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Abstract: The concentrations of pesticide residues were determined in 2,164 samples of 46 fruits species, collected over a 4-year period. Fruits originated from 59 countries, including Serbia (N = 199). Pesticide residues were determined by the liquid chromatography tandem mass spectrometry (LC-MS/MS) after extraction by a modified QuEChERS protocol. A total of 173 pesticide residues were detected. 62.57% of fruit samples had pesticide residues at or above 0.01 mg/kg, and 4.67% of samples exceeded the maximum residue limits (MRLs) set by the Serbian regulation. MRL values were most often exceeded in pomegranate and citrus fruits (grapefruit and mandarin). Most frequently found pesticide was imazalil (detected in 624 samples, 28.84%) with the highest concentration (93.870 mg/kg) in a grapefruit sample. Multiple pesticides were detected in 50.92% of the fruit samples, and two grapefruit samples contained up to 44 pesticide residues.

Keywords: fruits; pesticide residues; maximum residue levels; food safety

1. Introduction

Pesticides play a significant role in food production. They protect or increase yields and may increase the number of times each year a crop can be grown on the same land. Pesticides are used to protect crops against insects, weeds, fungi and other pests. Since they are designed to be biologically active, pesticides are potentially toxic to humans and can have both acute and chronic health effects, depending on the quantity and ways in which a person is exposed [1]. For this reason, pesticide residue levels in food are regulated by national and European legislation. These comprehensive legislative frameworks define rules for the approval of active substances, their uses in plant protection products and their permissible residues in food. To ensure a high level of consumer protection, legal limits, or so-called 'maximum residue levels' (MRLs) are established in Regulation (EC) No 396/2005 [2]. European Union harmonized MRLs are set for more than 1,300 pesticides covering 378 food products/food groups [3]. This regulation is being continuously amended by several Regulations and Commission Regulations to update the commodities included and their residue levels, based on the most recent knowledge from the Member States, EFSA and the Commission. In Serbia, Regulation on the ''maximum residue levels of pesticides in food'' have changed few times over the past 10 years [4–6], with the aim of aligning the national legislation with the EU regulation. The latest Serbian Regulation [7] on the ''maximum residue levels of pesticides in food'' is fully harmonized with the European Union Regulations.

There have been many surveys of pesticide residues in fruits/food recently [3,8–18]. Summary of the studies published in available literature dealing with pesticide residues in fruit (from 2010 onwards) are presented in Supplementary material 1 Table S1. The overall conclusion of these studies

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is that there is a widespread pesticide presence currently in fruits/food in general. The pesticides are frequently detected above the LOQ, however MRL is seldom exceeded. And some of the pesticide residues were detected with concentrations above their MRL. Also, pesticides that are found in these studies are banned and/or unauthorized in many countries because of their high toxicity. Therefore, pesticide residues control is an important activity intended to prevent, reduce or eliminate the chemical hazard in food.

The objective of this study was to investigate the concentrations of pesticide residues in fruits (Table 1), which are collected as a part of the national monitoring program for pesticide residues in Serbia and to compare these levels with maximum residue levels established by the Serbian Regulation [4,5].

2. Materials and Methods

Over 4-year period, concentrations of pesticide residues were determined in 2,164 samples of fresh fruits (Table 1). The analyses were conducted by an accredited state laboratory (A BIO TECH LAB). The method for sample preparation and analysis of the concentrations of pesticide residues in the collected fresh fruits was conducted as described in detail in Kecojević et al. [19]. A total of 173 (Table 2) pesticide residues were detected in these 2,164 samples. The limit of quantitation (LOQ) for all pesticide residues was 0.005 mg/kg (LOQ for cabbage, Kecojević et al. [19]), while reporting limit (RL) was 0.01 mg/kg. Generally, Serbian as well as EU MRLs for pesticide residues in fruits are in the range of 0.01–10 mg/kg, depending on the compound. Only for a few pesticides MRLs are up to 15 and 20 mg/kg. The results were evaluated according to the RL and MRLs that have been established by Serbian regulation.

Table 1. Characteristics of the analysed fruit samples and number of fruit samples without and with pesticide residues.

Name of the fruit samples	Country of origin	No. of samples	No. of samples without residues (< 0.01 mg/kg)	%	No. of samples with residues at or above the 0.01 mg/kg	%	No. of samples with residues above the MRL	%
Almond	Spain (N = 4), United States of America (N = 1)	6	5	83.33	1	16.67	0	0
Apple	Albania (N = 11), Austria (N = 3), Bosnia and Herzegovina (N = 3), Bulgaria (N = 1), Chile (N = 1), Croatia (N = 13), France (N = 1), Greece (N = 4), Hungary (N = 3), Italy (N = 32), North Macedonia (N = 12), Poland (N = 171), Serbia (N = 88), Slovenia (N = 2), The Netherlands (N = 4), Turkey (N = 2)	351	126	35.90	225	64.10	12	3.42
Apricot	Bulgaria (N = 1), Greece (N = 4), Italy (N = 2), Serbia (N = 6), Spain (N = 2)	15	10	66.67	5	33.33	0	0
Aronia	Serbia (N = 1)	1	1	100	0	0	0	0
Avocado	Chile (N = 1), Colombia (N = 2), Israel (N = 1), Kenya (N =	19	12	63.16	7	36.84	1	5.26

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	4), Peru (N = 6), South Africa (N = 1), Tanzania (N = 2), Turkey (N = 1), Zimbabwe (N = 1)							
Banana	Brazil (N = 2), Colombia (N = 41), Costa Rica (N = 35), Dominican Republic (N = 1), Ecuador (N = 47), Ghana (N = 1), Guatemala (N = 8), Honduras (N = 7), Italy (N = 1), Mexico (N = 19), Panama (N = 6)	168	70	41.67	98	58.33	0	0
Blackberry	Serbia (N = 2)	2	1	50.00	1	50.00	0	0
Blueberry	Argentina (N = 1), Serbia (N = 1), Spain (N = 1), Peru (N = 1), The Netherlands (N = 1)	5	4	80.00	1	20.00	0	0
Brazil nut	Bolivia (N = 2)	2	2	100	0	0	0	0
Carambola	Malesia (N = 2)	2	2	100	0	0	0	0
Cashew	Vietnam (N = 1)	1	1	100	0	0	0	0
Chestnut	China (N = 1), Serbia (N = 1)	2	2	100	0	0	0	0
Clementine	Egypt (N = 1), Italy (N = 5), Spain (N = 7), Turkey (N = 3)	16	8	50.00	8	50.00	0	0
Coconut	Ivory Coast (N = 1)	1	0	0	1	100	0	0
Currants	The Netherlands (N = 2)	2	0		2	100	0	0
Date palm	Iran (N = 7), Israel (N = 1)	8	6	75.00	2	25.00	0	0
Fig	Turkey (N = 1)	1	1	100	0	0	0	0
Grapefruit	Cyprus (N = 2), Greece (N = 3), Israel (N = 1), Mexico (N = 2), South Africa (N = 33), Swaziland (N = 1), Turkey (N = 71), Zimbabwe (N = 2)	115	13	11.30	102	88.70	21	18.26
Grape	Bosnia and Herzegovina (N = 2), Chile (N = 1), Greece (N = 1), India (N = 2), Italy (N = 18), North Macedonia (N = 111), Serbia (N = 8), South Africa (N = 1), Turkey (N = 8)	152	99	65.13	53	34.87	2	1.32
Hazelnut	Croatia (N = 3), Georgia (N = 1), Turkey (N = 1)	5	4	80.00	1	20.00	0	0
Japanese apple	Albania (N = 1), Spain (N = 6)	9	8	88.89	1	11.11	0	0
Kiwi	Chile (N = 7), Greece (N = 21), Italy (N = 16), New Zealand (N = 4), North Macedonia (N = 2)	50	33	66.00	17	34.00	0	0
Kumquat	Israel (N = 1), Italy (N = 2), South Africa (N = 1)	4	2	50.00	2	50.00	0	0
Lemon	Argentina (N = 45), Egypt (N = 1), Greece (N = 12), Italy (N = 2), South Africa (N = 15), Spain (N = 32), Turkey (N = 107), Uruguay (N = 3)	217	42	19.35	175	80.65	4	1.84

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Lime	Brazil (N = 1), China (N = 1), Guatemala (N = 2), Mexico (N = 21), South Africa (N = 1), The Netherlands (N = 1), Turkey (N = 1)	28	4	14.29	24	85.71	4	14.29
Lychee	Chile (N = 1)	1	1	100	0	0	0	0
Mandarin	Albania (N = 4), Croatia (N = 14), Cyprus (N = 4), Egypt (N = 2), Greece (N = 42), Italy (N = 3), Morocco (N = 1), Spain (N = 12), Swaziland (N = 1), Turkey (N = 111)	194	60	30.93	134	69.07	14	7.22
Mango	Brazil (N = 9), Burkina Faso (N = 1), Dominican Republic (N = 1), Israel (N = 1), Ivory Coast (N = 1), Mali (N = 2), Peru (N = 7), Senegal (N = 2)	24	15	62.50	9	37.50	0	0
Orange	Egypt (N = 32), Greece (N = 125), Morocco (N = 9), Italy (N = 3), South Africa (N = 46), Spain (N = 38), The Netherlands (N = 1), Turkey (N = 55), Uruguay (N = 3), Zimbabwe (N = 12)	324	98	30.25	226	69.75	7	2.16
Passion fruit	South Africa (N = 1)	1	1	100	0	0	0	0
Peach	France (N = 1), Greece (N = 32), Italy (N = 3), Serbia (N = 13), Spain (N = 7)	56	32	57.14	24	42.86	0	0
Peach (nectarine)	Albania (N = 2), Belgium (N = 1), Greece (N = 14), Italy (N = 4), North Macedonia (N = 3), Serbia (N = 5), Spain (N = 7)	36	23	63.89	13	36.11	0	0
Peanut	Argentina (N = 4), China (N = 4)	8	7	87.50	1	12.50	0	0
Pear	Argentina (N = 2), Belgium (N = 6), Bosnia and Herzegovina (N = 2), China (N = 3), Greece (N = 2), Italy (N = 9), Poland (N = 9), Serbia (N = 30), South Africa (N = 4), Spain (N = 3), The Netherlands (N = 24), Turkey (N = 1)	95	27	28.42	68	71.58	6	6.32
Pineapple	Colombia (N = 13), Costa Rica (N = 25), Ecuador (N = 1), Italy (N = 1), Ivory Coast (N = 1)	41	11	26.83	30	73.17	3	7.32
Pistachio	Turkey (N = 1)	1	1	100	0	0	0	0
Pitaya	Thailand (N = 1), Vietnam (N = 1)	2	2	100	0	0	0	0

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Plum	Albania (N = 3), Greece (N = 3), Italy (N = 2), Moldova (N = 1), North Macedonia (N = 3), Serbia (N = 14)	26	15	57.69	11	42.31	0	0
Pomegranate	Argentina (N = 2), Egypt (N = 1), Greece (N = 7), Peru (N = 6), Turkey (N = 50)	66	24	36.36	42	63.64	26	39.39
Pomelo	China (N = 12)	12	4	33.33	8	66.67	0	0
Quince	Greece (N = 1)	1	1	100	0	0	0	0
Raspberry	Morocco (N = 2), Serbia (N = 3), Spain (N = 2), The Netherlands (N = 1)	8	4	50.00	4	50.00	0	0
Sour cherry	Hungary (N = 8), Serbia (N = 6)	14	8	57.14	6	42.86	1	7.14
Strawberry	Albania (N = 8), Germany (N = 1), Greece (N = 13), Poland (N = 3), Serbia (N = 15), Spain (N = 5), Turkey (N = 1)	46	11	23.91	35	76.09	0	0
Sweet cherry	Greece (N = 6), Hungary (N = 1), Italy (N = 1), North Macedonia (N = 1), Poland (N = 1), Romania (N = 3), Serbia (N = 6), Spain (N = 1)	20	4	20.00	16	80.00	0	0
Walnut	Bulgaria (N = 2), Russia (N = 2), Ukraine (N = 1), United States of America (N = 1)	6	5	83.33	1	16.67	0	0

MRL, maximum residue level.

Table 2. The frequency of the detected pesticide residues and their concentrations in fruit samples.

Pesticide name (N = 173)	Types of pesticide	Frequency of detection in 2,164 samples	%	No. of samples with residues above MRL	%	Range min-max (mg/kg)
2-Phenylphenol	Fungicide	44	2.03	0	0	0.010 – 7.028
Abamectin	Insecticide	2	0.09	0	0	0.010
Acephate	Insecticide	5	0.23	0	0	0.010 – 0.011
Acetamiprid	Insecticide	171	7.90	21 (apple; grapefruit, N = 2; mandarin; pomegranate, N = 17)	12.21	0.010 – 1.418
Acetochlor	Herbicide	2	0.09	0	0	0.010
Acibenzolar-S-methyl	Fungicide	31	1.43	4 (grapefruit, N = 3; mandarin)	12.90	0.010 – 0.114
Acrinathrin	Insecticide	2	0.09	0	0	0.011 – 0.020
Aldicarb	Insecticide	27	1.25	0	0	0.010 – 0.018
Aldicarb sulfone	Insecticide	2	0.09	0	0	0.010
Ametryn	Herbicide	12	0.55	0	0	0.010
Amitraz	Insecticide	58	2.68	5 (pomegranate)	9	0.010 – 1.339
Atrazine	Herbicide	10	0.46	0	0	0.010 – 0.018
Azinphos-ethyl	Insecticide	6	0.28	1 (grapefruit)	16.67	0.010 – 0.982
Azinphos-methyl	Insecticide	7	0.32	0	0	0.010 – 0.042
Azoxystrobin	Fungicide	96	4.44	0	0	0.010 – 0.717
Bendiocarb	Insecticide	3	0.14	0	0	0.010
Bifenazate	Insecticide	6	0.28	0	0	0.011 – 0.020

Bifenthrin	Insecticide	18	0.83	0	0	0.010 – 0.081
Biphenyl	Fungicide	1	0.05	0	0	0.010
Bitertanol	Fungicide	5	0.23	1 (avocado)	20.00	0.012 – 0.152
Boscalid	Fungicide	154	7.12	1 (pomegranate)	0.65	0.010 – 2.989
Buprofezin	Insecticide	79	3.65	0	0	0.010 – 0.589
Butachlor	Herbicide	1	0.05	0	0	0.012
Butoxycarboxim	Insecticide	5	0.23	5 (grapefruit, N = 2; pomegranate, N = 3)	100	0.034 – 0.037
Carbaryl	Insecticide	29	1.34	0	0	0.010
Carbendazim	Fungicide	185	8.55	15 (apple, N = 3; grapefruit; lemon; orange, N = 2; pear, n = 2; pomegranate, N = 6)	8.06	0.010 – 2.670
Carbofuran	Insecticide	1	0.05	1 (mandarin)	100	0.033
Carboxin	Fungicide	2	0.09	0	0	0.010
Carfentrazone-ethyl	Herbicide	6	0.28	0	0	0.010 – 0.012
Chlorantraniliprole	Insecticide	24	1.11	0	0	0.010 – 0.121
Chlorothalonil	Fungicide	5	0.23	1 (grape)	20.00	0.010 – 12.500
Chlorotoluron	Herbicide	22	1.02	8 (grapefruit, N = 2; mandarin; pomegranate, N = 5)	36.36	0.010 – 0.928
Chlorpropham	Herbicide	2	0.09	0	0	0.010
Chlorpyrifos	Insecticide	145	6.70	10 (grapefruit, N = 8; grape; pomegranate)	6.90	0.010 – 2.338
Chlorpyrifos-methyl	Insecticide	27	1.25	1 (grapefruit)	3.70	0.011 – 0.944
Clethodim	Herbicide	1	0.05	0	0	0.010
Clofentezine	Insecticide	5	0.23	0	0	0.011 – 0.084
Clothianidin	Insecticide	13	0.60	0	0	0.010 – 0.045
Cyazofamid	Fungicide	3	0.14	0	0	0.054 – 0.111
Cyfluthrin	Insecticide	1	0.05	0	0	0.012
Cymoxanil	Fungicide	8	0.37	0	0	0.010 – 0.023
Cypermethrin	Insecticide	10	0.46	2 (pomegranate)	18.18	0.011 – 0.301
Cyproconazole	Fungicide	2	0.09	0	0	0.010 – 0.016
Cyprodinil	Fungicide	38	1.76	7 (mandarin; pomegranate, N = 6)	18.42	0.011 – 0.606
Deltamethrin	Insecticide	20	0.92	12 (grapefruit; mandarin; pomegranate, N = 10)	60.00	0.010 – 0.326
Diazinon	Insecticide	3	0.14	0	0	0.010
Dicrotophos	Insecticide	1	0.05	0	0	0.010
Difenoconazole	Fungicide	30	1.39	2 (pomegranate)	6.67	0.010 – 0.174
Diflubenzuron	Insecticide	8	0.37	2 (pear)	25.00	0.010 – 0.073
Dimethoate	Insecticide	8	0.37	1 (apple)	12.50	0.010 – 0.047
Dimethomorph	Fungicide	65	3.00	1 (grapefruit)	1.54	0.010 – 0.737
Dimoxystrobin	Fungicide	8	0.37	0	0	0.010
Dinotefuran	Insecticide	10	0.46	1 (pomegranate)	10.00	0.010 – 0.038
Diphenylamine	Fungicide	1	0.05	0	0	0.010
Emamectin	Insecticide	2	0.09	0		0.020 – 0.044
Emamectin B1a	Insecticide	4	0.18	0	0	0.010 – 0.025
Emamectin B1b	Insecticide	5	0.23	1 (pear)	20.00	0.010 – 0.016
Eprinomectin	Insecticide	2	0.09	0	0	0.010
Ethiofencarb	Insecticide	12	0.55	3 (grapefruit)	25.00	0.010 – 0.069
Ethirimol	Fungicide	5	0.23	0	0	0.010 – 0.038
Ethofumesate	Herbicide	20	0.92	0	0	0.010 – 0.038

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Etofenprox	Insecticide	1	0.05	0	0	0.141
Etoxazole	Insecticide	19	0.88	1 (pomegranate)	5.26	0.010 – 0.024
Famoxadone	Fungicide	3	0.14	0	0	0.040 – 0.292
Fenamidone	Fungicide	1	0.05	0	0	0.042
Fenamiphos	Insecticide	3	0.14	0	0	0.012 – 0.016
Fenazaquin	Insecticide	3	0.14	0	0	0.010
Fenbuconazole	Fungicide	4	0.18	0	0	0.010 – 0.033
Fenhexamid	Fungicide	18	0.83	0	0	0.010 – 0.645
Fenoxycarb	Insecticide	1	0.05	0	0	0.013
Fenpropimorph	Fungicide	7	0.32	0	0	0.010 – 0.067
Fenpyroximate	Insecticide	5	0.23	0	0	0.010 – 0.047
Fenthion	Insecticide	1	0.05	0	0	0.010
Fenuron	Herbicide	2	0.09	0	0	0.010
Fenvalerate	Insecticide	51	2.36	31 (lemon; mandarin, N = 9; orange, N = 3; pomegranate, N = 18)	60.78	0.010 – 1.247
Flonicamid	Insecticide	9	0.42	0	0	0.010 – 0.086
Fluazifop-butyl	Herbicide	1	0.05	0	0	0.010
Fludioxonil	Fungicide	154	7.12	2 (pear; pineapple)	1.30	0.010 – 5.984
Flufenacet	Herbicide	3	0.14	0	0	0.021 – 0.035
Flufenoxuron	Insecticide	2	0.09	0	0	0.015 – 0.032
Fluopyram	Fungicide	2	0.09	0	0	0.068 – 0.152
Fluoxastrobin	Fungicide	4	0.18	0	0	0.010 – 0.018
Flutolanil	Fungicide	2	0.09	0	0	0.010
Flutriafol	Fungicide	7	0.32	0	0	0.013 – 0.039
Formothion	Insecticide	17	0.79	10 (apple, N = 8; mandarin, N = 2)	58.82	0.010 – 0.396
Hexaconazole	Fungicide	5	0.23	0	0	0.010
Hexythiazox	Insecticide	5	0.23	0	0	0.013 – 0.032
Imazalil	Fungicide	624	28.84	10 (grapefruit, N = 3; lemon, N = 2; mandarin, N = 2; orange, N = 2; pomegranate)	1.60	0.010 – 93.349
Imidacloprid	Insecticide	213	9.84	0	0	0.010 – 0.327
Indoxacarb	Insecticide	24	1.11	4 (pomegranate)	16.67	0.010 – 0.080
Ipconazole	Fungicide	1	0.05	0	0	0.010
Iprodione	Fungicide	3	0.14	2 (orange)	66.67	0.019 – 0.551
Iprovalicarb	Fungicide	2	0.09	0	0	0.011 – 0.050
Isoprocarb	Insecticide	1	0.05	0	0	0.010
Isoproturon	Herbicide	1	0.05	0	0	0.010
Ketoconazole	Fungicide	19	0.88	0	0	0.010
Kresoxim-methyl	Fungicide	4	0.18	0	0	0.013 – 0.047
Lambda-cyhalothrin	Insecticide	8	0.37	0	0	0.010 – 0.098
Lufenuron	Insecticide	60	2.77	2 (grapefruit; pomegranate)	3.33	0.011 – 0.787
Malaoxon	Insecticide	3	0.14	0	0	0.058 – 1.067
Malathion	Insecticide	22	1.02	0	0	0.010 – 0.707
Mandipropamid	Fungicide	4	0.18	0	0	0.038 – 0.655
Mepanipyrim	Fungicide	13	0.60	8 (grapefruit, N = 3; mandarin; pomegranate, N = 4)	61.54	0.010 – 0.103
Mepronil	Fungicide	1	0.05	1 (grapefruit)	100	0.026
Metaflumizone	Insecticide	3	0.14	0	0	0.010 – 0.050
Metalaxyl	Fungicide	31	1.43	0	0	0.010 – 0.580

Metalaxyl-M	Fungicide	10	0.46	0	0	0.010 – 0.347
Methabenzthiazuron	Herbicide	5	0.23	0	0	0.010
Methamidophos	Insecticide	36	1.66	15 (grapefruit, N = 3; mandarin; orange; pear; pomegranate, N = 9)	41.67	0.010 – 2.048
Methidathion	Insecticide	1	0.05	0	0	0.012
Methiocarb	Insecticide	12	0.55	0	0	0.010 – 0.176
Methomyl	Insecticide	52	2.40	3 (grapefruit)	5.77	0.010 – 0.593
Methoxyfenozide	Insecticide	94	4.34	0	0	0.010 – 1.129
Metobromuron	Herbicide	5	0.23	2 (grapefruit)	40.00	0.010 – 0.598
Metrafenone	Fungicide	1	0.05	0	0	0.051
Metribuzin	Herbicide	42	1.94	2 (grapefruit)	4.76	0.010 – 0.335
Monocrotophos	Insecticide	3	0.14	0	0	0.010
Myclobutanil	Fungicide	34	1.57	0	0	0.011 – 0.290
Nitenpyram	Insecticide	1	0.05	0	0	0.010
Novaluron	Insecticide	7	0.32	2 (mandarin; orange)	28.57	0.010 – 0.013
Nuarimol	Fungicide	3	0.14	2 (grapefruit; mandarin)	66.67	0.010 – 0.043
Omethoate	Insecticide	4	0.18	1 (sour cherry)	25.00	0.010 – 0.060
Oxadixyl	Fungicide	13	0.60	6 (grapefruit, N = 4; mandarin; pomegranate)	46.15	0.010 – 0.595
Oxamyl	Insecticide	10	0.46	10 (grapefruit; lime, N = 4; mandarin; pomegranate, N = 4)	100	0.038 – 3.161
Penconazole	Fungicide	18	0.83	0	0	0.011 – 0.175
Permethrin	Insecticide	1	0.05	0	0	0.020
Phenmedipham	Herbicide	1	0.05	0	0	0.010
Phosmet	Insecticide	10	0.46	0	0	0.010 – 0.284
Picoxystrobin	Fungicide	43	1.99	19 (grapefruit, N = 16; mandarin; pomegranate, N = 2)	44.19	0.010 – 2.439
Piperonyl-butoxide	Insecticide	2	0.09	1 (pineapple)	50.00	0.010 – 0.130
Pirimicarb	Insecticide	32	1.48	0	0	0.010 – 0.110
Pirimiphos-methyl	Insecticide	12	0.55	10 (grapefruit, N = 3; mandarin, N = 2; pomegranate, N = 5)	83.33	0.010 – 0.480
Prochloraz	Fungicide	143	6.61	2 (pomegranate; sour cherry)	1.40	0.010 – 3.905
Promecarb	Insecticide	7	0.32	5 (grapefruit, N = 2; mandarin; pomegranate, N = 2)	71.43	0.010 – 0.039
Prometon	Herbicide	4	0.18	0	0	0.010
Prometryn	Herbicide	4	0.18	3 (grapefruit)	75.00	0.010 – 0.106
Propargite	Insecticide	4	0.18	1 (grapefruit)	25.00	0.010 – 0.316
Propham	Herbicide	59	2.73	3 (lime; pomegranate, N = 2)	5.08	0.010 – 0.085
Propiconazole	Fungicide	113	5.22	3 (pomegranate)	2.65	0.010 – 3.143
Propoxur	Insecticide	32	1.48	2 (pomegranate)	6.25	0.010 – 0.127
Prothioconazole	Fungicide	97	4.48	5 (grapefruit, N = 3; mandarin, N = 2)	5.15	0.010 – 0.586
Pymetrozine	Insecticide	2	0.09	0	0	0.010 – 0.019
Pyracarbolid	Fungicide	5	0.23	1 (grapefruit)	20.00	0.012 – 0.017
Pyraclostrobin	Fungicide	93	4.30	0	0	0.010 – 0.153
Pyridaben	Insecticide	23	1.06	0	0	0.010 – 0.135
Pyrimethanil	Fungicide	245	11.32	2 (pomegranate)	0.82	0.010 – 6.633
Pyriproxyfen	Insecticide	138	6.38	0	0	0.010 – 0.150
Quizalofop-p-ethyl	Herbicide	1	0.05	0	0	0.034
Siduron	Herbicide	1	0.05	0	0	0.010

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Spinetoram B	Insecticide	2	0.09	0	0	0.014 – 0.017
Spirodiclofen	Insecticide	16	0.74	0	0	0.010 – 0.195
Spiromesifen	Insecticide	29	1.34	9 (grapefruit, N = 3; mandarin; pomegranate, N = 5)	31.03	0.010 – 0.464
Spirotetramat	Insecticide	14	0.65	0	0	0.010 – 0.226
Spiroxamine	Fungicide	9	0.42	0	0	0.010 – 0.181
Sulfentrazone	Herbicide	4	0.18	2 (grapefruit)	50.00	0.010 – 0.026
Tebuconazole	Fungicide	116	5.36	1 (pineapple)	0.86	0.010 – 1.000
Tebufenozide	Insecticide	34	1.57	0	0	0.010 – 0.051
Tebufenpyrad	Insecticide	9	0.42	0	0	0.010 – 0.061
Tebuthiuron	Herbicide	11	0.51	7 (grapefruit, N = 2; mandarin; pomegranate, N = 4)	63.64	0.010 – 0.079
Teflubenzuron	Insecticide	50	2.31	0	0	0.010 – 0.025
Terbutryn	Herbicide	6	0.28	3 (grapefruit)	50.00	0.010 – 0.044
Tetraconazole	Fungicide	17	0.79	0	0	0.010 – 0.065
Thiabendazole	Fungicide	337	15.57	0	0	0.010 – 4.814
Thiacloprid	Insecticide	63	2.91	2 (grapefruit; pomegranate)	3.17	0.010 – 0.154
Thiamethoxam	Insecticide	16	0.74	0	0	0.010 – 0.034
Thiophanate-methyl	Fungicide	32	1.48	0	0	0.010 – 0.683
Triadimefon	Herbicide	1	0.05	0	0	0.016
Triadimenol	Fungicide	3	0.14	0	0	0.010 – 0.028
Tricyclazole	Fungicide	3	0.14	3 (grapefruit)	100	0.049 – 0.074
Trifloxystrobin	Fungicide	24	1.11	2 (pomegranate)	8.33	0.010 – 0.144
Triflumuron	Insecticide	2	0.09	0	0	0.022 – 0.048
Triticonazole	Fungicide	3	0.14	0	0	0.010
Zoxamide	Fungicide	7	0.32	3 (grapefruit)	42.86	0.014 – 1.094

MRL, maximum residue level.

3. Results and discussion

The individual concentrations of the analyzed pesticide residues in all samples of fruits (N = 2,164) are shown in the Supplementary material 2 (individual results). All pesticide residues at or above the reporting limit (RL ≥ 0.01 mg/kg) are reported.

In this study, a total of 2,164 samples of fresh fruits were analyzed for pesticide residue. A yearly total of 136 (6.28%), 651 (30.08%), 687 (31.75%) and 690 (31.89%) of these samples were analyzed in 2016 (Serbian fruits: 57 samples; imported fruits: 79 samples), 2017 (Serbian fruits: 38 samples; imported fruits: 613 samples), 2018 (Serbian fruits: 53 samples; imported fruits: 634 samples) and 2019 (Serbian fruits: 51 samples; imported fruits: 639 samples), respectively. Detailed characteristics like common name, country of origin and number of samples (without and with pesticide residues) of the analyzed samples are shown in Table 1. The evaluation of the obtained results of 2,164 different fruit samples has shown (Table 1) that 62.57% (1,354 out of the 2,164 samples) of all samples contained pesticide residues (RL ≥ 0.01 mg/kg) and 37.43% (810 out of the 2,164 samples) of the samples contained no pesticide residues (RL < 0.01 mg/kg). All samples of aronia (N = 1), Brazil nut (N = 2), carambola (N = 2), cashew (N = 1), chestnut (N = 2), fig (N = 1), lychee (N = 1), passion fruit (N = 1), pistachio (N = 1), pitaya (N = 2) and quince (N = 1) were pesticide-free. The detection rates (when the sample size ′′N′′ is greater than 30) of pesticide residues in peach (nectarine) (N = 36), pineapple (N = 41), strawberry (N = 46), kiwi (N = 50), peach (N = 56), pomegranate (N = 66), pear (N = 95), grapefruit (N = 115), grape (N = 152), banana (N = 168), mandarin (N = 194) lemon (N = 217), orange (N = 324) and apple (N = 351) samples were 36.11%, 73.17%, 76.09%, 34.00%, 42.86%, 63.64%, 71.58%, 88.70%, 34.87%, 58.33%, 69.07%, 80.65%, 69.75% and 64.10%, respectively. All pesticide residues detected in almond (N = 6), apricot (N = 15), aronia (N = 1), banana (N = 168), blackberry (N = 2), blueberry (N = 5), Brazil nut (N = 2), carambola (N = 2), cashew (N = 1), chestnut (N = 2), clementine (N = 16), coconut

(N = 1), currants (N = 2), date palm (N = 8), fig (N = 1), hazelnut (N = 5), Japanese apple (N = 9), kiwi (N = 50), kumquat (N = 4), lychee (N = 1), mango (N = 24), passion fruit (N = 1), peach (N = 56), peach (nectarine) (N = 36), peanut (N = 8), pistachio (N = 1), pitaya (N = 2), plum (N = 26), pomelo (N = 12), quince (N = 1), raspberry (N = 8), strawberry (N = 46), sweet cherry (N = 20) and walnut (N = 6) were below or at the MRLs. The MRLs for pesticide residues were exceeded in 101 out of the 2,164 (4.67%) samples: apple (12 out of the 351 samples, 3.42%; Bosnia and Herzegovina: N = 2, North Macedonia: N = 2, Poland: N = 3, Serbia: N = 5), avocado (1 out of the 19 samples, 5.26%; Peru: N = 1), grapefruit (21 out of the 115 samples, 18.26%; South Africa: N = 4; Turkey: N = 17), grapes (2 out of the 152 samples, 1.32%; North Macedonia: N = 2), lemon (4 out of the 217 samples, 1.84%; Argentina: N = 1, Turkey: N = 2), lime (4 out of the 28 samples, 14.29%; Guatemala: N = 1, Mexico: N = 2, The Netherlands: N = 1), mandarin (14 out of the 194 samples, 7.22%; Spain: N = 2, Swaziland: N = 1, Turkey: N = 11), orange (7 out of the 324 samples, 2.16%; Spain: N = 1, Turkey: N = 6), pear (6 out of the 95 samples, 6.32%; Poland: N = 2, Serbia: N = 4), pineapple (3 out of the 41 samples, 7.32%; Colombia: N = 1, Costa Rica: N = 2), pomegranate (26 out of the 66 samples, 39.39%; Turkey: N = 26) and sour cherry (1 out of the 14 samples, 7.14%; Serbia: N = 1).

The frequency of the detected pesticide residues in fruit samples are shown in Table 2. A total of 173 pesticide residues (distributed as: 49.13% insecticides, 35.84% fungicides and 15.03% herbicides) were detected in all the fruit samples (Table 2). Imazalil, thiabendazole, pyrimethanil, imidacloprid, carbendazim, acetamiprid, boscalid, fludioxonil, chlorpyrifos, prochloraz, pyriproxyfen, tebuconazole, propiconazole, prothioconazole, azoxystrobrin, methoxyfenozide and pyraclostrobin were the pesticide residues most frequently found (occurrence in more than 90 analyzed samples, > 4%) and were detected in 624 (28.84%), 337 (15.57%), 245 (11.32%), 213 (9.84%), 185 (8.55%), 171 (7.90%), 154 (7.12%), 154 (7.12%), 145 (6.70%), 143 (6.61%), 138 (6.38%), 116 (5.36%), 113 (5.22%), 97 (4.48%), 96 (4.44%), 94 (4.34%) and 93 (4.30%) samples, respectively. Of the 173 pesticide residues, 64 (36.99%) of them were detected at least once in fruit samples in level higher than MRLs. A total of 309 pesticide residues (133 in pomegranate, 43.04%; 95 in grapefruit, 30.74%; 33 in mandarin, 10.68%; 13 in apples, 4.21%; 11 in orange, 3.56%; 7 in pear, 2.27%; 5 in lime, 1.62%; 4 in lemon, 1.29%; 3 in pineapple, 0.97%; 2 in grape, 0.65%; 2 in sour cherry, 0.65; 1 in avocado, 0.32%) were found in the 101 fruit samples containing residues above MRLs. The other 109 (63.01%) pesticide residues did not exceed their MRL values. The most frequent pesticide residues found to exceed the MRL were butoxycarboxim (100%, 5 out of 5 samples), carbofuran (100%, 1 out of 1 sample), deltamethrin (60.00%, 12 out of 20 samples), fenvalerate (60.78%, 31 out of 51 samples), formothion (58.82%, 10 out of 17 samples), iprodione (66.67%, 2 out of 3 samples), mepanipyrim (61.54%, 8 out of 13 samples), mepronil (100%, 1 out of 1 sample), nuariomol (66.67%, 2 out of 3 samples), oxamyl (100%, 10 out of 10 samples), piperonyl-butoxide (50.00%, 1 out of 2 samples), pirimiphos-methyl (83.33%, 10 out of 12 samples), promecarb (71.43%, 5 out of 7 samples), prometryn (75.00%, 3 out of 4 samples), sulfentrazone (50.00%, 2 out of 4 samples), tebuthiuron (63.64%, 7 out of 11 samples), terbutryn (50.00%, 3 out of 6 samples) and tricyclazole (100%, 3 out of 3 samples). Among the mostly detected pesticide residues, imazalil was found at the highest concentration (93.349 mg/kg, 18.67 times higher than MRL) in grapefruit.

An overview of the number of residue residues per sample are shown in Table 3a and 3b. Many samples contained several pesticide residues. A total of 5,078 individual pesticide residues were found in the 1,354 fruit samples containing residues. Of the 2,164 samples analyzed, a single pesticide residue was detected in 252 (11.65%) samples and two, three, four, five and six pesticide residues in 278 (12.85%), 227 (10.49%), 203 (9.38%), 145 (6.70%) and 103 (4.76%) samples, respectively. Seven or more pesticide residues were detected in 6.75% of the samples. The samples with highest number of pesticide residues were two samples of grapefruit both with 44 pesticide residues.

Table 3. a. Number of pesticide residues in an individual sample.

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No. of pesticide residues	0	1	2	3	4	5	6	7	8	9	10	11
No. of samples	810	252	278	227	203	145	103	65	34	19	7	2
%	37.43	11.65	12.85	10.49	9.38	6.70	4.76	3.00	1.57	0.88	0.32	0.09
No. of samples with residues above the MRL	0	7 (7 with 1)	17 (13 with 1; 4 with 2)	10 (7 with 1; 3 with 2)	12 (4 with 1; 6 with 2; 1 with 3; 1 with 4)	8 (3 with 1; 2 with 2; 2 with 3; 1 with 5)	15 (7 with 1; 6 with 2; 1 with 3; 1 with 4)	7 (3 with 1; 1 with 2; 2 with 3; 1 with 5)	8 (3 with 1; 3 with 2; 1 with 3; 1 with 4)	5 (3 with 1; 1 with 2; 1 with 4)	1 (1 with 1)	0

Table 3. b. Number of pesticide residues in an individual sample.

No. of pesticide residues	12	13	15	17	26	29	30	31	33	36	39	44
No. of samples	4	4	1	1	1	1	1	1	1	1	1	2
%	0.18	0.18	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.09
No. of samples with residues above the MRL	2 (1 with 1; 1 with 2)	0	0	0	1 (1 with 16)	1 (1 with 17)	1 (1 with 11)	1 (1 with 17)	1 (1 with 18)	1 (1 with 16)	1 (1 with 20)	1 (1 with 19; 1 with 22)

4. Conclusions

In this study, pesticide residues were determined in 2,164 samples of the most popularly consumed fruits in Serbia (during 2016–2019). There were 1,354 (62.57%) samples contaminated with pesticide residues, of which 101 (4.67%) samples were higher than the MRLs. Among the 101 fruit samples with MRL exceedances, pomegranate was the fruit with the highest number of MRL exceedances (26 samples, 25.74%), followed by grapefruit with 21 samples (20.79%), mandarin with 14 samples (13.86%), apple with 12 samples (11.88%), orange with 7 samples (6.93%), pear with 6 samples (5.94%), lemon and lime with 4 samples each (3.96%), pineapple with 3 samples (2.97%), grapes with 2 samples (1.98%) and avocado and sour cherry with 1 sample each (0.99%). Pomegranate, grapefruit and mandarin showed the highest number of samples with multiple pesticide residues higher than MRLs. These results highlight the need to continuously monitor pesticide residues in fruits in order to fully protect public health.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org. Supplementary material 1 Table S1: Summary of studies dealing with detection of pesticide residue in fresh fruits/food of plant origin.; Supplementary material 2 Individual results.

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