In the presented study a total of 104 samples of herbal material (herbage of thyme, savory, sage, rock rose, marjoram, horsetail, oregano, basil; seeds of flax; roots of liquorice, valerian and lovage, flowers of coneflower and camomile and fruits of fennel and caraway) were analysed for the content of 250 pesticides. Residues of 16 pesticides were identified in 72.1% of the analysed herbal samples. In 11 of the analysed samples of thyme herbage and in one sample of basil herbage concentrations exceeding the maximum allowable levels were demonstrated. Residues of the identified substances were detected most frequently in samples of thyme (66.34%), compared to the other groups of analysed herbal material where the percentage share of samples containing the compounds sought was at the level of approximately 20%.

Keywords: pesticide residues; herbal components; high performance liquid chromatography (HPLC) with tandem mass spectrometry (MS/MS); maximum residue limits

1. Introduction

The use of herbs for medicinal purposes has a very long history and still constitutes a high proportion of the traditional therapeutic methods in use all over the world. The World Health Organisation (WHO) estimated that approximately 80% of the world’s population uses herbal products for therapeutic purposes, most frequently in the form of extracts from plants or of the active components of plants [1]. Commercialisation of herbal products is related to their extensive application in various production sectors, such as: food, pharmaceuticals, nutraceuticals, herbal agents, diet supplements, perfumes and fragrances, cosmetics or aromatising products [2,3].

In recent years, the international market noted a doubled demand for medicinal plants. According to the WHO the current demand for plant-derived medical products amounts to 14 thousand million dollars a year, and by the year 2050 it will have increased to five billion dollars [3]. The observed growth of interest in the use of herbal products in developed countries is the result of the assumption that “natural” implies “harmless”. However, with the increasing popularity and global expansion of the market of herbal materials, the safety of herbal products is becoming a serious problem relating to public health [4].

In view of the above, the demand for herbs creates the interest of the agricultural branch. The production of herbs in Poland has a well-established tradition. The contribution of the Polish production of herbs in the European production is approximately 30%. Polish agriculture has the largest area of herbal cultivations in Europe (30,000 hectares), and the number of producers oscillates around the level of 20,000 farms annually [5]. Currently, about 70 species of herb plants are grown. The Polish herbal industry uses about 130 species of plants from a natural collection (10,000 tons of collected raw material) and about 60 species from crops (50,000 tons). In Poland, 29 original varieties of herbs are grown. The owner and breeder of 22 of them is the Institute of Natural Fibers and Medicinal Plants in Poznań. The vast majority of the material produced is purchased by the processing of companies, and the average purchase is 20,000 tons per year [5,6]. In Poland, the following raw materials are most often
obtained from lowland positions: thyme herb, lemon balm leaf, peppermint leaf and herb, valerian root and rhizome, chamomile basket, plantain leaf, fennel fruit, sage leaf, cumin fruit, marigold flower and milk thistle fruit. In the mountainous part of Poland, mainly roots are produced: angelica, purple coneflower, lovage and marshmallow.

On average, 10% of Polish farms grow herbs, but one half of the total declare interest in such cultivations, which indicates a high production potential. Farmers consider herbs to be economically attractive crop plants, under conditions of guaranteed purchasing and good prices [5]. Therefore, the cultivation of herbal plants is a prospective direction for agricultural activity and constitutes an important supplement to the income of Polish farmers. Intensification of cultivation and a focus on obtaining high yields of good quality crop plants often results in contamination of the products with the chemical agents used in agriculture. Therefore, it is now extremely important to analyse foods of plant origin for chemical contaminants, including pesticide residues. Plant protection agents are commonly used in all sectors of agricultural production to control pests, as well as to improve yields and yield quality. They are also applied post-harvest, to extend the period of storage and to maintain desired product properties [7]. Caring for food safety for consumers, many countries have implemented programmes for the monitoring and official control of food regarding pesticide content, in accordance with the maximum allowable levels of these compounds [8].

To ensure correct and reliable results of determination of pesticide residues in food of plant origin, including samples of herbal products, it is important to apply specific and selective analytical methods which currently include the QuEChERS (Quick Easy Cheap Effective Rugged Safe) method, combined with the techniques of gas chromatography (GC) and high performance liquid chromatography (HPLC) with mass spectrometry detector MS and tandem mass spectrometry (MS/MS) [9–12]. There is little published data on residues of plant-protection products in herbal raw materials produced in Poland. As reported by Malinowska and Jankowski [13] and Dyjak et al. [14], preparations containing active substances such as azoxystrobin, diphenconazole chlorpyrifos-ethyl, diphenyloamine and tebuconazole have, to date, been used on crops in Poland.

Studies aimed at the determination of the presence of pesticides in herbal materials from agricultural production are important in their quality evaluation. These provide information on a given group of agricultural materials over a specific period of time, with emphasis on continuous improvement of that status which also, on the other hand, is affected by the relevant legislative regulations.

In view of the above, the objective of this study was to estimate the content of pesticide residues in various herbal materials originating from cultivations 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 2016–2017. The minimum weight of a sample was 3 kg. The total number of samples was 104: 74 samples of thyme herbage, eight samples of flax seed, three samples of root of liquorice, three samples of herbage of savory, two samples of herbage of common sage, two samples of root of valerian, two samples of herbage of rock rose, two samples of flower of coneflower, and one sample each of herbage of marjoram, horsetail, oregano, basil, flower of camomile, fruit of fennel and caraway and root of lovage.

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, benzoilprop ethyl, bifenthrate, bromacil, bromoxynil, bromuconazole, buprofezine,
butoxycarboxin, CAP, carbaryl, carbendazim, carbetamide, arbofuran, carboxin, chlorantraniliprole, chloridazon, chlorotoluron, chlorpyrifos, chlorosulfuron, clodimoxane, clothianidin, coumaphos, cyanazine, cyanofenphos, cycloate, cyxomoxan, cyfenothrin, DEF, demeton-s-methyl, demeton-S-methylsulphon, desethyl atrazin, desisopropyl atrazin, desmediphem, desmetryn, diafenthiuron, dialifos, diazinon, dicamba, dichlofluanid, dichloprop (2,4-DP), diclorvos, dicrotophos, diflubenzuron, dimefuron, dimethachlor, dimethamide, dimethoate, dimethomorph, diniconazole, diphenamide, diphenylamine, disulfoton, dalilimfos, diuron, DMF, dodine, epoxiconazole, etaconazole, ethofencarb, ethirimol, ethofenprox, etoxazole, etrimphos, fenamidone, fenamiphos, fenazaquin, fenbuconazole, fenhexamid, fenoxap-p-ethyl, fenoxycarb, fenpropimorph, fenpyroximate, fenthion, fenthion sulfon, fenuron, fipronil, flazasulfuron, florasulam, fluazifop, fluazifop-p-butyl, fluazinam, fludioxonil, flufenacet, flufenoxuron, fluometuron, fluroxypyr, flurtamone, fluthiazole, flutriafol, fonofos, fosthiazate, fuberidazol, furathiocarb, halfenprox, haloxyfop, haloxyfop methyl, haloxyfop-2-ethylhexyl, heptenophos, hexafluron, hexazinone, hymexazin, imazalil, imazamox, imazaquin, imidacloprid, indoxacarb, iprodione, iprovalicarb, isazofos, isocarbamide, isothiozin, isoproturon, isoxaflutole, linuron, lufenuron, malaoxon, malathion, MCPA, MCPB, MCPP mecoprop, mecarbam, mepanipyr, metacycylic, metalaxyl, metazachlor, metconazol, methabenzthiazuron, methacrifos, methamidophos, methidathion, methiocarb, methoprene, methoxyfenozide, metobromuron, metolachlor, metolachlor S, metosulam, metoxuron, metrafenon, monocrotophos, monolinuron, monuron, myclobutanil, nicosulfuron, nitenpyram, norflurazon, novaluron, omethoate, oxamyl, oxycarboxin, oxydemethon methyl, paraaoxon ethyl, paraaoxon methyl, parathion ethyl, pebulate, penconazole, pencurion, phenkaptan, phentachlor, phenothrin, phenoate, phorate, phosalone, phosmet, phosphamidon, phoxim, picofenox, pirimicarb, pirimiphos methyl, prochloraz, profenofos, prometryn, propamocarb, pronalin, propaquizafop, propophos, prosulfuron, pyraclostrobin, pyrafufen ethyl, pyridaphenthion, pyriproxyfen, quinmerac, quinapazof-p-ethyl, resmethrine, rimsulfuron, sebuthylazin, sethoxydim, simazine, simetryn, spinosad A, spinosad D, spirotetramat, spiroxamin, sulfoton, sulprofos, tebuconazole, tebufluoroide, tebufenpyrad, tebutam, tephenbenzuron, tepraloxydim, terbutarel, terbutaline, thalb掌ine desethyl, thalb掌ine, tetramethrin, thiabendazole, thiacyprid, thiamethoxam, thiodicarbox, thiophanate methyl, toclofos methyl, tolyfluandren, triallate, triametaphos, triazophos, trichlorofon, triclopyr, trifloxystrobin, triflumuron, triforine.

Standard solutions of pesticide in acetonitrile, with concentration of approximately 1000 mg/L were prepared. Next, standard solutions of a mixture of pesticides in acetonitrile, with concentration of about 35 mg/L, 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 temperature lower than $-20^\circ C$.

### 2.3. Pesticides Analysis

The content of pesticide residues in the analysed samples was assayed at the Central Agroecological Laboratory of the University of Life Sciences in Lublin, following a modified procedure developed in accordance with the standard PN-EN 15662 [15], with the use of the QuEChERS method combined with LC–MS/MS analysis. The procedure applied in the study was approved by the Polish Centre of Accreditation (PCA 1375).

### 2.4. Preparation of Samples

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 homogenise 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 homogenise, of 10 mL of acetonitrile (Merck) and 100 µL of internal standard of triphenylphosphate (Merck) (10 µg/mL) assayed in the mode of positive ionisation...
and 100 µL of internal standard of bis-nitrophenyl urea (Merck) (10 µg/mL) 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 (3000 rpm). 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 (3000 rpm). The extract prepared in this manner was transferred to the autosampler vial and subjected to chromatographic analysis.

2.5. 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 were used. The mobile phase was composed of HPLC-grade water containing 5 mM ammonium acetate (eluant A) and HPLC-grade methanol containing 5 mM ammonium acetate (eluant 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 and an injection volume of 15 µL were used in the LC–MS/MS system.

The mass spectrometer was operated using an electrospray ionization (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, 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/product ion transitions for each target analyte.

3. Results

The analyses of pesticide residues in samples of herbal material covered 74 samples of thyme herbage, eight samples of flux seed, three samples of root of liquorice, three samples of herbage of savory, two samples of herbage of common sage, two samples of root of valerian, two samples of herbage of rock rose, two samples of flower of coneflower, and one sample each of herbage of marjoram, horsetail, oregano, basil, flower of camomile, fruit of fennel and caraway and root of lovage. The analyses demonstrated that among the 104 analysed samples pesticide residues were detected in 75 samples (72.1%), while in 29 samples (27.9%) no presence of those substances was found. In 11 analysed samples of thyme herbage and in one sample of basil herbage, in which the presence of the sought compounds was identified, their levels exceeded the maximum allowable concentrations. The occurrence of the analysed contaminants in the particular kinds of analysed samples of herbal material is presented in Table 1.

Among the samples in which pesticide residues were identified, the presence of a single such substance was detected in 24 samples. Residues of two or more pesticides were found in 51 samples (68%). The presence of two pesticides was noted in a total of 18 samples (24%), in 11 samples the presence of three pesticides was found (14.67%), and in 12 and nine samples, respectively, the presence of four and five pesticides was detected (16% and 12%). One of the analysed samples contained a combination of six identified compounds (Figure 1).
Table 1. Number of samples with and without detected pesticides residues for each analysed herb sample.

| Herb Samples            | Samples Analysed | No Residues Found | Residues Found < MRL | Residues Found > MRL |
|-------------------------|------------------|-------------------|----------------------|----------------------|
| Herbage of thyme        | 74               | 5                 | 58                   | 11                   |
| seeds of flax           | 8                | 7                 | 1                    | 0                    |
| Roots of liquorice      | 3                | 3                 | 0                    | 0                    |
| Herbage of savory       | 3                | 3                 | 0                    | 0                    |
| Herbage of sage         | 2                | 2                 | 0                    | 0                    |
| Roots of valerian       | 2                | 1                 | 1                    | 0                    |
| Herbage of rock rose    | 2                | 2                 | 0                    | 0                    |
| Flowers of coneflower   | 2                | 1                 | 1                    | 0                    |
| Herbage of marjoram     | 1                | 1                 | 0                    | 0                    |
| Herbage of horsetail    | 1                | 1                 | 0                    | 0                    |
| Herbage of oregano      | 1                | 1                 | 0                    | 0                    |
| Herbage of basil        | 1                | 1                 | 0                    | 0                    |
| Flowers of camomile     | 1                | 1                 | 0                    | 0                    |
| Fruits of fennel        | 1                | 1                 | 0                    | 0                    |
| Fruits of caraway       | 1                | 0                 | 1                    | 0                    |
| Roots of lovage         | 1                | 0                 | 1                    | 0                    |

MRL—maximum residue level.

Co-occurrence of pesticide residues was noted in 48 samples of thyme herbage (64%) and in one sample of herbage of basil, flower of coneflower, fruit of caraway, flax seed, and root of valerian and lovage (1.3%) (Table 2). In the case of the analysed samples of herbal material the most-frequently-detected combination was that of a fungicide and a herbicide (azoxystrobin and linuron)—34 samples (45.3%), a combination of two fungicides and a herbicide (azoxystrobin, carbendazim and linuron)—detected in 16 samples (21.3%), and combinations of two fungicides with two herbicides (azoxystrobin, linuron, metalaxyl and metalaxyl M)—found in eight samples (10.7%). In seven of the analysed samples of herbal material (9.3%) the presence of a combination of two fungicides with three herbicides was detected (azoxystrobin, carbendazim, linuron, metalaxyl and metalaxyl M), while in three samples (4%)—the combination of a fungicide, a herbicide and an insecticide (azoxystrobin, linuron and dimethoate) was detected—Table 2.
Table 2. Pesticide residue concentrations in examined food samples.

| No. | Samples of Herb | Pesticide Residue | MRL (mg/kg) | LOQ (mg/kg) | Concentration (mg/kg) and Uncertainty | Rating |
|-----|-----------------|-------------------|-------------|-------------|--------------------------------------|--------|
| 1   | Herbage of thyme | Azoxystrobin      | 490.0       | 0.005       | 0.054 ± 0.011                        | <MRL   |
|     |                  | Carbendazim       | 0.7         | 0.002       | 0.26 ± 0.052                         |        |
|     |                  | Linuron           | 7.0         | 0.005       | 0.051 ± 0.016                        |        |
|     |                  | Metalaxyl         | 14.0 *      | 0.002       | 0.020 ± 0.006                        |        |
|     |                  | Metalaxyl M       |             |             | <LOQ = 0.002                         |        |
| 2   | Herbage of thyme | Azoxystrobin      | 2.0         | 0.005       | 0.068 ± 0.014                        | <MRL   |
|     |                  | Carbendazim       | 70.0        | 0.002       | 0.017 ± 0.005                        |        |
|     |                  | Linuron           | 0.1         | 0.005       | 0.032 ± 0.010                        |        |
|     |                  | Metalaxyl         | 1.0         | 0.002       | 0.032 ± 0.009                        |        |
|     |                  | Metalaxyl-M       | 2.0 *       | 0.002       | 0.031 ± 0.010                        |        |
|     |                  | Trifloxystrobin   | 15.0        | 0.002       | 0.020 ± 0.004                        |        |
| 3   | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.060 ± 0.012                        | <MRL   |
|     |                  | Linuron           | 1.0         | 0.005       | 0.023 ± 0.007                        |        |
|     |                  | Metalaxyl         | 2.0 *       | 0.002       | 0.026 ± 0.008                        |        |
|     |                  | Metalaxyl M       |             |             | <LOQ = 0.002                         |        |
| 4   | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.042 ± 0.008                        | <MRL   |
|     |                  | Linuron           | 1.0         | 0.005       | 0.019 ± 0.006                        |        |
|     |                  | Metalaxyl         | 2.0         | 0.002       | 0.022 ± 0.006                        |        |
|     |                  | Metalaxyl-M       | 2.0 *       | 0.002       | 0.019 ± 0.006                        |        |
|     |                  | Pyraclostrobin    |             |             | 0.088 ± 0.023                        |        |
| 5   | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.028 ± 0.006                        | <MRL   |
|     |                  | Linuron           | 1.0         | 0.005       | 0.010 ± 0.003                        |        |
|     |                  | Pyraclostrobin    | 2.0         | 0.002       | 0.21 ± 0.05                          |        |
| 6   | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.043 ± 0.009                        | <MRL   |
|     |                  | Linuron           | 1.0         | 0.005       | 0.051 ± 0.015                        |        |
|     |                  | Metalaxyl         | 2.0         | 0.02        | 0.15 ± 0.04                          |        |
|     |                  | Metalaxyl-M       | 2.0 *       | 0.002       | 0.14 ± 0.04                          |        |
| 7   | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.090 ± 0.018                        | <MRL   |
|     |                  | Linuron           | 1.0         | 0.005       | 0.018 ± 0.006                        |        |
| 8   | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.033 ± 0.007                        | <MRL   |
|     |                  | Linuron           | 1.0         | 0.005       | 0.029 ± 0.009                        |        |
|     |                  | Metalaxyl         | 2.0         | 0.02        | 0.034 ± 0.010                        |        |
|     |                  | Metalaxyl-M       | 2.0 *       | 0.002       | 0.030 ± 0.009                        |        |
| 9   | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.056 ± 0.011                        | <MRL   |
|     |                  | Carbendazim       |             |             | 0.68 ± 0.080                         | <MRL   |
|     |                  | Dimethoate        | 0.02        | 0.002       | 0.020 ± 0.006                        | <MRL   |
|     |                  | Linuron           | 1.0         | 0.005       | 0.013 ± 0.004                        | <MRL   |
| 10  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.12 ± 0.02                          | <MRL   |
|     |                  | Carbendazim       | 0.1         | 0.002       | 0.051 ± 0.015                        | <MRL   |
|     |                  | Linuron           | 1.0         | 0.005       | 0.014 ± 0.004                        | <MRL   |
| 11  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.19 ± 0.04                          | <MRL   |
|     |                  | Isoproturon       | 0.05        | 0.002       | 0.19 ± 0.05                          | <MRL   |
| 12  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.062 ± 0.012                        | <MRL   |
|     |                  | Carbendazim       | 0.1         | 0.002       | 0.066 ± 0.020                        | <MRL   |
| 13  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.18 ± 0.04                          | <MRL   |
| 14  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.051 ± 0.010                        | <MRL   |
| 15  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.061 ± 0.012                        | <MRL   |
|     |                  | Linuron           | 1.0         | 0.005       | 0.028 ± 0.009                        | <MRL   |
| No. | Samples of Herb | Pesticide Residue | MRL (mg/kg) | LOQ (mg/kg) | Concentration (mg/kg) and Uncertainty | Rating |
|-----|-----------------|-------------------|-------------|-------------|---------------------------------------|--------|
| 16  | Herbage of thyme | Azoxystrobin      | 70          | 0.002       | 0.083 ± 0.017                         | <MRL   |
|     |                 | Carbendazim       | 0.1         | 0.005       | 0.019 ± 0.006                         | >MRL   |
|     |                 | Linuron           | 1.0         | 0.002       | 0.021 ± 0.006                         | >MRL   |
|     |                 | Metalaxyl         | 2.0 *       | 0.002       | 0.018 ± 0.006                         | <MRL   |
| 17  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.045 ± 0.009                         | <MRL   |
|     |                 | Carbendazim       | 0.1         | 0.005       | 0.022 ± 0.007                         | >MRL   |
|     |                 | Linuron           | 1.0         | 0.002       | 0.093 ± 0.027                         | >MRL   |
|     |                 | Metalaxyl         | 2.0 *       | 0.002       | 0.085 ± 0.026                         | <MRL   |
| 18  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.044 ± 0.009                         | <MRL   |
|     |                 | Carbendazim       | 0.1         | 0.002       | 0.076 ± 0.023                         | >MRL   |
| 19  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.17 ± 0.03                           | <MRL   |
|     |                 | Flutriafol        | 0.02        | 0.002       | 0.20 ± 0.05                           | <MRL   |
| 20  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.061 ± 0.012                         | <MRL   |
|     |                 | Metalaxyl         | 2.0 *       | 0.002       | 0.045 ± 0.013                         | <MRL   |
|     |                 | Metalaxyl-M       | 2.0 *       | 0.002       | 0.046 ± 0.014                         | <MRL   |
| 21  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.11 ± 0.02                           | <MRL   |
|     |                 | Linuron           | 1.0         | 0.005       | 0.019 ± 0.006                         | <MRL   |
| 22  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.041 ± 0.008                         | <MRL   |
|     |                 | Carbendazim       | 0.1         | 0.002       | 0.37 ± 0.070                          | >MRL   |
| 23  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.11 ± 0.02                           | <MRL   |
| 24  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.11 ± 0.02                           | <MRL   |
|     |                 | Carbendazim       | 0.1         | 0.002       | 1.7 ± 0.25                            | >MRL   |
|     |                 | Chlorotoluron     | 0.02        | 0.002       | 0.041 ± 0.010                         | >MRL   |
| 25  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.039 ± 0.008                         | <MRL   |
|     |                 | Carbendazim       | 0.1         | 0.002       | 0.92 ± 0.15                           | >MRL   |
|     |                 | Linuron           | 1.0         | 0.005       | 0.027 ± 0.008                         | <MRL   |
| 26  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.062 ± 0.012                         | <MRL   |
|     |                 | Linuron           | 1.0         | 0.005       | 0.013 ± 0.004                         | <MRL   |
|     |                 | Metalaxyl         | 2.0 *       | 0.002       | 0.022 ± 0.006                         | <MRL   |
|     |                 | Metalaxyl-M       | 2.0 *       | 0.002       | 0.020 ± 0.006                         | <MRL   |
| 27  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.052 ± 0.010                         | <MRL   |
| 28  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.042 ± 0.008                         | <MRL   |
|     |                 | Carbendazim       | 0.1         | 0.002       | 0.077 ± 0.02                          | >MRL   |
|     |                 | Metalaxyl         | 2.0 *       | 0.002       | 30.030 ± 0.009                        | >MRL   |
|     |                 | Metalaxyl-M       | 2.0 *       | 0.002       | 0.026 ± 0.008                         | >MRL   |
| 29  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.11 ± 0.02                           | <MRL   |
|     |                 | Dimethoate        | 0.02        | 0.002       | 0.010 ± 0.003                         | <MRL   |
|     |                 | Linuron           | 1.0         | 0.005       | 0.019 ± 0.006                         | <MRL   |
|     |                 | Pirimiphos methyl | 0.02        | 0.002       | 0.042 ± 0.012                         | <MRL   |
| 30  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.042 ± 0.008                         | <MRL   |
|     |                 | Carbendazim       | 0.1         | 0.002       | 0.89 ± 0.10                           | >MRL   |
|     |                 | Linuron           | 1.0         | 0.005       | 0.046 ± 0.014                         | >MRL   |
| 31  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.019 ± 0.004                         | <MRL   |
|     |                 | Carbendazim       | 0.1         | 0.002       | 0.063 ± 0.019                         | >MRL   |
|     |                 | Chlorotoluron     | 0.02        | 0.002       | 0.048 ± 0.012                         | >MRL   |
|     |                 | Linuron           | 1.0         | 0.005       | 0.019 ± 0.006                         | >MRL   |
| 32  | Herbage of thyme | Azoxystrobin      | 70.0        | 0.005       | 0.053 ± 0.011                         | <MRL   |
|     |                 | Carbendazim       | 0.1         | 0.002       | 0.14 ± 0.04                           | >MRL   |
|     |                 | Dimethoate        | 0.02        | 0.002       | 0.21 ± 0.05                           | >MRL   |
|     |                 | Linuron           | 1.0         | 0.005       | 0.033 ± 0.010                         | <MRL   |
| No. | Samples of Herb | Pesticide Residue | MRL (mg/kg) | LOQ (mg/kg) | Concentration (mg/kg) and Uncertainty | Rating |
|-----|----------------|-------------------|-------------|-------------|--------------------------------------|--------|
| 33  | Herbage of thyme | Azoxystrobin     | 70.0        | 0.005       | 0.15 ± 0.03                          | <MRL   |
|     |                 | Linuron           | 1.0         | 0.002       | 0.018 ± 0.006                       | >MRL   |
|     |                 | Flutriafol        | 0.02        | 0.002       | 0.10 ± 0.03                         | >MRL   |
|     |                 | Metalaxyl         | 2.0 *       | 0.002       | 0.11 ± 0.03                         | >MRL   |
|     |                 | Metalaxyl-M       |             |             | 0.10 ± 0.03                         | >MRL   |
| 34  | Herbage of thyme | Azoxystrobin     | 70.0        | 0.005       | 0.17 ± 0.03                          | <MRL   |
|     |                 | Linuron           | 1.0         | 0.002       | 0.022 ± 0.007                       | <MRL   |
|     |                 | Trifloxystrobin   | 15.0        | 0.002       | 0.018 ± 0.004                       | <MRL   |
| 35  | Herbage of thyme | Azoxystrobin     | 70.0        | 0.005       | 0.097 ± 0.019                       | <MRL   |
|     |                 | Linuron           | 1.0         | 0.002       | 0.011 ± 0.003                       | <MRL   |
|     |                 | Metalaxyl         | 2.0 *       | 0.002       | 0.018 ± 0.005                       | <MRL   |
| 36  | Herbage of thyme | -                 | -           | -           | -                                    |        |
| 37  | Herbage of thyme | -                 | -           | -           | -                                    |        |
| 38  | Herbage of thyme | Atoxystrobin     | 490.0       | 0.005       | 0.026 ± 0.005                       | <MRL   |
|     |                 | Acetamiprid       | 21.0        | 0.002       | 0.082 ± 0.016                       | <MRL   |
|     |                 | Carbendazim       | 0.7         | 0.002       | 0.31 ± 0.064                        | <MRL   |
|     |                 | Linuron           | 7.0         | 0.005       | 0.037 ± 0.012                       | <MRL   |
| 39  | Herbage of thyme | Atoxystrobin     | 490.0       | 0.005       | 0.082 ± 0.016                       | <MRL   |
|     |                 | Linuron           | 7.0         | 0.005       | 0.023 ± 0.007                       | <MRL   |
| 40  | Herbage of thyme | Atoxystrobin     | 490.0       | 0.005       | 0.094 ± 0.019                       | <MRL   |
| 41  | Herbage of thyme | Atoxystrobin     | 490.0       | 0.005       | 0.072 ± 0.014                       | <MRL   |
|     |                 | Linuron           | 7.0         | 0.005       | 0.069 ± 0.021                       | <MRL   |
| 42  | Herbage of thyme | Atoxystrobin     | 490.0       | 0.005       | 0.18 ± 0.04                         | <MRL   |
| 43  | Herbage of thyme | Atoxystrobin     | 490.0       | 0.005       | 0.053 ± 0.011                       | <MRL   |
|     |                 | Carbendazim       | 0.7         | 0.002       | 0.13 ± 0.04                         | <MRL   |
|     |                 | Linuron           | 7.0         | 0.005       | 0.020 ± 0.006                       | <MRL   |
| 44  | Herbage of thyme | Atoxystrobin     | 490.0       | 0.005       | 0.040 ± 0.008                       | <MRL   |
|     |                 | Linuron           | 7.0         | 0.005       | 0.016 ± 0.005                       | <MRL   |
| 45  | Herbage of thyme | Atoxystrobin     | 490.0       | 0.005       | 0.15 ± 0.03                         | <MRL   |
| 46  | Herbage of thyme | Atoxystrobin     | 490.0       | 0.005       | 0.27 ± 0.05                         | <MRL   |
|     |                 | Pirimiphos methyl| 0.14        | 0.002       | 0.019 ± 0.005                       | <MRL   |
| 47  | Herbage of thyme | Atoxystrobin     | 490.0       | 0.005       | 0.047 ± 0.009                       | <MRL   |
|     |                 | Linuron           | 7.0         | 0.005       | 0.012 ± 0.004                       | <MRL   |
| 48  | Herbage of thyme | Linuron           | 7.0         | 0.005       | 0.045 ± 0.014                       | <MRL   |
| 49  | Herbage of thyme | Atoxystrobin     | 490.0       | 0.005       | 0.057 ± 0.011                       | <MRL   |
|     |                 | Carbendazim       | 0.7         | 0.002       | 0.67 ± 0.09                         | <MRL   |
|     |                 | Linuron           | 7.0         | 0.005       | 0.053 ± 0.016                       | <MRL   |
|     |                 | Metalaxyl         | 2.0 *       | 0.002       | 0.41 ± 0.08                         | <MRL   |
|     |                 | Metalaxyl-M       |             | 0.0002      | 0.39 ± 0.08                         | <MRL   |
| 50  | Herbage of thyme | Atoxystrobin     | 490.0       | 0.005       | 0.038 ± 0.008                       | <MRL   |
| 51  | Herbage of thyme | Atoxystrobin     | 490.0       | 0.005       | 0.095 ± 0.019                       | <MRL   |
|     |                 | Carbendazim       | 0.7         | 0.002       | 0.15 ± 0.05                         | <MRL   |
|     |                 | Linuron           | 7.0         | 0.005       | 0.033 ± 0.010                       | <MRL   |
|     |                 | Metalaxyl         | 2.0 *       | 0.002       | 0.11 ± 0.03                         | <MRL   |
|     |                 | Metalaxyl-M       |             | 0.002       | 0.096 ± 0.030                       | <MRL   |
| 52  | Herbage of thyme | Atoxystrobin     | 490.0       | 0.005       | 0.020 ± 0.004                       | <MRL   |
Table 2. Cont.

| No. | Samples of Herb | Pesticide Residue | MRL (mg/kg) | LOQ (mg/kg) | Concentration (mg/kg) and Uncertainty | Rating |
|-----|----------------|-------------------|-------------|-------------|---------------------------------------|--------|
| 53  | Herbage of thyme | Azoxystrobin | 490.0 | 0.005 | 0.056 ± 0.011 | <MRL |
|     |                 | Chlorotoluron | 0.14 | 0.002 | 0.034 ± 0.008 | |
|     |                 | Linuron | 7.0 | 0.005 | 0.017 ± 0.005 | |
|     |                 | Metalaxyl | 2.0 * | 0.002 | 0.055 ± 0.016 | |
|     |                 | Metalaxyl-M |          | 0.002 | 0.047 ± 0.015 | |
| 54  | Herbage of thyme | Azoxystrobin | 490.0 | 0.005 | 0.024 ± 0.005 | <MRL |
| 55  | Herbage of thyme | Azoxystrobin | 490.0 | 0.005 | 0.089 ± 0.018 | <MRL |
|     |                 | Carbendazim | 0.7 | 0.002 | 0.19 ± 0.06 | |
|     |                 | Linuron | 7.0 | 0.005 | 0.027 ± 0.008 | |
|     |                 | Metalaxyl | 2.0 * | 0.002 | 0.047 ± 0.014 | |
|     |                 | Metalaxyl-M |          | 0.002 | 0.043 ± 0.013 | |
| 56  | Herbage of thyme | Metalaxyl | 2.0 * | 0.002 | 0.012 ± 0.003 | <MRL |
|     |                 | Metalaxyl-M |          | 0.002 | <LOQ = 0.002 | |
| 57  | Herbage of thyme | Carbendazim | 0.7 | 0.002 | 0.41 ± 0.08 | <MRL |
| 58  | Herbage of thyme | Azoxystrobin | 490.0 | 0.005 | 0.092 ± 0.018 | <MRL |
| 59  | Herbage of thyme | Carbendazim | 0.7 | 0.002 | 0.23 ± 0.07 | <MRL |
| 60  | Herbage of thyme | Azoxystrobin | 490.0 | 0.005 | 0.047 ± 0.009 | <MRL |
| 61  | Herbage of thyme | Carbendazim | 0.7 | 0.002 | 0.61 ± 0.09 | <MRL |
| 62  | Herbage of thyme | Dimethoate | 0.14 | 0.002 | 0.054 ± 0.014 | <MRL |
| 63  | Herbage of thyme | Carbendazim | 0.7 | 0.002 | 0.071 ± 0.02 | <MRL |
|     |                 | Metalaxyl | 2.0 * | 0.002 | 0.41 ± 0.08 | |
|     |                 | Metalaxyl-M |          | 0.002 | 0.39 ± 0.08 | |
| 64  | Herbage of thyme | Azoxystrobin | 490.0 | 0.005 | 0.061 ± 0.012 | <MRL |
|     |                 | Dimethoate | 0.14 | 0.002 | 0.051 ± 0.013 | |
| 65  | Herbage of thyme | Azoxystrobin | 490.0 | 0.005 | 0.080 ± 0.016 | <MRL |
| 66  | Herbage of thyme | Carbendazim | 0.7 | 0.002 | 0.62 ± 0.09 | <MRL |
| 67  | Herbage of thyme | Azoxystrobin | 490.0 | 0.005 | 0.011 ± 0.002 | <MRL |
|     |                 | Linuron | 7.0 | 0.005 | 0.055 ± 0.017 | |
| 68  | Herbage of thyme | Carbendazim | 0.7 | 0.002 | 0.67 ± 0.09 | <MRL |
| 69  | Herbage of thyme | Carbendazim | 0.7 | 0.002 | 0.56 | <MRL |
|     |                 | Linuron | 7.0 | 0.005 | 0.18 ± 0.06 | |
|     |                 | Metalaxyl | 2.0 * | 0.002 | 0.37 ± 0.07 | |
|     |                 | Metalaxyl-M |          | 0.002 | 0.35 ± 0.07 | |
| 70  | Herbage of thyme | Carbendazim | 0.7 | 0.002 | 0.53 ± 0.07 | <MRL |
|     |                 | Metalaxyl | 2.0 * | 0.002 | 0.22 ± 0.06 | |
|     |                 | Metalaxyl-M |          | 0.002 | 0.22 ± 0.07 | |
| 71  | Herbage of thyme | Linuron | 7.0 | 0.005 | 0.09 ± 0.03 | <MRL |
| 72  | Herbage of thyme | - | - | - | - | |
| 73  | Herbage of thyme | - | - | - | - | |
| 74  | Herbage of thyme | - | - | - | - | |
| 75  | Herbage of savory | - | - | - | - | |
| 76  | Herbage of savory | - | - | - | - | |
| 77  | Herbage of savory | - | - | - | - | |
| 78  | Herbage of sage | - | - | - | - | |
| 79  | Herbage of sage | - | - | - | - | |
| 80  | Herbage of rock rose | - | - | - | - | |
Table 2. Cont.

| No. | Samples of Herb | Pesticide Residue | MRL (mg/kg) | LOQ (mg/kg) | Concentration (mg/kg) and Uncertainty | Rating |
|-----|----------------|-------------------|-------------|-------------|---------------------------------------|--------|
| 81  | Herbage of rock rose | -                  | -           | -           | -                                     | -      |
| 82  | Herbage of marjoram  | -                  | -           | -           | -                                     | -      |
| 83  | Herbage of horsetail | -                  | -           | -           | -                                     | -      |
| 84  | Herbage of oregano   | -                  | -           | -           | -                                     | -      |
| 85  | Herbage of basil     | Carbendazim        | 0.1         | 0.002       | 0.35 ± 0.06                           | >MRL   |
|     |                 | Metalaxyl          | 2.0 *       | 0.002       | 0.060 ± 0.017                         | >MRL   |
|     |                 | Metalaxyl-M        | 0.002       | 0.002       | 0.056 ± 0.017                         | >MRL   |
| 86  | Flowers of camomile  | -                  | -           | -           | -                                     | -      |
| 87  | Flowers of coneflower| -                  | -           | -           | -                                     | -      |
| 88  | Flowers of coneflower| Azoxystrobin       | 70          | 0.005       | 0.022 ± 0.004                         | <MRL   |
|     |                 | Fludioxonil        | 15          | 0.0001      | 0.27 ± 0.10                           | <MRL   |
| 89  | Fruits of fennel     | -                  | -           | -           | -                                     | -      |
| 90  | Fruits of caraway    | Imazalil           | 1.0         | 0.002       | 0.091 ± 0.018                         | <MRL   |
|     |                 | Tebuconazole       | 1.5         | 0.005       | 0.061 ± 0.016                         | <MRL   |
| 91  | Seeds of flax       | -                  | -           | -           | -                                     | -      |
| 92  | Seeds of flax       | -                  | -           | -           | -                                     | -      |
| 93  | Seeds of flax       | -                  | -           | -           | -                                     | -      |
| 94  | Seeds of flax       | -                  | -           | -           | -                                     | -      |
| 95  | Seeds of flax       | -                  | -           | -           | -                                     | -      |
| 96  | Seeds of flax       | -                  | -           | -           | -                                     | -      |
| 97  | Seeds of flax       | Imidacloprid       | 0.081       | 0.005       | 0.05 ± 0.02                           | <MRL   |
| 98  | Seeds of flax       | -                  | -           | -           | -                                     | -      |
| 99  | Roots of liquorice  | -                  | -           | -           | -                                     | -      |
| 100 | Roots of liquorice  | -                  | -           | -           | -                                     | -      |
| 101 | Roots of liquorice  | -                  | -           | -           | -                                     | -      |
| 102 | Roots of valerian   | -                  | -           | -           | -                                     | -      |
| 103 | Roots of valerian   | Azoxystrobin       | 0.3         | 0.005       | 0.026 ± 0.005                         | <MRL   |
| 104 | Roots of lovage     | Linuron            | 1.0         | 0.005       | 0.02 ± 0.01                           | <MRL   |

MRL—maximum residue level; LOQ—the limit of quantification; * sum of metalaxyl and metalaxyl-M.

In the analysed samples the presence of residues of a total of 16 pesticides was detected. The most-frequently identified ones were azoxystrobin—detected in 59 samples (78.7%), linuron—assayed in 36 samples (48%), carbendazim—detected in 29 samples (38.7%), metalaxyl and metalaxyl M—found in 21 samples (28%) and dimethoate—detected in five samples (6.7%). The frequency of occurrence of the detected pesticides is presented in Figure 2. From among 250 compounds sought in the presented...
experiment, the presence of 16 pesticides (6.4%) was detected in the analysed samples, which means that no presence of 234 pesticides from the examined group of plant protection agents was found.

In 11 analysed samples of thyme herbage the maximum allowable concentration levels were exceeded for five identified active substances— isoproturon (assayed value of 0.19 mg/kg at maximum residue level (MRL)—0.05 mg/kg), carbeddazim (assayed values of 0.68; 0.52; 0.30; 0.37; 1.7; 0.92; 0.89 and 0.14 mg/kg at MRL—0.1 mg/kg), chlorotoluron (assayed values of 0.041 and 0.048 mg/kg at MRL—0.02 mg/kg), dimethoate (assayed value of 0.21 mg/kg at MRL—0.02 mg/kg) and flutriafol (assayed value of 0.10 mg/kg at MRL—0.02 mg/kg)—Table 2.

In the presented study the percentage of samples of herbal material containing pesticide residues (72%) correlates with results obtained by other authors (Table 3). In a study on fresh herbs and vegetables purchased at local supermarkets it was demonstrated that 91.7% of the samples contained residues of active substances.

In a monitoring study on Chinese medicines prepared on the base of herbal materials [21–24] showed that from 72.8% to 97.5% of the analysed samples contained at least one pesticide, while in later reports [25–28] from 36.73% to 100% of the analysed samples of herbs contained residues of active substances.

4. Discussion

In the presented study the percentage of samples of herbal material containing pesticide residues (72%) correlates with results obtained by other authors (Table 3). In a study on fresh herbs and vegetables purchased at local supermarkets it was demonstrated that 91.7% of the samples contained residues of plant protection agents [14]. In a monitoring study on Egyptian herbs, vegetables and fruits in the aspect of the content of identified substances [16], pesticide residues were found in 73% of the analysed samples, while in a later study, in 54.55% of all analysed samples [17]. The results of this study find support also in another study on the estimation of the content of pesticide residues in samples of herbs and spices, in which their authors noted the presence of contaminants in 59% of the samples [18]. Similar results concerning the content of contaminants in samples of herbs were obtained by Siméon et al. [19] in a study on herbal material used in animal feeds, and also by Di Bella et al. [20] in a study on Italian and Tunisian herbs, in which contamination with those substances was at the level of 63% and 55% of the analysed samples, respectively. Analysis of pesticide residues in Chinese medicines prepared on the base of herbal materials [21–24] showed that from 72.8% to 97.5% of the analysed samples contained at least one pesticide, while in later reports [25–28] from 36.73% to 100% of the analysed samples of herbs contained residues of active substances.
The number of detected pesticide residues in the presented study varied from one to six compounds in a single sample—Table 2. The highest percentage was that of samples containing from one to two identified compounds, at 32% and 24%, respectively, while a significantly smaller number of samples were found in the group containing from three to five pesticide residues—12% to 16%, with a single sample representing the presence of six active compounds. The results of the presented study support earlier reports on research on herbs, in which the numbers of compounds detected in individual samples varied from one to nine [17,25]. In the study on Egyptian herbs, fruits and vegetables, 43.18% of the samples were contaminated with residues of one substance, 6.06% with residues of two pesticides, and 5.3% with residues of more than two contaminants. Among the analysed samples of herbs, three samples contained residues of four pesticides, and one sample of marjoram, residues of five different active substances [17].

Among the 74 samples of thyme analysed in this study, only five of them (27.88%) did not contain any residues of plant protection agents. The remaining 69 analysed samples (93.24%) contained pesticides, which is in support of the studies by Reinhold et al. [18] and by Di Bella et al. [20], who demonstrated similar levels of pesticide residues in the analysed samples of that herbal species, at 82% and 50%, respectively. In our study, the compounds identified most frequently in the analysed samples of thyme were azoxystrobin, linuron, carbendazim, metalaxyl and metalaxyl M, and dimethoate, while in the studies by other authors, cymoxanil, dimethoate and tebuconazole [18,29].

Azoxystrobin, so often identified in the presented studies, is a systemic fungicide commonly used in agriculture. It is a broad-spectrum substance, protecting plants against fungal diseases (Oomycetes, Ascomycetes, Basidiomycetes and Deuteromycetes). Its fungicidal activity results from the inhibition of mitochondrial respiration in fungi. This is achieved by the prevention of electron transfer between cytochrome b and cytochrome c. Because of its novel mode of action, azoxystrobin is effective against pathogens which have developed reduced sensitivity to other fungicides [30]. Linuron is a herbicide from the group of urea derivatives. It is characterized by soil action and is recommended for controlling dicotyledonous weeds. Linuron penetrates into the plant mainly through the roots and to a lesser extent through the leaves. It moves in xylem and causes disturbances of photosynthesis [31]. Linuron was withdrawn from use in 2018.

Numerical data contained in research reports concerning the observed presence of various pesticide residues in herbal samples is presented in Figure 3. Analysing the frequency of occurrence of the particular active substances in the analysed group of herbs, the most-frequently-detected pesticides were: hexachlorobenzene (16%), chlorpyrifos (16%), quintozene, (12%), carbendazim (12%), malathion (12%), dimethoate (8%), tebuconazole (8%), profenos (8%), benzene hexachloride—α-BHC (8%) and pentachloronitrobenzene—PCNB (8%). Two of those—carbendazim and dimethoate—were also among the most-frequently-identified pesticides in the presented study—Figure 2.

In the group of analysed herbal samples, the sought compounds were detected most frequently in samples of thyme (66.34%). In the group of 69 analysed samples of that material, in which the presence of pesticide residues was identified, in 11 samples (15.9%) the maximum allowable residue concentration levels were exceeded. This confirms the results of a study by Reinholds et al. [18], in which the concentrations of pesticide residues in 10% of samples of oregano and in 46% of samples of thyme were above the allowable levels. The results of the presented study are in conformance with earlier reports on studies on herbs, in which the percentage of samples with exceeded maximum permitted concentration of pesticide residues varied from 6% to 18% [14,16,19,21,24].
Table 3. Summary of the most-frequently-detected pesticides in different herbs samples reported in the literature.

| No. | Type of Sample                          | Number of Samples | Number of Samples with Detected Residues | Number of Analysed Pesticides | No. of Detected Pesticides | Most Frequently-Found Pesticide | % (1) | % (2) | References |
|-----|----------------------------------------|-------------------|-----------------------------------------|-------------------------------|---------------------------|---------------------------------|-------|-------|------------|
| 1   | Herbs                                  | 300               | 177                                     | 134                          | 24                        | Cymoksanyl Dimetoat              | 59.00 | 17.91 | [18]       |
|     |                                        |                   |                                         |                              |                           | Tebukonazol Tetrakonazol Chlorpyrifos |      |       |            |
| 2   | Herbal raw materials in feed           | 92                | 58                                      | Not defined                  | 47                        | Cypermethrin Carbendazim         | 63.00 | Not defined | [19]       |
| 3   | Italian and Tunisian herbs             | 80                | 47                                      | 140                          | 50                        | Alachlor Metalaxy M              | 58.75 | 35.71 | [20]       |
| 4   | Chinese herbal medicines               | 294               | 108                                     | 162                          | 42                        | Chlorpyrifos                     | 36.73 | 25.93 | [25]       |
| 5   | Egyptian herbs and spices              | 303               | Not defined                             | 22                           | 18                        | Malathion Dimetoat               | Not defined | 81.82 | [30]       |
| 6   | Egyptian herbs, vegetables and fruits  | 132               | 72                                      | 241                          | 17                        | Malathion Carbendazim            | 54.55 | 7.05  | [17]       |
| 7   | Chinese herbal medicines               | 132               | 74                                      | 103                          | 51                        | Hexsachlorobenzene Quinozene     | 56.06 | 49.51 | [27]       |
| 8   | Egyptian herbs                         | 391               | 286                                     | 26                           | 12                        | Malathion Profenofos             | 73.00 | 46.15 | [16]       |
| 9   | Chinese herbal medicines               | 92                | 67                                      | 18                           | 13                        | Benzene hexachloride (α-BHC)     | 72.80 | 72.2  | [24]       |
|     |                                        |                   |                                         |                              |                           | Pentachloronitrobenzene (PCNB)   |       |       |            |
| 10  | Chinese herbal medicines               | 40                | 30                                      | 20                           | 5                         | Hexsachlorobenzene Quinozene     | 75.00 | 25.00 | [21]       |
| 11  | Chinese herbal medicines               | 280               | 212                                     | 18                           | 13                        | Benzene hexachloride (α-BHC)     | 75.80 | 72.20 | [24]       |
| 12  | Herbs                                  | 30                | 2/3                                     | 155                          | 3                         | Diphenyloamine Tebukonazol       | 6.67-10.00 | 1.94  | [13]       |
Table 3. Cont.

| No. | Type of Sample                  | Number of Samples | Number of Samples with Detected Residues | Number of Analysed Pesticides | No. of Detected Pesticides | Most Frequently-Found Pesticide | % (1)  | % (2)  | References |
|-----|--------------------------------|-------------------|-----------------------------------------|------------------------------|----------------------------|---------------------------------|--------|--------|-----------|
| 13  | Plant used in traditional Chinese medicine | 138               | 95                                      | 116                          | 55                         | Carbendazim, Carbofuran         | 68.84  | 47.41  | [28]      |
| 14  | Traditional Chinese medicine    | 20                | 20                                      | 55                           | 6                          | Quintozene, Chlorothalonil, Chlorpyrifos | 100.00 | 10.91  | [26]      |
| 15  | Herbs                          | 12                | 11                                      | Not defined                   | 18                         | Azoxystrobin, Difenoconazole, α-Hexachlorocyclohexane, γ-Hexachlorocyclohexane, γ-HCH | 91.70  | Not defined | [14] |
| 16  | Herbal medicines               | 40                | 39                                      | 7                            | 6                          | α-HCH, γ-HCH                     | 97.50  | 85.71  | [23]      |

(1) The percentage of total number of analysed samples in the total number of detected pesticides. (2) The percentage of detected pesticides in the total number of pesticides analysed.
where the percentage of samples containing the sought compounds was at the level of approximately 20%. Special attention should be paid to possible contamination of analysed samples with azoxystrobin, linuron and carbendazim. Analysed samples of thyme contained the largest number and diversity of identified pesticide residues, compared to the remaining samples, which raises concern about the quality of those food components. The results of the study emphasise the importance of monitoring of pesticide residues in herbs, especially in the case of thyme which was identified as the most contaminated matrices in that group of products. The percentage share of samples containing pesticide residues in thyme was decidedly at the highest level.

5. Conclusions

In relation to the growing importance of the use of herbal plants in various domains of human life, studies in the area of analysis of pesticide residues play a significant role in the estimation of quality of that raw material. The results obtained indicate that the occurrence of pesticide residues in the analysed products from Polish cultivations cannot be considered a serious threat to human and animal health. However, the observed instances of exceeded maximum allowable concentrations of the residues in a small number of samples indicate the necessity of permanent monitoring of the content of pesticide residues in herbal matrices. To ensure high quality of food and safety of consumer health, efforts should also be aimed at the implementation of strict regulations concerning the maximum allowable concentrations of those compounds that are of key importance, with a view to the reduction of potential risk involved in the use of herbal products.

Figure 3. The most-frequently-detected compounds in fruit and vegetable samples (see literature reports in Table 3).
Recently, organic farming has been proposed in the cultivation of herbs. It involves the use of crop rotation and appropriate cultivation techniques and selection of resistant species and varieties. Organic farming rules exclude the possibility of using synthetic pesticides. Therefore, monitoring research may be relevant to determine how trends in herb production change. In conventional cultivation, pesticide residues in herbs are also determined by improper use by farmers (use of excessive amounts and non-compliance with waiting periods). Unfortunately, available studies indicate that MRLs were exceeded in herbs from conventional crops. In addition, the problem of using plant protection products not authorized in Poland is also noticeable. Therefore, research into the assessment of pesticide residues is of particular importance for improving the quality of herbal products.

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