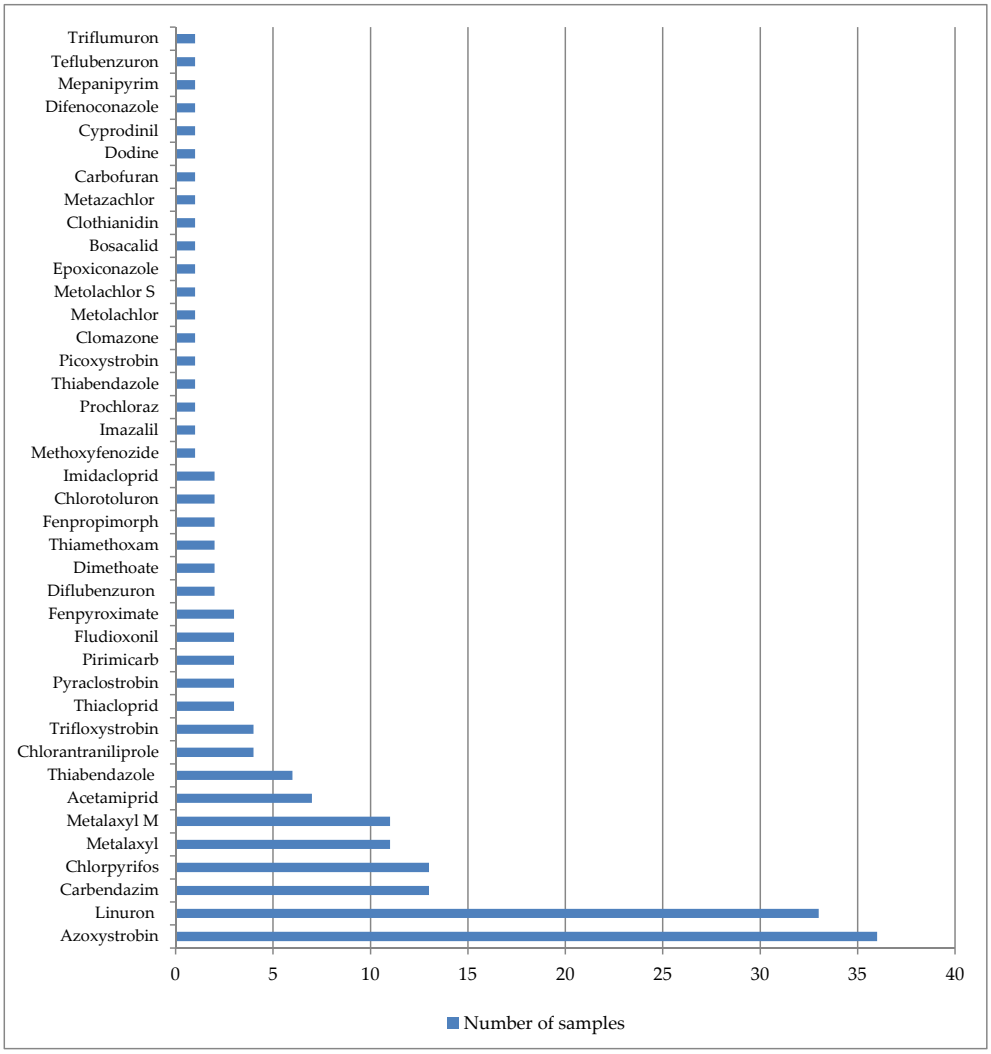

Figure 1. Pesticide occurrence frequency in analysed samples.

4. Discussion

In the presented study, the percentage share of samples containing pesticide residues (42.9–66.7%) correlates with the results obtained by other authors for the criterion "kind of sample"—Table 3. In studies concerned with vegetables, the percentage share of samples in which pesticide residues were noted varied from 15.9% to 77.8% (Table 1). Similar results were obtained in studies including fruit samples, for which the presence of pesticide residues was from 33.3 % to 77.4% of cases (Table 3). Referring to earlier results from studies covering samples of fruits and vegetables, it was demonstrated that pesticide residues in vegetables were less frequently found than in fruits [13,14], which is also supported by the results obtained in the presented experiment. Similar data were published by the European Food Safety Authority (EFSA) in 2014 and 2015, in the area of control studies on pesticide residues in food products in the member states of the European Union, indicating the presence of pesticide residues in 49–53% of samples of vegetables. Comparative studies on conventional and organic cultivations also confirmed a higher frequency of occurrence of pesticide residues in samples of fruits (75% and 25.8%) in relation to samples of vegetables (32% and 8.7%) [15,16]. The cause for this is attributed by those authors to the probability of application of a higher concentration of plant protection agents with extended effect duration, as well as to the use of various spraying technologies which may contribute to an increased accumulation of pesticide residues in fruits. A compilation of numerical data concerning the observed presence of various pesticide residues in food samples is presented in Figure 2. In the study, the own group of pesticides was most often determined as fungicides—47.5%, while every third designated plant protection product was an insecticide (32.5%). Fungicides dominated in samples from domestic primary production, tested by Dyjak et al. [17] in 2017 and Nowacka et al. [18] in 2011, as they constituted 45.5% and 63.9% respectively, and insecticides—24.5% and 32.5%. Also, in studies conducted by Szpyrk et al. [19], fungicides occurred as the most common pesticide residues. Analysing the frequency of occurrence of various pesticide residues in samples of fruits and vegetables (Figure 2), the most frequently identified pesticides were: chlorpyrifos (25%), cypermethrin (16.7%), imazalil (16.7%), azoxystrobin (12.5%), carbendazim (12.5%), imidacloprid (8.3%), cyprodinil (8.3%), permethrin (8.3%) and pyridaben (8.3%), enosulfan (4.2%), difenoconazole (4.2%), haloxyfop-R-Methyl (4.2%), boscalid (4.2%), chlorothalonil (4.2%), phosalone (4.2%), ∑-HCH (4.2%), diazinon (4.2%), enthoprophos (4.2%), pendimethalin (4.2%), acequinocyl (4.2%), iprodione (4.2%), bifenthrin (4.2%), deltamethrin (4.2%), metalaxyl (4.2%), and thiabendazole (4.2%). Four of those—azoxystrobin, carbendazim, chlorpyrifos, and metalaxyl—were also among the most frequently identified pesticides in the presented study (Figure 1). Authors conducting research on the presence of pesticide residues in plant samples also confirm the presence of those pesticides in samples of fruits and vegetables, in food of plant origin, in diet supplements, and also in plant samples used in Chinese medicine (Table 3). In the group of analysed fruits, pesticide residues were most frequently identified in samples of blackcurrant (44.4%), which is also reported in a study conducted in Poland in the years 2010–2015, in which the highest percentage level of pesticide residues among all of the analysed samples was demonstrated in blackcurrant—50% [15,20], and in black and red currant—40.9% [14]. In the presented study, the level of detected pesticide residues in herbs (52.9%) and spices (42.7%) correlates with the results obtained in study by Reinholds et al. [21] and Kowalska [11], who demonstrated the presence of pesticides in 59% and 71% of analysed samples of herbs and spices. The number of detected pesticide residues in herbs varied from 1 to 7 compounds in an individual sample of thyme (Table 2). Only in 3 (7.7%) among the 39 analysed samples of thyme was no presence found of the plant protection agents from the group analysed in their experiment. The remaining 36 samples contained pesticides, which is also confirmed by the study of Reinholds et al. [21], which showed similar values of pesticide residues in the analysed samples of that raw material (82%). In our study, the most frequently identified pesticides were linuron and azoxystrobin, while in studies by other authors, presence of plant procection, such as cymoxanil, dimethoate, and tebuconazole, was found [21–23]. Studies conducted in Poland have demonstrated the presence of the same pesticides in the analysed herb samples—azoxystrobin and linuron [11].

In the group of analysed spices, the sought compounds were detected most frequently in samples of black pepper (44.4%). In 4 out 7 analysed samples, the presence of pesticide residues was found, which is supported by the study by Ferrer-Amate et al. [24], and Reinholds et al. [21], who obtained similar results for samples of that spice.

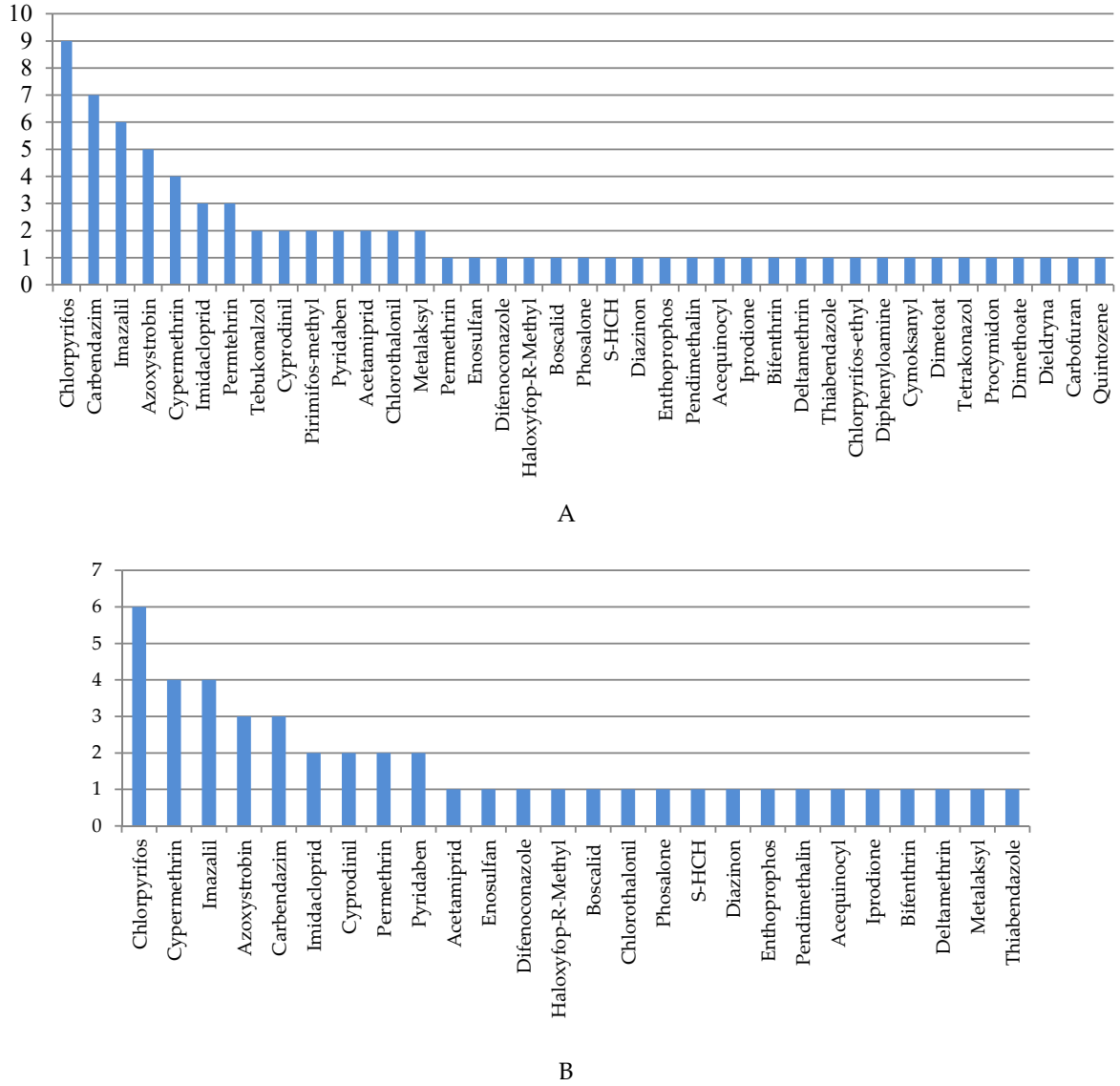

Figure 2. The most frequently detected pesticide residues in samples of plant origin according to literature data, (**A**) in all samples, (**B**) in fruit and vegetable samples (literature reports in Table 3).

Table 3. Summary of the most frequently detected pesticides in different food samples reported in the literature.

No.	Food Category	No. of Samples	No. of Samples with Detected Residues	No. of Analysed Pesticides	No. of Detected Pesticides	Most Frequently Found Pesticide	% (1)	% (2)	References
1	Vegetables	1057	168	86	43	Permethrin Enosulfan	15.9	50.0	[25]
2	Vegetables	30	5	283	4	Cypermethrin Chlorpyrifos Difenoconazole	16.7	1.4	[26]
3	Vegetables (bean)	178	39	58	39	Cyprodinil, Haloxyfop-R-Methyl	21.9	67.2	[27]
4	Vegetables	365	118	130	15	Chlorpyrifos Cypermethrin	32.3	11.5	[28]
5	Vegetables	138	47	242	17	Azoxystrobin Boscalid Chlorothalonil	34.1	7.0	[29]
6	Vegetables (tomato)	20	8	30	6	Azoxystrobin Cyprodinil	40.0	20.0	[8]
7	Vegetables	90	70	18	14	Chlorpyrifos Phosalone	77.8	77.8	[10]
8	Vegetables	20	Not defined	48	23	Σ-HCH, Permethrin	-	47.9	[30]
9	Fruit (peach)	1150	383	31	22	Chlorpyrifos Diazinon	33.3	71.0	[31]
10	Omija fruit and juice	420	143	33	4	Enthoprophos Pendimethalin	34.1	12.1	[32]
11	Yuza fruits and tea	155	120	7	3	Carbendazim Acequinocyl	77.4	42.9	[7]
12	Fruits and vegetables	199	46	74	Not defined	Imazalil Iprodione Azoxystrobin	23.1	-	[33]
13	Fruits and vegetables	20	5	82	36	Pyridaben	25.0	43.9	[34]
14	Fruits and vegetables	144	46	60	15	Carbendazim Acetamiprid	31.9	25.0	[20]
15	Fruits and vegetables	866	293	102	30	Imazalil	33.8	29.4	[35]

Table 3. *Cont.*

No.	Food Category	No. of Samples	No. of Samples with Detected Residues	No. of Analysed Pesticides	No. of Detected Pesticides	Most Frequently Found Pesticide	% (1)	% (2)	References
16	Fruits and vegetables	3009	1135	22	22	Cypermethrin	37.7	100.0	[36]
17	Fruits and vegetables	1463	689	121	44	Bifenthrin Pyridaben	47.1	36.4	[37]
18	Fruits and vegetables	13,556	6548	229	15	Carbendazim Chlorpyrifos	48.3	6.6	[6]
19	Fruits and vegetables	150	88	34	16	Deltamethrin Imidacloprid Cypermethrin Chlorpyrifos Metalaksyl	58.7	47.1	[38]
20	Fruits and vegetables	724	586	326	83	Thiabendazole Imazalil	80.9	25.5	[5]
21	Fruits and vegetables	17	17	100	26	Imazalil Imidacloprid	100.0	26.0	[9]
22	Herbs	30	2/3	155	3	Chlorpyrifos-ethyl Diphenyloamine Tebukonazol	6.7–10.0	1.9	[22]
23	Herbs and spices	300	177	134	24	Cymoksanyl Dimetoat Tebukonazol Tetrakonazol	59.0	17.9	[21]
24	Herbs	104	75	250	16	Azoxystrobin Linuron Carbendazim	72.1	6.4	[11]
25	Foods of plant origin and drinks	126	42	47	18	Chlorpyrifos Procymidon Primifos-methyl Dimethoate Dieldryna	33.3	38.3	[39]

Table 3. *Cont.*

No.	Food Category	No. of Samples	No. of Samples with Detected Residues	No. of Analysed Pesticides	No. of Detected Pesticides	Most Frequently Found Pesticide	% (1)	% (2)	References
26	Fruit juices	106	46	53	9	Carbendazim Imazalil	43.4	17.0	[3]
27	Fruit juices	21	10	174	21	Imidacloprid Acetamiprid	47.6	12.0	[40]
28	Fruit-based soft drinks	94	85	30	11	Carbendazim Imazalil	90.4	36.7	[4]
29	Cereals	89	14	110	3	Primifos-methyl	15.7	2.7	[41]
30	Cereals	380	145	292	Not defined	Permethrin Tebukonazol	38.0	-	[23]
31	Chinese herbal medicines	294	108	162	42	Chlorpyrifos	36.7	25.9	[42]
32	Plant used in traditional Chinese medicine	138	95	116	55	Carbendazim Carbofuran	68.8	47.4	[43]
33	Traditional Chinese medicine	20	20	55	6	Quintozene Chlorothalonil Chlorpyrifos	100.0	10.9	[44]
34	Dried botanical dietary supplements	Not defined	Not defined	236	73	Carbendazim Metalaxyl Azoxystrobin	-	30.9	[45]
35	Food samples	31	9	44	8	Acetamiprid Azoxystrobin	29.0	18.8	[46]

(1) The percentage of total number of analysed sample to the total number of detected pesticides. (2) The percentage of detected pesticides to the total number of pesticides analysed.

The literature review revealed the presence of metalaxyl and carbendazim in samples of black pepper, which was also observed in our experiment. In none of the analysed samples of herbs were exceeded levels of concentration (above the MRL) observed, which does not support the results obtained by Reinholds et al. [21] and Kowalska [11], where the concentrations of pesticide residues in 10% [21] of samples of oregano and in 46% [21] and 15% [11] of samples of thyme were above the permissible values. The literature review, in the aspect of the content of pesticide residues in samples of juices, demonstrated that the percentage share of samples in which the sought compounds were identified varied from 43.40% to 90.43% [3,4,40], which is in conformance with the results obtained in this study for the samples of fruit and vegetable juices—50%. In our own study, the most frequently assayed pesticides were acetamiprid, boscalid, clothianidin, and tebucanozole (Table 2), while in the literature reports—acetamiprid, carbendazim, and imazalil (Table 3). In the analysed samples of cereals, no presence of pesticide residues was found. Literature data concerning studies on pesticide residues in cereals in Poland in the years 2009–2013 report the presence of those compounds in the range from 15.73% to 38% of the analysed samples [23,41]. In the presented study, only 3 cereal samples were analysed, which constituted as little as 1.9% of the total number of analysed samples, and that number did not constitute a representative value in relation to the remaining kinds of samples. Summing up the results obtained in this study, it should be emphasised that 51.9% of the samples of plant materials and food products originating from the eastern part of Poland contained pesticide residues, but their levels did not exceed the higher permissible concentrations. Most frequently, pesticide residues were detected in fruit samples (66.7%), compared to the remaining groups of analysed products, where the percentage share of samples containing the sought compounds was at the level of approximately 50% in each group. Special note should be taken of the possible contamination with thiacloprid and trifloxystrobin in fruits of blackcurrant, carbendazim in apples, and azoxystrobin and fludioxonil in strawberries. The analysed samples of fruits contained the largest number and diversity of identified pesticide residues, compared to the remaining samples, which raises concern relating to the quality of those food components. Pesticide cocktails found in food pose a serious threat to people and the environment. Mixtures of pesticides can have far more harmful effects than exposure to individual chemicals, both in humans and other species, such as insects, fish, and birds [47,48]. Pesticides are found in millions of different combinations at different concentrations in our food and landscape. It is probably impossible to create a system sufficiently advanced to be able to assess the full spectrum of health and environmental effects resulting from long-term exposure to hundreds of different pesticides. The results of this study emphasise the importance of monitoring of pesticide residues in herbs and spices, especially in the case of thyme and black pepper, which were identified as the most contaminated matrices in that group of products, in which the percentage share of samples containing pesticide residues was at the level of 80% and 44%, respectively.

5. Conclusions

Studies in the area of analysis of pesticide residues are highly important in the estimation of quality of raw materials of plant origin, as well as food. The results obtained in this study indicate that the occurrence of pesticide residues in the analysed products cannot be considered to be a serious threat to human and animal health. Nevertheless, constant monitoring of the content of pesticide residues and strict regulations concerning the highest permissible concentrations of those compounds in food samples are of key importance for the alleviation of potential risk to the health and life of consumers. Due to the harmful effects of the cocktail effect of pesticides, perhaps the only way to minimise the risks to health and the environment is to significantly reduce the overall use of pesticides. There is also a need to introduce urgently needed measures to support farmers to significantly reduce pesticide use and switch to organic farming systems in which synthetic pesticides are replaced by botanical pesticides or chemical control is completely avoided.

Supplementary Materials: The following are available online at http://www.mdpi.com/2077-0472/10/6/192/s1, Table S1: List of pesticides determined in the positive ionization mode, Table S2: List of pesticides determined in the negative ionization mode.

Author Contributions: G.K. and R.K. conceived the research idea and experimental protocol; G.K. coordinated the research; G.K. and R.K. wrote the manuscript; G.K. and R.K. managed writing—review and editing; G.K., U.P., and R.K. had the supervision task; G.K., U.P., and R.K. were involved in crop management and performed the determinations of biochemical and physiological analyses; G.K. managed the data statistical processing; G.K., U.P., and R.K. were involved in bibliographic search. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare that they have no conflicts of interest to disclose.

References

1. Damalas, C.A.; Eleftherohorinos, I.G. Pesticide Exposure, Safety Issues, and Risk Assessment Indicators. *Int. J. Environ. Res. Public Health* **2011**, *8*, 1402–1419. [PubMed]
2. Akoto, O.; Gavor, S.; Appah, M.K.; Apau, J. Estimation of human health risk associated with the consumption of pesticide-contaminated vegetables from Kumasi, Ghana. *Environ. Monit. Assess.* **2015**, *187*, 244. [CrossRef] [PubMed]
3. Ferrer, C.; Martínez-Bueno, M.J.; Lozano, A.; Fernández-Alba, A.R. Pesticide residue analysis of fruit juices by LC–MS/MS direct injection. One year pilot survey. *Talanta* **2011**, *83*, 1552–1561. [CrossRef]
4. Gilbert-López, B.; Jaén-Martos, L.; García-Reyes, J.F.; Villar-Pulido, M.; Polgar, L.; Ramos-Martos, N.; Molina-Díaz, A. Study on the occurrence of pesticide residues in fruit-based soft drinks from the EU market and morocco using liquid chromatography–mass spectrometry. *Food Control* **2012**, *26*, 341–346. [CrossRef]
5. Hjorth, K.; Johansen, K.; Holen, B.; Andersson, A.; Christensen, H.B.; Siivinen, K.; Toome, M. Pesticide residues in fruits and vegetables from South America–A Nordic project. *Food Control* **2011**, *22*, 1701–1706. [CrossRef]
6. Jardim, A.N.O.; Caldas, E.D. Brazilian monitoring programs for pesticide residues in food–Results from 2001 to 2010. *Food Control* **2012**, *25*, 607–616.
7. Lee, K.-G.; Lee, S.-K. Monitoring and risk assessment of pesticide residues in yuza fruits (Citrus junos Sieb. ex Tanaka) and yuza tea samples produced in Korea. *Food Chem.* **2012**, *135*, 2930–2933.
8. Melo, A.; Cunha, S.C.; Mansilha, C.; Aguiar, A.; Pinho, O.; Ferreira, I.M.P.L.V.O. Monitoring pesticide residues in greenhouse tomato by combining acetonitrile-based extraction with dispersive liquid–liquid microextraction followed by gas-chromatography–mass spectrometry. *Food Chem.* **2012**, *135*, 1071–1077.
9. Núñez, O.; Gallart-Ayala, H.; Ferrer, I.; Moyano, E.; Galceran, M.T. Strategies for the multi-residue analysis of 100 pesticides by liquid chromatography–triple quadrupole mass spectrometry. *J. Chromatogr. A* **2012**, *1249*, 164–180.
10. Sinha, S.N.; Vasudev, K.; Vishnu Vardhana Rao, M. Quantification of organophosphate insecticides and herbicides in vegetable samples using the "Quick Easy Cheap Effective Rugged and Safe" (QuEChERS) method and a high-performance liquid chromatography–electrospray ionisation–mass spectrometry (LC–MS/MS) t. *Food Chem.* **2012**, *132*, 1574–1584. [CrossRef]
11. Kowalska, G. Pesticide Residues in Some Polish Herbs. *Agriculture* **2020**, *10*, 154. [CrossRef]
12. PN-EN 15662. *Foods of Plant Origin-Determination of Pesticide Residues Using GC-MS and/or LC-MS/MS Following Acetonitrile Extraction/Partitioning and Cleanup by Dispersive SPE-QuEChERS-Method*; Polish Committee for Standardization: Warszawa, Poland, 2008.
13. Góralczyk, K.; Struciński, P.; Korcz, W.; Czaja, K.; Hernik, A.; Snopczyński, T.; Ludwicki, J.K. The survey of pesticide residues in food of plant origin in Poland, 2004–2007. *Ann. Natl. Inst. Hyg.* **2009**, *60*, 113–119.
14. Szpyrka, E.; Kurdziel, A.; Rupar, J.; Słowik-Borowiec, M. Pesticide residues in fruit and vegetable crops from the central and eastern region of Poland. *Rocz. Panstw. Zakl. Hig.* **2015**, *66*, 107–113.
15. Gnusowski, B.; Nowacka, A.; Walorczyk, S.; Lozowicka, B.; Szpyrka, E. Pesticide residues in organic food of plant origin in Poland in 2010. *Prog. Plant Prot.* **2012**, *52*, 127–132.

16. Barański, M.; Średnicka-Tober, D.; Volakakis, N.; Seal, C.; Sanderson, R.; Stewart, G.B.; Benbrook, C.; Biavati, B.; Markellou, E.; Giotis, C.; et al. Higher antioxidant and lower cadmium concentrations and lower incidence of pesticide residues in organically grown crops: A systematic literature review and meta-analyses. *Br. J. Nutr.* **2014**, *112*, 794–811. [CrossRef]
17. Dyjak, K.; Michota-Katulska, E.; Zegan, M. Pilotażowe badania pozostałości pestycydów w wybranych świeżych ziołach i warzywach przyprawowych zakupionych w krajowych supermarketach. *Zywn. Nauk. Technol. Jakosc/Food. Sci. Technol. Qual.* **2017**, *24*, 126–138.
18. Nowacka, A.; Gnusowski, B.; Walorczyk, S.; Drożdżyński, D.; Raczkowski, M.; Hołodyńska, A.; Frąckowiak, D.; Wójcik, A.; Ziółkowski, A.; Przewoźniak, M.; et al. Pozostałości środków ochrony roślin w płodach rolnych (2011). *Post. Ochr. Roślin* **2012**, *52*, 1106–1116.
19. Szpyrka, E.; Kurdziel, A.; Matyaszek, A.; Podbielska, M.; Rupar, J.; Słowik-Borowiec, M. Pozostałości środków ochrony roślin w płodach rolnych z terenu południowo-wschodniej Polski (2013). *Prog. Plant Prot.* **2014**, *54*, 283–287.
20. Stachniuk, A.; Szmagara, A.; Czeczko, R.; Fornal, E. LC-MS/MS determination of pesticide residues in fruits and vegetables. *J. Environ. Sci. Heal. Part B* **2017**, *52*, 446–457. [CrossRef]
21. Reinholds, I.; Pugajeva, I.; Bavrins, K.; Kuckovska, G.; Bartkevics, V. Mycotoxins, pesticides and toxic metals in commercial spices and herbs. *Food Addit. Contam. Part B* **2017**, *10*, 5–14. [CrossRef]
22. Malinowska, E.; Jankowski, K. Pesticide residues in some herbs growing in agricultural areas in Poland. *Environ. Monit. Assess.* **2015**, *187*, 775. [CrossRef]
23. Malinowska, E.; Jankowski, K.; Sosnowski, J.; Wiśniewska-Kadżajan, B. Pesticide residues in cereal crop grains in Poland in 2013. *Environ. Monit. Assess.* **2015**, *187*, 329. [CrossRef]
24. Ferrer-Amate, C.; Unterluggauer, H.; Fischer, R.J.; Fernández-Alba, A.R.; Masselter, S. Development and validation of a LC–MS/MS method for the simultaneous determination of aflatoxins, dyes and pesticides in spices. *Anal. Bioanal. Chem.* **2010**, *397*, 93–107. [CrossRef]
25. EL-Saeid, M.H.; Selim, M.T. Multiresidue Analysis of 86 Pesticides Using Gas Chromatography Mass Spectrometry: II-Nonleafy Vegetables. *J. Chem.* **2013**, *2013*, 727149. [CrossRef]
26. Skovgaard, M.; Renjel Encinas, S.; Jensen, O.C.; Andersen, J.H.; Condarco, G.; Jørs, E. Pesticide Residues in Commercial Lettuce, Onion, and Potato Samples From Bolivia—A Threat to Public Health? *Environ. Health Insights* **2017**, *11*, 117863021770419. [CrossRef]
27. Li, Z.; Li, Y.; Liu, X.; Li, X.; Zhou, L.; Pan, C. Multiresidue Analysis of 58 Pesticides in Bean Products by Disposable Pipet Extraction (DPX) Cleanup and Gas Chromatography–Mass Spectrometry Determination. *J. Agric. Food Chem.* **2012**, *60*, 4788–4798. [CrossRef]
28. Łozowicka, B.; Jankowska, M.; Kaczyński, P. Pesticide residues in Brassica vegetables and exposure assessment of consumers. *Food Control* **2012**, *25*, 561–575. [CrossRef]
29. Słowik-Borowiec, M.; Szpyrka, E.; Rupar, J.; Podbielska, M.; Matyaszek, A. Occurrence of pesticide residues in fruiting vegetables from production farms in south-eastern region of Poland. *Ann. Natl. Inst. Hyg.* **2016**, *67*, 359–365.
30. Srivastava, A.K.; Trivedi, P.; Srivastava, M.K.; Lohani, M.; Srivastava, L.P. Monitoring of pesticide residues in market basket samples of vegetable from Lucknow City, India: QuEChERS method. *Environ. Monit. Assess.* **2011**, *176*, 465–472. [CrossRef]
31. Danis, T.G.; Karagiozoglou, D.T.; Tsakiris, I.N.; Alegakis, A.K.; Tsatsakis, A.M. Evaluation of pesticides residues in Greek peaches during 2002–2007 after the implementation of integrated crop management. *Food Chem.* **2011**, *126*, 97–103. [CrossRef]
32. Jeong, H.R.; Lim, S.J.; Cho, J.Y. Monitoring and risk assessment of pesticides in fresh omija (Schizandra chinensis Baillon) fruit and juice. *Food Chem. Toxicol.* **2012**, *50*, 385–389. [CrossRef]
33. Mutengwe, M.T.; Chidamba, L.; Korsten, L. Monitoring Pesticide Residues in Fruits and Vegetables at Two of the Biggest Fresh Produce Markets in Africa. *J. Food Prot.* **2016**, *79*, 1938–1945. [CrossRef]
34. Dong, J.; Pan, Y.-X.; Lv, J.-X.; Sun, J.; Gong, X.-M.; Li, K. Multiresidue Method for the Determination of Pesticides in Fruits and Vegetables Using Gas Chromatography-Negative Chemical Ionization-Triple Quadrupole Tandem Mass Spectrometry. *Chromatographia* **2011**, *74*, 109–119. [CrossRef]
35. Knežević, Z.; Serdar, M.; Ahel, M. Risk assessment of the intake of pesticides in Croatian diet. *Food Control* **2012**, *23*, 59–65. [CrossRef]

36. Drouillet-Pinard, P.; Boisset, M.; Périquet, A.; Lecerf, J.-M.; Casse, F.; Catteau, M.; Barnat, S. Realistic approach of pesticide residues and French consumer exposure within fruit & vegetable intake. *J. Environ. Sci. Health Part B* **2010**, *46*, 84–91.
37. Camino-Sánchez, F.J.; Zafra-Gómez, A.; Ruiz-García, J.; Bermúdez-Peinado, R.; Ballesteros, O.; Navalon, A.; Vílchez, J.L. UNE-EN ISO/IEC 17025:2005 accredited method for the determination of 121 pesticide residues in fruits and vegetables by gas chromatography–tandem mass spectrometry. *J. Food Compos. Anal.* **2011**, *24*, 427–440. [CrossRef]
38. Jallow, M.F.A.; Awadh, D.G.; Albaho, M.S.; Devi, V.Y.; Ahmad, N. Monitoring of Pesticide Residues in Commonly Used Fruits and Vegetables in Kuwait. *Int. J. Environ. Res. Public Health* **2017**, *14*, 833. [CrossRef]
39. Nasreddine, L.; Rehaime, M.; Kassaify, Z.; Rechmany, R.; Jaber, F. Dietary exposure to pesticide residues from foods of plant origin and drinks in Lebanon. *Environ. Monit. Assess.* **2016**, *188*, 485. [CrossRef]
40. Tran, K.; Eide, D.; Nickols, S.M.; Cromer, M.R.; Sabaa-Srur, A.; Smith, R.E. Finding of pesticides in fashionable fruit juices by LC–MS/MS and GC–MS/MS. *Food Chem.* **2012**, *134*, 2398–2405. [CrossRef]
41. Łozowicka, B.; Miciński, J.; Zwierzchowski, G.; Kowalski, I.M.; Szarek, J. Monitoring study of pesticide residues in cereals and foodstuff from Poland. *Polish J. Environ. Stud.* **2012**, *21*, 1703–1712.
42. Harris, E.S.J.; Cao, S.; Littlefield, B.A.; Craycroft, J.A.; Scholten, R.; Kaptchuk, T.; Fu, Y.; Wang, W.; Liu, Y.; Chen, H.; et al. Heavy metal and pesticide content in commonly prescribed individual raw Chinese Herbal Medicines. *Sci. Total Environ.* **2011**, *409*, 4297–4305.
43. Chen, L.; Song, F.; Liu, Z.; Zheng, Z.; Xing, J.; Liu, S. Multi-residue method for fast determination of pesticide residues in plants used in traditional chinese medicine by ultra-high-performance liquid chromatography coupled to tandem mass spectrometry. *J. Chromatogr. A* **2012**, *1225*, 132–140. [CrossRef] [PubMed]
44. Du, G.; Song, Y.; Wang, Y. Rapid simultaneous determination of multiple pesticide residues in traditional Chinese medicines using programmed temperature vaporizer injection-fast gas chromatography coupled with mass spectrometry. *J. Sep. Sci.* **2011**, *34*, 3372–3382. [CrossRef] [PubMed]
45. Chen, Y.; Al-Taher, F.; Juskelis, R.; Wong, J.W.; Zhang, K.; Hayward, D.G.; Zweigenbaum, J.; Stevens, J.; Cappozzo, J. Multiresidue Pesticide Analysis of Dried Botanical Dietary Supplements Using an Automated Dispersive SPE Cleanup for QuEChERS and High-Performance Liquid Chromatography–Tandem Mass Spectrometry. *J. Agric. Food Chem.* **2012**, *60*, 9991–9999. [PubMed]
46. Yang, A.; Park, J.-H.; Abd El-Aty, A.M.; Choi, J.-H.; Oh, J.-H.; Do, J.-A.; Kwon, K.; Shim, K.-H.; Choi, O.-J.; Shim, J.-H. Synergistic effect of washing and cooking on the removal of multi-classes of pesticides from various food samples. *Food Control* **2012**, *28*, 99–105.
47. Rizzatti, V.; Briand, O.; Guillou, H.; Gamet-Payrastre, L. Effects of pesticide mixtures in human and animal models: An update of the recent literature. *Chem. Biol. Interact.* **2016**, *254*, 231–246. [CrossRef]
48. Hernández, A.F.; Gil, F.; Lacasaña, M. Toxicological interactions of pesticide mixtures: An update. *Arch. Toxicol.* **2017**, *91*, 3211–3223.