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Preharvest Treatments with Low-Risk Plant Protection Products Can Help Apple Growers Fulfill the Demands of Supermarket Chains Regarding Pesticide Residues and Marketing Apples under 0-Residue Brands

Andrej Paušič *, Mihaela Roškarič and Mario Lešnik

Department of Phytomedicine, Faculty of Agriculture and Life Sciences, University of Maribor, Pivola 10, 2311 Hoče, Slovenia
* Correspondence: andrej.pausic@um.si

Abstract: As a result of worried consumer pressure, European supermarket chains (ESC) have developed very strict rules about the number and concentration of pesticide active substance residues (AS) accepted in fruits. So-called fruit quality toxicological burden indicators were developed. If fruit suppliers do not comply with ESC requirements, their fruit is often rejected. It is becoming increasingly difficult for apple producers to meet all the requirements of the ESC, so they need new residue reduction tools. One of the options to lower the concentrations of residue on apples is a preharvest application of low-risk preparations (LRP) based on potassium bicarbonate ($KHCO_3$) = PBC, coconut di-ethanol amide ($(CH_3(CH_2)_nC(=O)N(CH_2CH_2OH)_2)$ = DEA, hydrogen peroxide (H_2O_2) = HP, and a mixture of microbes (EM) that have the ability to dissolve or disintegrate the AS residue. Trials were carried out to test the concept mentioned above. The application of LRP during the last four weeks of preharvest significantly reduced the residue concentration of pesticide AS in apples. Reduction rates among 25 active substances ranged from 0 to 100%, depending on the combination of LRP and AS. HP had the highest capacity to accelerate AS degradation, PB was the second most efficient, and DEA and EM displayed a low residue disintegration ability. The application of the tested LRP can enable apple growers to produce fruits with significantly lower residue concentrations and allows them to comply more successfully with strict ESC rules based on the calculations of toxicological burden indicators.

Keywords: hydrogen peroxide; potassium bicarbonate; effective microbes; detergent; pesticide residues; fruit marketing rules

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1. Introduction

To produce high quality apples in conditions of constant disease and pest pressure, growers need to frequently apply pesticides, often more than 20 times per season, and the fruits, therefore, contain a lot of pesticide residue at harvest. The pesticide residue statistics for European markets show that at least 50% of the analyzed apple samples from official surveys carried out by EU member states contain pesticide residues at a level higher than 0.01 mg/kg; approx. 1% of the samples contain residues over the MRL limit (legally permitted maximum residue limit in mg kg^{-1}), and 3–7% of apple samples contain more than five residues of pesticide active substances (a.s.) [1]. The publications of nongovernment organizations (such as regional Pesticide Action Network associations) in the form of so-called "Dirty dozen" lists illustrate residue situations as much worse than official EU member state surveys present. In these surveys, apples are very often listed at the top as the most contaminated fruits. The health impacts of consuming fruit with multiple residues are of great concern to consumers, and the residue concentration information significantly impacts consumers' decisions about where and from whom they will buy fruit [2,3].

As a result of this consumer pressure, European supermarket chains (ESC) have developed very strict rules about the levels of residue that fruit can contain and also about the highest concentrations thereof. They developed the so-called fruit quality toxicological burden indicators. An example of these requirements for German supermarket chains is available at https://www.port-international.de/new-standards-for-use-of-pesticides/ (accessed on 4 April 2023). Limits posed by the ESC on the levels of residue and about a.s. concentrations are far lower than the legal permitted limits expressed in MRL or ARFD (Acute reference dose in mg kg^{-1} bw^{-1}) [4].

According to the information obtained from Slovenian fruit suppliers, the common rules of EU retailers and supermarket chains (i.e., ALDI, HOFER, LIDL, TESCO, COOP, ECOPLAZA, EDEKA, REWE, etc.) can be broadly summarized as follows:

(a) The fruit should not contain more than 3–5 residues of pesticide a.s. detected at a level higher than 0.01 $mgkg^{-1}$. Some ESCs started to implement a limit of 0.005 mg kg^{-1} for counting the number of allowed found residues (=No. a.s.);
(b) The concentration of each a.s. may not exceed 33–70% of its MRL (=% MRL);
(c) The cumulative sum of the MRL % values of all found a.s. should not exceed the sum 60–80% (=$\sum$% MRL of all detected a.s. together);
(d) The concentration of each a.s. should not exceed 50–80% of its ARFD (=% ARFD);
(e) The cumulative sum of the ARFD % values of all found a.s. should not exceed the sum 60–80% (=$\sum$% ARFD of all detected a.s. together).

If the fruit supplier does not comply with one of the listed requirements, their fruits are often rejected. It is becoming increasingly difficult for apple producers to meet all the requirements of the ESC because the limits are constantly pushed downwards and also because the ESCs compare their requirements among each other. The use of stricter rules is a mechanism of attracting consumers to buy fruits in their stores and not in the stores of their competitors. ESCs are ranked by consumer associations (see example data on UK Ranking of Supermarkets on pesticides at https://www.pan-uk.org/supermarkets// (accessed on 3 April 2023). Farmers are complaining that the limits are too low and do not have any scientific background in pesticide risk studies, whereas consumers claim that the existing methods in pesticide residue risk studies do not correctly address the risk of long-term exposure to multiple residues (so-called “cocktail effect”) [5]. We have three distinct stakeholder groups; toxicological scientists and the state regulatory system, farmers, and consumer organizations, which are somehow disconnected despite trying to come closer via the system of stakeholder cooperation.

Farmers are advised to adopt spray programs, especially in the second part of the season. One possible adaptation in the second part of the season is the frequent use of alternative products used in organic production systems. This approach is welcomed in 0.0-residue fruit production systems [6,7]. The 0.0-residue concept is compatible with upgraded integrated production systems, which are intensively researched and economically evaluated [8,9]. Some alterative products used in 0.0-residue production systems have a direct effect on the dissipation kinetics of applied pesticide residues. By applying such products, we can lower the concentrations of chemical pesticide residues at harvest to reach ESC rules, despite pesticides already being applied frequently during the first part of the season. Organic acids are useful preparations for the aforementioned purpose, as well as certain mineral salts and clays, microbe-based biostimulant preparations, and detergents. This approach of lowering the pesticide residue levels in fruit at harvest via preharvest application of alternative plant protection products is under development; publications explaining the details of its performance are not yet available.

Apple producers around the world have very similar problems when considering active substances, which are often found in too high concentrations at harvest. These substances are: captan, dithianon, boscalid, fludioxonil, pirimicarb, spirotetramat, chlorantraniliprole, trifloxystrobin, pyrimethanil, tebuconazole, chlorpyrifos, and others [10,11].

The mentioned substances are often listed in the European National Food Pesticide Residue Survey Statistics. Technologies to remove residues in fruit and vegetables during storage were developed by performing chemical and physical cleaning [12], but in many EU countries, competent authorities oppose the massive use of chemicals in fruit storage and rather support the application of alternative plant protection preparations during preharvest.

The aim of our trial was to test the system of pesticide decomposition acceleration in apples by applying products that have the ability to dissolve, disintegrate, or bind pesticide residues prior to harvest. The preparations were safe low-risk chemicals, biostimulators, or microbes, which do not leave any residues and are not phytotoxic to apples. We chose four products that are already used in apple production worldwide and serve as controls for certain pests and diseases as biostimulants, or to clean fruits from insect-secreted honeydew and sooty blotch caused by a great variety of saprophytic fungi. These are: potassium bicarbonate ($KHCO_3$), natural coconut detergent (coconut di-ethanolamide), hydrogen peroxide, and a mixture of microorganisms. We wanted to test if sequential applications of the listed products close to harvesting could significantly reduce pesticide residues in apples and if the application can help apple producers to fulfill the demands of supermarket chains more successfully.

2. Materials and Methods

2.1. Preparations Used to Speed Up the Disintegration of Pesticide Residues on Apples

The tested preparations were applied separately at appointed plots at a dose of 10 L or kg of product per hectare. Each was applied repeatedly four times during the preharvest period at one-week intervals (see Table 1). The trial was carried out in 2019 and was repeated in 2020. The first preparation to be tested was potassium bicarbonate (PBC) (99% $KHCO_3$) VitiSan® produced by Biofa (Germany). It is generally used to control several fungal diseases in organic apple production. The second was the LDC® detergent produced by NeoLife (Netherlands). LDC consists of a mixture of mono- and di-ethanolamine salts of linear dodecyl benzene sulfonate, a non-ionic surfactant, and of free natural coconut di-ethanolamide (4%; $(CH_3(CH_2)_nC(=O)N(CH_2CH_2OH)_2)$). In some countries, it serves as a pest control agent (mites, aphids, psyllids) for the removal of honeydew excreted by insects, or to stop the development of sooty blotch caused by a variety of saprophytic fungi and yeasts. It is well known for its use in cosmetic products. The third product was hydrogen peroxide (HP) H_2O_2 (35%) Stabilized peroxide® produced by Belinka (Slovenia). Peroxide is used to control certain fungi causing storage rot, as a stimulant for the prevention of climate-related stress and as a plant resistance activator. The fourth product was the microbial biostimulant EM Naturally Active® produced in Poland at the consortium of the GrenLife company. This preparation belongs to the Effective Microorganism technology EM® developed in Japan [13]. The EM preparation contains several species of photosynthetic bacteria (*Rhodopseudomonas* spp., *Rhodobacter* spp.), bacteria from the genus *Azotobacter* sp., lactic bacteria (*Lactobacillus* spp. and *Streptococcus* spp.), yeasts (*Saccharomyces* spp.), and actinomycetes (*Streptomyces* spp.). A similar set of microorganisms is also used in preparations for the microbial decontamination of polluted water [14].

2.2. Apple Orchard, Application of Pesticides, and Tested Plant Protection Products

The experiment was performed at a 13-year-old Golden delicious orchard (in 2019). Trees were grafted on M9 rootstock and were growing at the experimental station at the Faculty of Agriculture and Life Sciences in Hoče near Maribor, Slovenia (GIS 46°30.5′50.00″ N, 15°37′39.06″ E). The slender spindle-trained trees were planted at a distance of 3.2 m between rows and 0.8 m within rows. This amounted to 3.900 trees per hectare with a height of 3.5 m, a 90 cm width of green wall, and 9300 m^3 of tree row volume. The pesticides were applied at equal rates to all trial plots with the standard orchard trailed sprayer Andreoli Eco Simplex (Andreoli Eng., Novi Di Moden, Italy), delivering 350 l of spray per hectare. The spray was generated with Albuz ATR 80 nozzles (Solcera Albuz, Évreux, France) operating at a pressure of 7 bars and producing droplets with a volume median diameter between 130–160 μm. The preparations for the disintegration of pesticide residues were applied with a Stihl SR 430 backpack mist blower (Stihl AG, Waiblingen, Germany) at a water volume of 1000 l ha^{-1} to ensure a good wetting of all the tree crows and fruit parts (more than 90 droplet impact per cm^{-2} and more than 75% coverage determined by use of water sensitive papers). The tested plant protection products are listed in Table 1.

Table 1. Pesticide formulation, application period, and weather parameters for the period from last application till harvest period—sampling date 13. 9. (2019) and 15. 9. (2020).

Formulation	Active Substance	Application Date		ADT (°C)		CP (mm)		NDAH (day)	
		2019	2020	2019	2020	2019	2020	2019	2020
Affirm (1)	Emamectin	27. 7.	28. 7.	20.4	20.8	161	102	49	50
Bellis (3)	Boscalid	28. 6.	1. 7.	20.8	20.5	239	245	78	77
Coragen (5)	Chlorantraniliprole	28. 6.	1. 7.	20.8	20.5	239	245	78	77
Delan (3)	Dithianon	31. 5.	28. 3.	21.1	17.4	327	461	106	172
Delegate (6)	Spinetoram	18. 7.	19. 7.	20.9	20.8	176	140	58	59
Dithane (6)	Mancozeb	12. 4.	17. 4.	18.3	18.4	506	447	155	152
Envidor (2)	Spirodiclofen	13. 5.	15. 5.	19.9	19.4	438	382	124	124
Faban (3)	Dithianon + Pyrimethanil	13. 5.	15. 5.	19.9	19.4	438	382	124	124
Geoxe (1)	Fludioxonil	31. 8.	1. 9.	17.2	18.3	51	11	14	15
Imidan (6)	Phosmet	26. 5.	25. 5.	20.8	19.7	405	351	111	114
Laser (8)	Spinosad	28. 6.	1. 7.	20.8	20.5	239	245	78	77
Luna (2)	Fluopyram + Tebuconazole	21. 6.	19. 6.	20.9	20.5	313	281	85	89
Merpan (6)	Captan	7. 9.	9. 9.	15.5	19.5	24	0	7	7
Mospilan (2)	Acetamprid	27. 4.	27. 4.	19.0	18.7	493	430	140	142
Movento (2)	Spirotetramat	31. 5.	30. 5.	21.1	19.9	327	348	106	109
Nativo (2)	Trifloxystrobin + Tebuconazole	13. 6.	12. 6.	21.1	20.4	324	321	93	96
Ovitex (4)	Oil	16. 3.	20. 3.	17.0	16.8	620	468	182	180
Penncozeb (9)	Propineb	16. 3.	20. 3.	17.0	16.8	620	468	182	180
Pirimor (6)	Pirimicarb	13. 6.	12. 6.	21.1	20.4	324	321	93	96
Score (1)	Difenoconazole	17. 5.	25. 5.	20.3	19.7	408	351	120	114
Sercadis (3)	Fluxapyroxad + Difenconazole	5. 6.	4. 6.	21.2	20.1	325	344	101	104
Sivanto (2)	Flupiradifuron	5. 6.	4. 6.	21.2	20.1	325	344	101	104
Stroby (3)	Krezoxym-methyl	17. 5.	20. 5.	20.3	19.6	408	361	120	119
Syllit (7)	Dodin	26. 5.	25. 5.	20.8	19.7	405	351	111	114
Teppeki (4)	Flonicamid	12. 4.	17. 4.	18.3	18.4	506	477	155	152
Tercel (3)	Dithianon + Pyraclostrobin	10. 5.	10. 5.	19.8	19.2	441	398	127	129
Topas (1)	Penconazole	26.4.	10. 4.	18.9	18.1	493	456	141	159

Producers of plant protection formulations: 1—Syngenta, 2—Bayer, 3—BASF, 4—Belchim, 5—DuPont, 6—Adama, 7—Arysta Life Science, 8—Corteva, 9—NuFarm ADT—average daily temperature for the period from last product application til the day of sampling. CP—cumulative amount of rain from period of last product application til the day of sampling. NDAH—number of days from period of last product application til the day of sampling.

We tried to apply the same products at the same time within the seasons of both 2019 and 2020. The application dates in both seasons were not identical but were as similar as possible. The apple harvest time was also similar in both seasons. Data about the precipitation and average temperature for the period from the last application of products til harvest are also presented in Table 1. The timing of the individual pesticide application was chosen according to the advice given by the Slovenian State Advisory Service and the producers of the products (Bayer, Syngenta, BASF, and others). All GAP (good agricultural practice) and waiting period rules presented on the preparation label were respected. By performing the trial in a described way, we conducted trial in realistic practical circumstances. We applied the maximum dose according to the recommendations on the pesticide label. We chose the most frequently used pesticides to get dissipation rate data on as many a.s. as possible.

2.3. Analysis of Pesticide Residues and Data on MRL and ARFD Indicators

At harvest (13.9. in 2019 and 15.9. in 2020), the apple samples were collected and delivered to the laboratory. In each plot, 30 apples were picked from 8 trees in the middle of each plot from different positions of tree crowns. The analysis was performed in an internationally validated and recognized laboratory, Institut Dr. Wagner Lebensmittel Analytik GmbH in Austria, according to the EN ISO/IEC 17,025 [15]. The determination of residues was performed via highly sensitive analytical methods based on liquid or gas chromatography, coupled with mass spectrometry according to the standard EN 15662:2018 "Foods of Plant Origin—Multimethod for the Determination of Pesticide Residues Using GC-MS/MS and LC-MS/MS-based methods". The samples were prepared following acetonitrile extraction/partitioning and cleaned up via the dispersive SPE-modular QuEChERS-method. The limit for the detection of active substances was 0.001 mg kg^{-1} and the limit for quantification was 0.003 mg kg^{-1} with less than ±50% uncertainty of measurements according to EU guidance SANTE/12682/2019. The a.s. extraction efficacy was over 90%. The fruits were analyzed within one day after picking, after being stored at a temperature of 2 C. Data on MRL and ARFD were taken from the EU Pesticide Database [4]. Data on % of MRL and % of ARFD from the EFSA PRIMo v. 3.1 model for the dietary exposure evaluation of adults was provided by the laboratory where the residue analysis was performed [16,17].

With regards to pesticide residues, we calculated the pesticide residue concentration reduction rate % RR. In the tables with the results next to the columns with the comparisons between control plots and treated plots, there is also a column with data on the average rate of reduction of pesticide concentrations (RR in %). The relative rate of concentration reduction is calculated via the following formula (RR in %) = $100 - ((T/C) \times 100)$, where T represents the average a.s. concentration at a treated plot and C is the average concentration in an untreated control plot. If the calculated RR value had a negative value, it would indicate that the concentration measured in the treated plot was higher than in the control plot, and that a reduction in a.s. concentration did not occur. In those instances, the negative value was noted in the data set. We also calculated two types of overall reduction rates for all active substances together. At avg. % RRa, we took all the data into calculation without regarding the sign of value (+ and −). At avg. % RRb, we only took the data of the active substances with positive values into calculation.

2.4. Trial Design and Statistical Methods

Plots in a field trial were arranged according to a randomized block design with four repetitions. Each plot consisted of 50 trees in a row. The data was processed via the standard analysis of variance (one-way ANOVA general linear model; F-test). The difference significance among treatment means was tested via the Tukey HSD significance test ($p < 0.05$; parameters of MRL and ARFD) and the Student's t-test ($p < 0.05$; at parameters of pesticide concentration). Levene's test of homogeneity of variances was performed to assure the fulfillment of statistical requirements for the performance of ANOVA analysis. The Statgraphics Centurion XIX software (Statgraphics Technologies, Inc., Virginia, VA, USA) was used to perform the analysis.

Data on % of MRL, ∑% MRL, % of ARFD, and ∑% ARFD were expressed in percentages, so we applied some standard data transformations, such as the angle-arcsine-square-root and the square-red transformations, to fulfill the rule of the homogeneity of variances [18], but found that the same results were obtained when the analysis was performed without the transformation; untransformed values are shown in the tables with results and the significance markers shown in the tables are based on untransformed data.

3. Results

The data on active substance residue concentrations are presented in Tables 2–5.

Table 2. Average concentration of pesticide residue (±SE) in apples at picking time (mg kg^{-1}) in relation to treatment with hydrogen peroxide; four times preharvest at a rate of 10 L (35% HP) Stabilized peroxide®/1000 l water/ha.

Active Substance:	Season 2019			Season 2020		
	Control C	**Treated T**	**RR%**	**Control C**	**Treated T**	**RR%**
Acetamprid	0.012 ± 0.001 a	0.011 ± 0.000 a	5.7	0.025 ± 0.010 a	0.021 ± 0.011 a	16.4
Boscalid	0.037 ± 0.002 a	0.023 ± 0.006 b	37.8	0.042 ± 0.010 a	0.014 ± 0.002 b	67.7
Captan	0.209 ± 0.022 a	0.071 ± 0.042 b	65.9	0.293 ± 0.067 a	0.054 ± 0.031 b	81.7
Chlorantraniliprole	0.040 ± 0.019 a	0.013 ± 0.003 a	68.2	0.030 ± 0.015 a	0.010 ± 0.000 a	68.1
Difenconazole	0.007 ± 0.001 a	0.003 ± 0.000 b	57.1	0.012 ± 0.002 a	0.006 ± 0.001 b	52.8
Dithianon	0.208 ± 0.037 a	0.050 ± 0.016 b	76.0	0.253 ± 0.078 a	0.099 ± 0.015 b	61.1
Dodine	0.022 ± 0.004 a	0.008 ± 0.001 b	62.6	0.060 ± 0.019 a	0.009 ± 0.001 b	85.4
Emamectin	0.006 ± 0.001 a	0.003 ± 0.002 a	54.7	0.007 ± 0.001 a	0.001 ± 0.001 b	80.9
Flonicamid	0.004 ± 0.002 a	0.005 ± 0.001 a	−7.7	0.012 ± 0.000 a	0.004 ± 0.001 b	68.6
Fludioxonil	0.061 ± 0.008 a	0.025 ± 0.005 b	58.8	0.103 ± 0.027 a	0.007 ± 0.003 b	92.8
Fluopyram	0.024 ± 0.004 a	0.012 ± 0.001 b	47.9	0.048 ± 0.006 a	0.025 ± 0.008 b	48.2
Flupyradifurone	0.014 ± 0.006 a	0.006 ± 0.002 a	58.1	0.018 ± 0.005 a	0.007 ± 0.001 b	63.5
Fluxapiroxad	0.029 ± 0.002 a	0.026 ± 0.005 a	10.4	0.034 ± 0.002 a	0.022 ± 0.003 b	35.6
Kresoxim-Methyl	0.004 ± 0.001 a	0.004 ± 0.001 a	0.0	0.009 ± 0.002 a	0.003 ± 0.001 b	71.4
Mancozeb	0.040 ± 0.008 a	0.025 ± 0.010 a	38.8	0.070 ± 0.022 a	0.010 ± 0.001 b	86.2
Phosmet	0.009 ± 0.001 a	0.004 ± 0.002 b	50.0	0.011 ± 0.003 a	0.001 ± 0.001 b	87.3
Pyraclostrobin	0.028 ± 0.011 a	0.012 ± 0.004 a	55.9	0.044 ± 0.017 a	0.009 ± 0.000 b	79.4
Pirimicarb	0.012 ± 0.001 a	0.007 ± 0.002 b	44.4	0.024 ± 0.007 a	0.008 ± 0.003 b	67.9
Pyrimethanil	0.009 ± 0.001 a	0.010 ± 0.004 a	−7.4	0.039 ± 0.010 a	0.038 ± 0.012 a	2.5
Spinosad	0.006 ± 0.001 a	0.002 ± 0.001 b	69.4	0.008 ± 0.002 a	0.000 ± 0.000 b	100.0
Spinetoram	0.006 ± 0.001 a	0.001 ± 0.001 b	82.3	0.012 ± 0.004 a	0.000 ± 0.000 b	100.0
Spirodiclofen	0.040 ± 0.018 a	0.012 ± 0.002 a	70.6	0.060 ± 0.011 a	0.023 ± 0.005 b	60.9
Spirotetramat	0.011 ± 0.001 a	0.007 ± 0.002 a	39.4	0.025 ± 0.002 a	0.016 ± 0.004 b	38.2
Tebuconazole	0.026 ± 0.010 a	0.013 ± 0.002 a	50.6	0.033 ± 0.006 a	0.020 ± 0.002 b	38.8
Thiacloprid	0.006 ± 0.001 a	0.007 ± 0.000 a	−15.8	0.017 ± 0.001 a	0.015 ± 0.002 a	15.9
Trifloxystrobin			56.8			46.0
Avg. %RRa	0.019 ± 0.006 a	0.008 ± 0.003 a	43.5	0.021 ± 0.003 a	0.011 ± 0.001 b	62.2
Avg. %RRb			50.5			62.2

The values for each active substance in each year marked with the same letter do not differ significantly in relation to *t*-test ($p < 0.05$) results. Relative rate of concentration reduction (RR in %) = 100 − ((T/C) × 100). Meanings of average values avg. % RRa and avg. % RRb are described in Section 2.3.

Table 3. Average concentration of pesticide residues (±SE) in apples at picking time (mg kg^{-1}) in relation to treatment with PBC (potassium bicarbonate); four times preharvest at a rate of 10 kg of VitiSan®/1000 L water/ha.

Active Substance:	Season 2019			Season 2020		
	Control C	**Treated T**	**RR**	**Control C**	**Treated T**	**RR**
Acetamprid	0.012 ± 0.001 a	0.014 ± 0.001 a	−17.1	0.025 ± 0.010 a	0.055 ± 0.002 b	−121.6
Boscalid	0.037 ± 0.002 a	0.038 ± 0.004 a	−2.7	0.042 ± 0.010 a	0.033 ± 0.002 a	22.0
Captan	0.209 ± 0.022 a	0.071 ± 0.012 b	66.0	0.293 ± 0.067 a	0.036 ± 0.008 b	87.6
Chlorantraniliprole	0.040 ± 0.019 a	0.016 ± 0.001 a	59.0	0.030 ± 0.015 a	0.027 ± 0.011 a	8.0
Difenconazole	0.007 ± 0.001 a	0.006 ± 0.001 a	14.3	0.012 ± 0.002 a	0.011 ± 0.001 a	5.6
Dithianon	0.208 ± 0.037 a	0.050 ± 0.016 b	76.0	0.253 ± 0.078 a	0.072 ± 0.004 b	71.7
Dodine	0.022 ± 0.004 a	0.015 ± 0.005 a	31.8	0.060 ± 0.019 a	0.031 ± 0.013 a	47.9
Emamectin	0.006 ± 0.001 a	0.003 ± 0.002 a	54.7	0.007 ± 0.001 a	0.000 ± 0.000 b	100.0
Flonicamid	0.004 ± 0.002 a	0.008 ± 0.002 a	−84.6	0.012 ± 0.000 a	0.010 ± 0.002 a	11.4
Fludioxonil	0.061 ± 0.008 a	0.039 ± 0.002 a	36.0	0.103 ± 0.027 a	0.045 ± 0.005 b	56.2
Fluopyram	0.024 ± 0.004 a	0.023 ± 0.002 a	4.2	0.048 ± 0.006 a	0.039 ± 0.010 a	19.3
Flupyradifurone	0.014 ± 0.006 a	0.004 ± 0.002 a	58.1	0.018 ± 0.005 a	0.009 ± 0.003 a	48.7
Fluxapiroxad	0.029 ± 0.002 a	0.020 ± 0.003 b	29.7	0.034 ± 0.002 a	0.022 ± 0.000 b	35.6
Kresoxim-methyl	0.004 ± 0.001 a	0.006 ± 0.002 a	−58.3	0.009 ± 0.001 a	0.006 ± 0.002 a	39.3
Mancozeb	0.040 ± 0.008 a	0.035 ± 0.006 a	14.0	0.070 ± 0.022 a	0.045 ± 0.017 a	35.2

Table 3. *Cont.*

Active Substance:	Season 2019			Season 2020		
	Control C	Treated T	RR	Control C	Treated T	RR
Phosmet	0.009 ± 0.001 a	0.004 ± 0.002 b	50.0	0.011 ± 0.003 a	0.001 ± 0.001 b	90.5
Pyraclostrobin	0.028 ± 0.011 a	0.012 ± 0.004 a	55.9	0.044 ± 0.017 a	0.013 ± 0.003 a	70.2
Pirimicarb	0.012 ± 0.001 a	0.008 ± 0.003 a	30.6	0.024 ± 0.007 a	0.012 ± 0.002 a	51.4
Pyrimethanil	0.009 ± 0.001 a	0.010 ± 0.004 a	−7.4	0.039 ± 0.010 a	0.054 ± 0.005 a	−37.3
Spinosad	0.006 ± 0.001 a	0.003 ± 0.000 b	52.5	0.008 ± 0.002 a	0.002 ± 0.001 b	78.3
Spinetoram	0.006 ± 0.001 a	0.003 ± 0.001 b	43.8	0.012 ± 0.004 a	0.004 ± 0.002 a	63.9
Spirodiclofen	0.040 ± 0.018 a	0.011 ± 0.001 a	73.1	0.060 ± 0.011 a	0.037 ± 0.007 a	37.7
Spirotetramat	0.011 ± 0.001 a	0.014 ± 0.002 a	−27.3	0.025 ± 0.002 a	0.020 ± 0.002 b	22.4
Tebuconazole	0.026 ± 0.010 a	0.011 ± 0.000 a	57.1	0.033 ± 0.006 a	0.023 ± 0.006 a	39.6
Thiacloprid	0.006 ± 0.001 a	0.008 ± 0.000 a	−21.1	0.017 ± 0.001 a	0.016 ± 0.001 a	9.6
Trifloxystrobin	0.019 ± 0.006 a	0.010 ± 0.004 a	47.7	0.021 ± 0.003 a	0.012 ± 0.002 b	40.3
Avg. %RRa			24.5			35.9
Avg. %RRb			44.9			45.5

The values for each active substance in each year marked with the same letter do not differ significantly in relation to *t*-test ($p < 0.05$) results. Relative rate of concentration reduction (RR in %) = 100 − ((T/C) × 100). Meanings of average values avg. % RRa and avg. % RRb are described in Section 2.3.

Table 4. Average concentration of pesticide residues (±SE) in apples at picking times (mg kg^{-1}) in relation to treatment with EM (effective microorganisms); four times preharvest at a rate of 10 L of EM Naturally®/1000 L water/ha.

Active Substance:	Season 2019			Season 2020		
	Control C	Treated T	RR	Control C	Treated T	RR
Acetamprid	0.012 ± 0.001 a	0.008 ± 0.000 b	27.7	0.025 ± 0.010 a	0.021 ± 0.002 a	13.1
Boscalid	0.037 ± 0.002 a	0.017 ± 0.002 b	53.4	0.042 ± 0.010 a	0.028 ± 0.006 a	33.6
Captan	0.209 ± 0.022 a	0.167 ± 0.016 a	20.1	0.293 ± 0.067 a	0.185 ± 0.006 a	36.8
Chlorantraniliprole	0.040 ± 0.019 a	0.018 ± 0.003 a	54.8	0.030 ± 0.015 a	0.015 ± 0.001 a	50.1
Difenconazole	0.007 ± 0.001 a	0.007 ± 0.002 a	0.0	0.012 ± 0.002 a	0.012 ± 0.002 a	0.0
Dithianon	0.208 ± 0.037 a	0.018 ± 0.009 b	91.6	0.253 ± 0.078 a	0.097 ± 0.020 a	61.7
Dodine	0.022 ± 0.004 a	0.013 ± 0.000 b	41.9	0.060 ± 0.019 a	0.034 ± 0.006 a	43.7
Emamectin	0.006 ± 0.001 a	0.002 ± 0.000 b	61.1	0.007 ± 0.001 a	0.002 ± 0.001 b	76.2
Flonicamid	0.004 ± 0.002 a	0.007 ± 0.000 a	−54.0	0.012 ± 0.000 a	0.013 ± 0.001 a	-14.3
Fludioxonil	0.061 ± 0.008 a	0.033 ± 0.000 b	45.9	0.103 ± 0.027 a	0.048 ± 0.008 a	53.4
Fluopyram	0.024 ± 0.004 a	0.018 ± 0.004 a	24.9	0.048 ± 0.006 a	0.049 ± 0.003 a	−1.8
Flupyradifurone	0.014 ± 0.006 a	0.005 ± 0.000 a	64.6	0.018 ± 0.005 a	0.010 ± 0.002 a	45.2
Fluxapiroxad	0.029 ± 0.002 a	0.015 ± 0.000 b	46.9	0.034 ± 0.002 a	0.021 ± 0.004 b	38.6
Kresoxim-methyl	0.004 ± 0.001 a	0.005 ± 0.000 a	−25.9	0.009 ± 0.002 a	0.006 ± 0.000 a	32.1
Mancozeb	0.040 ± 0.008 a	0.022 ± 0.001 b	44.9	0.070 ± 0.022 a	0.028 ± 0.007 a	59.7
Phosmet	0.009 ± 0.001 a	0.004 ± 0.000 b	58.2	0.011 ± 0.003 a	0.002 ± 0.002 b	77.2
Pyraclostrobin	0.028 ± 0.011 a	0.015 ± 0.002 a	47.9	0.044 ± 0.017 a	0.016 ± 0.004 a	64.1
Pirimicarb	0.012 ± 0.001 a	0.008 ± 0.001 b	32.4	0.024 ± 0.007 a	0.012 ± 0.002 a	48.9
Pyrimethanil	0.009 ± 0.001 a	0.008 ± 0.000 a	7.7	0.039 ± 0.010 a	0.040 ± 0.004 a	−1.7
Spinosad	0.006 ± 0.001 a	0.003 ± 0.002 a	51.4	0.008 ± 0.002 a	0.002 ± 0.001 b	68.1
Spinetoram	0.006 ± 0.001 a	0.003 ± 0.000 b	45.1	0.012 ± 0.004 a	0.002 ± 0.001 b	85.2
Spirodiclofen	0.040 ± 0.018 a	0.019 ± 0.007 a	51.6	0.060 ± 0.011 a	0.041 ± 0.001 a	31.5
Spirotetramat	0.011 ± 0.001 a	0.009 ± 0.001 a	16.1	0.025 ± 0.002 a	0.019 ± 0.001 b	26.8
Tebuconazole	0.026 ± 0.010 a	0.010 ± 0.000 a	62.3	0.033 ± 0.006 a	0.021 ± 0.001 b	35.0
Thiacloprid	0.006 ± 0.001 a	0.006 ± 0.000 a	10.1	0.017 ± 0.001 a	0.016 ± 0.001 a	5.9
Trifloxystrobin	0.019 ± 0.006 a	0.009 ± 0.000 a	50.0	0.021 ± 0.003 a	0.012 ± 0.001 b	42.3
Avg. %RRa			35.8			38.9
Avg. %RRb			42.1			44.8

The values for each active substance in each year marked with the same letter do not differ significantly in relation to *t*-test ($p < 0.05$) results. Relative rate of concentration reduction (RR in %) = 100 − ((T/C) × 100). Meaning of average values avg. % RRa and avg. % RRb are described in Section 2.3.

Table 5. Average concentration of pesticide residues (±SE) in apples at picking times (mg kg^{-1}) in relation to treatment with LDC; four times preharvest at a rate of 10 L of LDC®/1000 L water/ha.

Active Substance:	Season 2019			Season 2020		
	Control C	Treated T	RR	Control C	Treated T	RR
Acetamprid	0.012 ± 0.001 a	0.011 ± 0.001 a	7.5	0.025 ± 0.010 a	0.031 ± 0.005 a	−24.9
Boscalid	0.037 ± 0.002 a	0.024 ± 0.001 b	35.3	0.042 ± 0.010 a	0.028 ± 0.002 a	35.1
Captan	0.209 ± 0.022 a	0.071 ± 0.000 b	65.9	0.293 ± 0.067 a	0.067 ± 0.013 b	77.2
Chlorantraniliprole	0.040 ± 0.019 a	0.015 ± 0.002 a	62.9	0.030 ± 0.015 a	0.015 ± 0.005 a	49.9
Difenconazole	0.007 ± 0.001 a	0.005 ± 0.001 a	26.5	0.012 ± 0.002 a	0.007 ± 0.001 b	45.7
Dithianon	0.208 ± 0.037 a	0.050 ± 0.000 b	76.0	0.253 ± 0.078 a	0.060 ± 0.010 b	76.4
Dodine	0.022 ± 0.004 a	0.015 ± 0.000 a	31.8	0.060 ± 0.019 a	0.033 ± 0.002 a	44.9
Emamectin	0.006 ± 0.001 a	0.003 ± 0.001 b	47.6	0.007 ± 0.001 a	0.004 ± 0.001 a	48.5
Flonicamid	0.004 ± 0.002 a	0.005 ± 0.002 a	−15.4	0.012 ± 0.001 a	0.005 ± 0.003 b	55.7
Fludioxonil	0.061 ± 0.008 a	0.030 ± 0.006 b	50.6	0.103 ± 0.027 a	0.052 ± 0.009 a	49.6
Fluopyram	0.024 ± 0.004 a	0.015 ± 0.001 b	38.8	0.048 ± 0.006 a	0.034 ± 0.003 b	30.6
Flupyradifurone	0.014 ± 0.006 a	0.013 ± 0.001 a	10.9	0.018 ± 0.005 a	0.014 ± 0.006 a	22.6
Fluxapiroxad	0.029 ± 0.002 a	0.017 ± 0.001 b	38.7	0.034 ± 0.002 a	0.017 ± 0.001 b	48.6
Kresoxim-Methyl	0.004 ± 0.001 a	0.002 ± 0.001 a	47.2	0.009 ± 0.002 a	0.004 ± 0.001 b	62.4
Mancozeb	0.041 ± 0.008 a	0.028 ± 0.000 a	30.6	0.070 ± 0.022 a	0.039 ± 0.022 a	44.7
Phosmet	0.009 ± 0.001 a	0.004 ± 0.000 b	50.0	0.011 ± 0.003 a	0.002 ± 0.001 b	84.7
Pyraclostrobin	0.028 ± 0.011 a	0.017 ± 0.002 a	38.9	0.044 ± 0.017 a	0.027 ± 0.002 a	39.1
Pirimicarb	0.012 ± 0.001 a	0.007 ± 0.000 b	39.8	0.024 ± 0.007 a	0.009 ± 0.001 b	62.7
Pyrimethanil	0.009 ± 0.001 a	0.010 ± 0.000 a	−7.4	0.039 ± 0.010 a	0.036 ± 0.004 a	10.0
Spinosad	0.006 ± 0.001 a	0.005 ± 0.002 a	22.7	0.008 ± 0.002 a	0.001 ± 0.001 b	85.2
Spinetoram	0.006 ± 0.001 a	0.005 ± 0.001 a	9.6	0.012 ± 0.004 a	0.004 ± 0.001 a	65.2
Spirodiclofen	0.040 ± 0.018 a	0.010 ± 0.001 a	74.4	0.060 ± 0.011 a	0.027 ± 0.004 b	55.6
Spirotetramat	0.011 ± 0.001 a	0.012 ± 0.002 a	−6.4	0.025 ± 0.002 a	0.019 ± 0.001 b	26.7
Tebuconazole	0.026 ± 0.010 a	0.011 ± 0.000 a	57.1	0.033 ± 0.006 a	0.028 ± 0.007 a	14.8
Thiacloprid	0.006 ± 0.001 a	0.006 ± 0.001 a	0.0	0.017 ± 0.001 a	0.017 ± 0.003 a	4.3
Trifloxystrobin	0.019 ± 0.006 a	0.013 ± 0.002 a	30.9	0.021 ± 0.003 a	0.016 ± 0.005 a	23.1
Avg. %RRa			33.3			43.8
Avg. %RRb			38.9			46.5

The values for each active substance in each year marked with the same letter do not differ significantly in relation to *t*-test ($p < 0.05$) results. Relative rate of concentration reduction (RR in %) = 100 − ((T/C) × 100). Meanings of average values avg. % RRa and avg. % RRb are described in Section 2.3.

3.1. Reduction of Residue Concentration in Apples Treated with Different Alternative Products Sprayed Four Times Preharvest

The effects of four applications of hydrogen peroxide (HP) in the average concentration of residues in apples at harvest are presented in Table 2. The application of HP significantly reduced the concentrations of boscalid, captan, difenconazole, dithianon, dodine, fludioxonil, flupyradifurone, phosmet, pirimicarb, spinosad, and spinetoram in both years and that of emamectin, flonicamid, fluopyram, fluxapiroxad, krezoxym-methyl, mancozeb, pyraclostrobin, spirodiclofen, tebuconazole, and tryfloxystrobin in just one of the two seasons. The application of HP reduced the average concentration of residues at more than two thirds of the tested a.s. The effect of preharvest potassium bicarbonate (PBC) application is shown in Table 3. In many a.s. (at 19 of 26 in 2019 and at 24 of 26 in 2020), the concentrations decreased but not statistically or significantly. A significant effect in both seasons was evident only in dithianon, fluxapyroxad, captan, phosmet, and spinosad. Some differences were noticed between seasons, but in acetamprid, emamectin, fludioxonil, spinetoram, spirotetramat, and trifloxystrobin, significant effects were observed in just one season. The rate of residue dissipation in apples treated with PBC was lower than in plots treated with HP. We assume that the degradation effect was noticed at those a.s. which were sensitive to alkaline hydrolysis (p.e. captan).

The ability of the microbe mixture EM to facilitate the dissipation kinetics of pesticide residues is demonstrated in Table 4. In 19 cases (in both seasons), there was a noticeable reduction in concentration, but less than at HP (33 cases) and little more than at PBC (16 cases).

The microbes (EM) were less effective as HP and were comparably as effective as PBC. They significantly reduced the residue concentrations only in emamectin, fluxapyroxad, phosmet, and spinetoram in both years and in acetamprid, boscalid, dithianon, dodin, fludioxonil, mancozeb, pirimicarb, spinosad, spiroteramat, tebuconazole, and trifloxystrobin in one of the two seasons. The consequences of four applications of LDC detergent on residue dissipation are shown in Table 5. Again, in 23 a.s. out of 26 in 2019 and in 25 out of 26 in 2020, a reduction in concentrations was detected, but it was only significant in nine in 2019 and in 12 in the 2020 season. We can see that reductions in the cases of captan, dithianon, phosmet, fluopyram, fluxapyroxad, and pirimicarb were significant in both seasons, and in boscalid, difenconazole, emamectin, flonicamid, fludioxonil, krezoxym-methyl, spinosad, spirodiclofen, and spirotetramat, significant reduction rates were noticed in just one of the two seasons.

3.2. Effects of Tested Preparations on Pesticide Residue Related ESC Fruit Quality Requirements

The standard requirements of ESC are presented in the introduction section. Table 6 shows the differences in certain parameters that are part of the standard requirements of ESC. In the 2019 season, we could see that the application of the tested products significantly decreased the detected average no. of a.s. with a concentration higher than 0.01 or 0.005 mg kg^{-1}. In the control plots, the average number of a.s., with a concentration higher than 0.01 or 0.005 mg kg^{-1}, was 16.8 and 23.8, respectively. In the 2020 season, it was 20.0 and 25.0, respectively. In both seasons, we tested 26 different a.s.. The highest effect on the reduction of the avg. number of found a.s. in season 2019 was observed in HP (16.8 control vs. 9.8 HP). In PBC, EM, and LDC, the reduction of the avg. number of found a.s. residues above the limit of 0.01 mg kg^{-1} was significant in 2019. In the 2020 season, only the HP application significantly reduced the number. of a.s. found at a level higher than 0.01 and 0.005 mg kg^{-1}, and the effect of the other three tested products was not significant at the parameter of the number of a.s. >0.01 mg kg^{-1} in 2020 (control 20.0 vs. 15.5 PBC, 19.3 EM and 15.3 LDC; Table 6), but it was significant at the parameter of the number of a.s. >0.005 mg kg^{-1} in that year.

Table 6. Values (±SE) of pesticide residue-related parameters requested by EU supermarket chains.

Variant:	No. a.s. >0.01 mg kg^{-1}	No. a.s. >0.005 mg kg^{-1}	No. a.s. >10% MRL	Σ % MRL	No. a.s. >10% ARFD	Σ % ARFD
2019						
Control	16.8 ± 1.31 a	23.8 ± 0.25 a	2.3 ± 0.48 a	106.4 ± 7.76 a	1.3 ± 0.25 a	54.2 ± 1.83 a
HP	9.8 ± 0.48 b	19.0 ± 1.35 b	0.3 ± 0.25 b	48.6 ± 9.01 b	0.0 ± 0.00 b	21.3 ± 2.93 b
PBC	10.8 ± 0.25 b	21.0 ± 1.47 ab	0.5 ± 0.29 b	60.2 ± 8.55 b	0.0 ± 0.00 b	24.1 ± 3.52 b
EM	10.0 ± 0.41 b	21.5 ± 0.65 ab	1.0 ± 0.00 b	52.7 ± 0.36 b	0.0 ± 0.00 b	23.2 ± 0.59 b
LDC	12.3 ± 0.85 b	22.0 ± 0.41 ab	1.0 ± 0.00 b	59.3 ± 2.21 b	0.0 ± 0.00 b	20.9 ± 0.25 b
2020						
Control	20.0 ± 2.35 a	25.0 ± 0.71 a	3.3 ± 0.95 a	151.4 ± 26.64 a	2.3 ± 0.25 a	72.3 ± 3.96 a
HP	8.5 ± 1.04 b	18.8 ± 0.63 c	0.5 ± 0.29 b	52.6 ± 2.45 b	0.3 ± 0.25 b	29.6 ± 5.85 b
PBC	15.5 ± 1.32 a	21.5 ± 0.29 b	1.3 ± 0.48 ab	77.3 ± 2.60 b	1.0 ± 0.00 b	45.1 ± 1.83 b
EM	19.3 ± 0.48 a	22.3 ± 0.25 b	0.3 ± 0.25 b	79.9 ± 9.18 b	0.3 ± 0.25 b	41.9 ± 0.48 b
LDC	15.3 ± 0.85 a	21.0 ± 0.91 bc	1.0 ± 0.00 b	90.5 ± 2.76 b	0.3 ± 0.25 b	41.3 ± 3.02 b

Columns within seasons marked with the same small letters do not differ statistically or significantly according to Tukey HSD tests ($p < 0.05$). The meaning of the parameters is explained in the introductory section.

In the 2020 season, the use of LDC detergent and PBC significantly reduced the number of a.s. with a concentration above the level of 0.005 mg kg^{-1} (25.0 control vs. 18.8 HP, 21.5 PBC, 21.0 LDC and 22.3 EM; Table 6). The results from both seasons were not completely comparable. We believe that a part of the differences could be explained by slightly different weather conditions (see Table 1). In 2020, we had less rain and maybe the rate of pesticide wash-off during the summer rains was lower.

The application of the tested preparations significantly lowered the parameter values of the number of a.s. with a concentration > 10% MRL and the number of a.s. >10% ARFD in both years and with all the tested preparations (see Table 6). The only exception was PBC in the 2020 season (3.3 control vs. 1.3 PBC), where the difference was not significant. These two parameters are less important for fruit growers and are not part of ESC requests.

The parameters ∑% MRL and ∑% ARFD are more important for growers and are the hardest to comply with. Despite the too high number of found a.s., non-compliance with the two aforementioned parameters is most often the reason that apples get rejected by the ESC (confirmed via consultation with fruit producers). In the 2019 season, the application of tested products reduced the value of the parameter ∑% MRL for 48.1% on average (54.3% in HP, 43.4% in PBC, 50.5% in EM, and 44.3% in LDC). This is a very good result. The highest reduction was noticed at the application of HP (106.4 vs. 48.6 in 2019 and 151.4 vs. 52.6 in 2020; see HP Table 6). In the 2020 season, the reduction of the ∑% MRL parameter was comparable to the 2019 season. In HP, a more than 50% reduction was significant (151.4 control vs. 52.6 HP; Table 6). A similar comment can be made for the parameter ∑% ARFD. In the 2019 season, all preparations provided a great and significant reduction in the values of this parameter (control 54.2% vs. 21.3% at HP, 24.1% at PBC, 23.2% at EM, and 20.9% at LDC; Table 6). A similar comment would be adequate for the 2020 season.

Consumer and non-governmental organizations are mostly focused on the ∑% ARFD parameter because they believe that this is a realistic measure of health risk caused by the consummation of apples with multiple residues. This belief does not have a proven scientific background. According to consumer organizations, exceeding the limit of 100% of the ∑% ARFD parameter means that theoretically, some acute negative health impacts could appear after consuming fruits with multiple residues [19,20].

Since the parameters ∑% MRL and ∑% ARFD are the most important for growers and are the hardest to comply with, we checked if apples produced in our trial variants complied with the rules of three supermarket chains (Kaufland Germany, Hofer Austria, Metro Germany). In Table 7, we can see how the application of the tested preparations can help in meeting the requirements of supermarket chains regarding the values of the ∑% MRL and ∑% ARFD parameters. It is evident that the use of HP and PBC made it possible to meet the requirement for the ∑% MRL parameter for Hofer. There was no problem in satisfying the ∑% ARFD requirement because apples from the untreated control also met the ∑% ARFD requirement (max. sum less than 80%). We can make the same comment about the Metro chain as the Hofer chain. The difference is apparent in the Kaufland retail chain, which has stricter requirements for the ∑% ARFD parameter (max. sum less than 50%). Apples from the untreated control treatment do not meet the requirement of the Kaufland trade chain, where the value of the parameter ∑% ARFD should be less than 50%. In this case, we can see that using the tested preparations was beneficial for complying with the rules of the Kaufland company.

Table 7. Information about the compliance of apples produced under different spray regimes, considering the rules of three supermarket chains. Mark C means that the apples comply with the upper limit of the parameter's value, and mark N means that the apples do not comply with the rules.

Variant:	HOFER	HOFER	METRO	METRO	KAUFLAND	KAUFLAND
Rule of Company	**Max. ∑% MRL = 80%**	**Max. ∑% ARFD = 80%**	**Max. ∑% MRL = 80%**	**Max. ∑% ARFD = 100%**	**Max. ∑% MRL = 80%**	**Max. ∑% ARFD = 50%**
2019						
Control	106.4 ± 7.76 N	54.2 ± 1.83 C	106.4 ± 7.76 N	54.2 ± 1.83 C	106.4 ± 7.76 N	54.2 ± 1.83 N
HP	48.6 ± 9.01 C	21.3 ± 2.93 C	48.6 ± 9.01 C	21.3 ± 2.93 C	48.6 ± 9.01 C	21.3 ± 2.93 C
PBC	60.2 ± 8.55 C	24.1 ± 3.52 C	60.2 ± 8.55 C	24.1 ± 3.52 C	60.2 ± 8.55 C	24.1 ± 3.52 C
EM	52.7 ± 0.36 C	23.2 ± 0.59 C	52.7 ± 0.36 C	23.2 ± 0.59 C	52.7 ± 0.36 C	23.2 ± 0.59 C
LDC	59.3 ± 2.21 C	20.9 ± 0.25 C	59.3 ± 2.21 C	20.9 ± 0.25 C	59.3 ± 2.21 C	20.9 ± 0.25 C
2020						
Control	151.4 ± 26.6 N	72.3 ± 3.96 C	151.4 ± 26.6 N	72.3 ± 3.96 C	151.4 ± 26.6 N	72.3 ± 3.96 N
HP	52.6 ± 2.45 C	29.6 ± 5.85 C	52.6 ± 2.45 C	29.6 ± 5.85 C	52.6 ± 2.45 C	29.6 ± 5.85 C
PBC	77.3 ± 2.60 C	45.1 ± 1.83 C	77.3 ± 2.60 C	45.1 ± 1.83 C	77.3 ± 2.60 C	45.1 ± 1.83 C
EM	79.9 ± 9.18 N	41.9 ± 0.48 C	79.9 ± 9.18 N	41.9 ± 0.48 C	79.9 ± 9.18 N	41.9 ± 0.48 C
LDC	90.5 ± 2.76 N	41.3 ± 3.02 C	90.5 ± 2.76 N	41.3 ± 3.02 C	90.5 ± 2.76 N	41.3 ± 3.02 C

Data on supermarket requirements was taken from a publication by Romanazzi et al. [21].

4. Discussion

4.1. Discussion on Effects of Applied Preparations on Pesticide Residue Concentration

The impact mechanisms of the tested products on pesticide removal or dissipation kinetics are different. In HP and PBC, the effects were quite similar to those described in studies on pesticide removal from fruit post-harvest and during processing in the food industry [22–24]. In HP, we expected intense oxidizing effects [25,26], and in PBC, we expected an alkaline hydrolysis effect [27,28]. With the use of LDC detergent, we washed the a.s. away without disintegration effects [28,29], and in microbes, we expected an active disintegration of residues, which can serve the microbes as a source of nutrients [30,31]. In all four LRPs, we influenced the pH values on the fruit surfaces and also the solubility of surface deposits.

LRP preparations were applied separately from the pesticides on the already established pesticide deposit on the fruit surface. The pH of the fruit surface and the pH of the solution of the LRP preparations both influence the decomposition dynamics of pesticide active substance residues, especially those susceptible to alkaline or acidic hydrolysis. We must consider that the pH of the fruit surface changes rapidly and dynamically. The length of the fruit wetness period, the pH of rainwater, the pH of fruit secretions, interactions between different pesticide formulations, and other factors dynamically change the pH on the fruit surface. We estimate that immediately after the application of HP and EM, the pH is slightly acidic; after the application of PBC and LDC, it is slightly basic. Captan and phosmet are well known to be susceptible to alkaline hydrolysis. Our data confirm that when using PBC, where we have the most basic pH, we significantly reduce the residue concentration of these two substances (66–87.6% captan and 50–90.5% phosmet; see Table 3). Intensive alkaline hydrolysis was not expected for dithianon, spinosad, and spinetoram, where the concentrations also fell a lot. The pH parameter also influences the solubility of pesticide residues and impacts washing-off processes.

In all four of the tested preparations, the greatest reduction was most often obtained in the case of a.s. that are contact-acting and do not penetrate deeply into the apple fruit tissue (e.g., captan and dithianon). It was expected that the applied alterative preparations would not interfere with the systemic acting a.s., which penetrate deeply into the apple tissue (e.g., tebuconazole and thiacloprid).

We gave general theoretical expectations regarding the differences in LRP's effect on contact or systemically active pesticide active substances. Different chemical reactions can occur between LRP and pesticides, which we cannot accurately present in detail. We gave an assessment that contact-acting active substances can be removed more easily because they are directly exposed to the action of LRP on the surface of the fruits. Still, we are aware that there are probably certain exceptions related to the pesticides' polarity and water solubility. In the cases of some active substances, it is also difficult to precisely define whether they belong to the group of systemic or contact-acting substances. Such are, for example, active substances that bind strongly to the epidermis of the fruit but do not move rapidly and deeply into the internal tissues of the fruit (e.g., boscalid and pyrimethanil). Surface-acting LRPs have a certain effect on such pesticides, despite the fact that they are already transported into the structure of the peel. The concentration of pesticide residues is the result of decomposition as well as wash-off from the fruit surface. LRPs may be able to break the bonds between the pesticide and the fruit epidermis, and so we have more intensive washing-off during the rain. With HP, there may be a possibility that it also passes into the tissues of the fruit, and it may also react with pesticide residues inside the fruit. What happens in the lenticels, which can be entry points for both pesticides and LRP, is very unclear. If we wanted answers to the questions mentioned above, we would have to carry out much more detailed research and take samples from different layers of the skin and the flesh of the fetus. This was not the purpose of the study.

In the literature, we can find data on the dissipation dynamic of the majority of tested active substances in the period from application to harvest [32–34], and data on the dissipation during storage [35,36], but almost no data are available on the effects of the tested alternative plant protection products on pesticide dissipation dynamics in apples in the preharvest period. Here, we have a lack of information. The available data on dissipation rates after treatment in storage, for example, at dipping apples into water solutions of HP or $NaHCO_3$, cannot be extrapolated to preharvest field conditions. The binding of a.s. onto the peel surface and further penetration into deeper layers of fruit peel is a very complex and dynamic process. The second phase, involving penetration deep into the fruit tissue, can take longer and depends on the weather conditions and structural features of the peel tissues [37]. This is why the time interval between pesticide application and the application of chemicals for the removal of residue plays an important role [38]. In the case of field treatments, we interfere with the penetration process earlier and can maybe remove more residue from the systemic acting pesticides than we can remove later with treatments in the storage facilities. In the case of HP, the exposure time in field conditions is quite short because HP disintegrates fast. It is not comparable to the usual storage dipping of apples. In the case of PBC, the exposure time in field conditions is longer than in usual storage treatments by $NaHCO_3$. The same applies for LDC and EM microbial products.

The highest impact on a.s. dissipation was observed in HP and moderate effects were noticed in PBC. The treatments with detergent or microbes had fewer intensive effects on the reduction of residue concentrations. In LDC, we expected more significant effects because detergents can loosen the structure of waxes on the apple peel and enable an easier disconnection of pesticide a.s. from the wax structures [39]. This could be important in a.s., which bond strongly with wax (i.e., trifloxystrobin, boscalid, fluxapyroxad, pyraclostrobin, pyrimethanil, and fludioxonil). In a published study [39], it was proven that detergents have significant potential to remove the mentioned systemic fungicide in storage treatments with dipping apples in a detergent solution for at least 5 min. A high potential of detergents for the removal of residues was presented in the same study [39]. The authors treated vegetables with specially in-lab-developed detergents. They also stated that there is an urgent need to provide new cleaning agents in the category of detergents, such as low-risk household chemicals or preparations for professional treatments in storage facilities.

Maybe the 10 L dose of LDC per hectare applied in our trial was too low. In some other trials, we observed that six sequential applications of LDC in one-week intervals in the middle of the growing season caused a severe phytotoxicity in pears and Fuji apples (not published). The protective wax layer on fruits and leaves was too far dissolved and the surface tissues were damaged by UV light (we probably induced sunburn). The same results were described by Curkovic, who studied the use of detergents in plant protection [40]. We cannot increase the hectare rate of LDC without running the risk of an increase in phytotoxicity. The microbial decomposition of residues in the preharvest period is a field of research significantly lacking in knowledge. There are almost no studies available that would provide data on the level of microbial disintegration of pesticide residues on fruit surfaces in case of their preharvest application. In our study, the influence of microbes on the dissipation of residues was not comparable to HP and LDC and was only partly comparable to PCB. Microbes can be considered as a relevant factor. For example, in some studies [31], it was shown how efficient yeast-based preparation and bacteria- (*Bacillus*) and fungi (*Trichoderma*)-based products can be useful in the degradation of residues of fluxapyroxad (by yeasts) and penthiopyrad (by fungi) deposited on the surface of apples. We think that the microbes have potential as a preharvest treatment to reduce pesticide residues; this is a neglected and underestimated approach to cope with residue problems. We applied microbes as preharvest agents to replace the use of chemical fungicides (p.e. *Bacillus*, *Aureobasidium*, *Pseudomonas*), but we did not use them to remove residues.

We know there is a constant trend of increasing the application frequency of alternative products in the second part of the growing season in so-called integrated "0.0-residue fruit" or "Clean fruit" production systems [41,42]. Check the concept of "Clean fruit" production at the Clean fruit project site (https://www.eitfood.eu/projects/cleanfruit (accessed on 3 April 2023). The results of our study show that the tested products can interfere with pesticide residue dissipation kinetics and their effects should be considered when anticipating the final level of residues at harvest and further in the planning of the marketing dynamics of individual fruit lots taken out of storage facilities. Many trials are needed to evaluate the real facilitation level of pesticide dissipation dynamics of the tested alternative products. The differences among seasons could be great because of the weather conditions and other factors. The amount of rain is very important after detergent application. Detergent wash efficacy can be increased if we activate a sprinkler irrigation system shortly after detergent application. The apple cultivar is also important, especially the structure and chemical composition of the fruit skin (e.g., properties of epicuticular waxes).

4.2. Discussion about Residue Related Fruit Quality Parameters with Respect to Supermarket Chain Demands

In the introduction section, we mentioned that apple producers have a lot of problems with fully complying with the requirements of supermarket chains. If they reduce the amount of applied pesticides too much, they can suffer unacceptable yield losses in the field and in storage [42,43]. Especially for apples not intended for long-term storage, it is important that they are almost completely residue-free at harvest time. The system we tested is also crucial for producers who market apples under different 0.0-residue brands. In marketing those apples, the producers sometimes provide statements such as "fruits without reportable or measurable residues." In practice, they mean that all residues are at a level lower than 0.01 or 0.005 mg kg^{-1}, sometimes even lower than 0.001 mg kg^{-1}. On the other hand, some consumers believe that the aforementioned claim means that residues are at a level lover than the limit of detection, which could be much lower than 0.001 mg kg^{-1}. So, in relation to the marketing strategy, the goal of modern 0.0-residue apple production systems is to at least get the residue levels lower than 0.005 mg kg or 0.003 mg kg^{-1}. Residues at the mentioned level are, at certain a.s., several hundred times lower than the permissible legal MRL and ARFD values. This is the health preservation contribution of 0.0-residue apple production systems. Many plant protection experts think that the expectations of supermarket chains have gone too far and that they put too much pressure on growers. Supermarket rules are a kind of negation of the state pesticide regulatory systems and the system of toxicological studies carried out during the registration procedures of pesticides. By analyzing the data from our trial, we can see that the application of the tested preparations lowers the number of detected substances and the cumulative $\sum$% MRL and $\sum$% ARFD values as well (see Tables 6 and 7). It seems that the use of the four tested preparations can actually help apple producers to fulfilll the requirements of supermarket chains. The greatest effect in lowering the parameter values was observed in treatments with HP. The results of the trials studying the $\sum$% MRL and $\sum$% ARFD parameters depend on the composition of the spray program and directly on the portion of substances that can be more easily removed (some contact-acting pesticides) vs. substances that enter deep into the fruit tissue. If we want to develop this system further, we need good planning of which a.s. to apply at certain parts of the season and which alternative products can be applied to facilitate its degradation. Therefore, we can make a predictive pre-calculation of residue concentrations to see if we are able to fulfill the demands of the supermarket chains. Software support to do this is already under development. An example of such smartphone software available for assisting grape growers is available on the Aplicación Móvil Control Plaguicidas website (https://twgroup.cl/portfolio/laboratorio/ (accessed on 3 April 2023).

4.3. Discussion about the Feasibility of Our Residue Removal Approach

The first step in further developing the presented approach is a full official registration of the products we have tested and many other potential candidate products for application in orchards. The purpose given at registration, presumably in the category of low-risk substances, could be the control of pests and diseases or plant biostimulation, and the pesticide residue removal could be listed as a side effect of their use. The registration status "product for removal of pesticide residues" still does not exist in EU legislation. Maybe this category of products could be developed under the umbrella of GRAS products (generally recognized as safe) [44]. The fastest method to legally obtain the approval for use would be potassium carbonate, which is already registered for use in apples. Sodium carbonate ($NaHCO_3$) is a well known agent for removing pesticide residues [29]. We tested it in previous field trials and found that it is much more phytotoxic than $KHCO_3$ and is therefore not as useful for field treatments as potassium carbonate. Both carbonates can be classified in the GRAS category of products.

Some questions arose during research. For example, a question arose about the toxicological effects of byproducts that develop during the reactions between pesticides and tested chemicals and microbes. Are those metabolites safe or do they also pose a health risk? We do not have answers to that. Metabolites should be analyzed and checked toxicologically. For HP and PBC, the common opinion is that treated fruits are safe for humans [45,46], but for EM microbes and detergent, there is much less data available. Detergents are used in the post-harvest manipulation of fruits, so we do have certain sets of data on the safety of the procedures in which they are used [47]. In the field of detergents, there are no notable developments in new regulatory procedures to register them for plant protection purposes. It is expected that they fit into the category of low-risk substances. Some drawbacks for the broader acceptance of detergents as low-risk plant protection products are presented in published research [40]. It was also mentioned that some detergents are less risky than others.

LRP products are used shortly before harvesting. For this reason, we certainly have some of their remains on the fruit surface when harvesting apples. There is absolutely no residue after the application of HP because it completely disintegrates in a short time. With PCB, we have residues that are certainly not harmful because the preparation has an official registration for the treatment of apple trees (in the preharvest periods as well). PCB is also a food additive. We know that fruit growers in some countries use LDC to remove honeydew from the fruit before harvesting. Some remains are definitely present on the fruit surface at harvest. Considering that LDC is allowed for application on the human body, we do not expect a high level of adverse effects from the remains on fruits. We know there is no relation between the acceptance of the substance as body contact material and the substance that can be ingested in a certain low amount. The use of EM microbial preparation is the most uncertain because there is a lack of information on the possible adverse effects of microbes. With microbes, concerns about the adverse impacts on tree microbiota and about the problem of the potential acceleration of antibiotic resistance in plant and human pathogenic bacteria may arise [48,49]

Special studies are needed to determine the risks of microbial inoculation and inhabitation of apples for consumers. EM microbial products were developed as biostimulants for use at the beginnings of seasons and not for preharvest treatments. Allergies can be one negative side effect of microbe application to fruits during preharvest [50]. EU regulations on the registration of biological microbe-based pesticides are becoming stricter and treatments with microbial biostimulants, such as EM products, will probably not be allowed in preharvest periods without passing through suitable risk evaluation procedures. This demand was already presented many years ago and is still in place [51].

Another important question is: what effects do the tested products have on fungal storage diseases? In the case of detergents, we know that they can partially dissolve the plant and fruit cuticle, which can make fruits more vulnerable to pathogen attacks during storage [52]. In storage treatments, detergents are purposefully used to dissolve surface waxes to partially increase the exposure of microorganisms to chemicals (p.e. to chlorine) [47]. Detergents partly remove fungicides, which protect fruits against microbes in storage. For example, we noticed a significant disintegration of fludioxonil, which is applied to protect fruit during storage. The treated apples from our trail plots were put in storage at a limited amount and the development of storage diseases was monitored. Treatments with tested preparations did not have an effect on the number of apples that were attacked by fungi from the genera *Penicillium*, *Botrytis*, *Neofabrea*, *Monilia,* and others. These effects should also be studied in detail to make sure that we do not cause an increase in fungal-caused storage diseases induced by cuticle damage. Potential yield loss and additional costs with the spray program can significantly impact the feasibility of the approach. The cost of four applications of LRPs varies between countries and is estimated to be between 190 and 310€ ha^{-1}. This is a relevant cost, but we must also consider the financial loss that occurs if we cannot market the apples because of their non-compliance with supermarket chain rules.

5. Conclusions

The data on the lowered concentrations of pesticide residues in apples treated with the tested preparations show that their potential to remove a significant proportion of pesticide residues prior to harvest is worth considering. Due to the high variability of residue concentrations found in fruits in field conditions, differences between treated and control plots were often not statistically significant, but we nonetheless believe that the studied preparations could serve as a fairly safe and simple method of reducing pesticide residues before harvest and thus enable fruit growers to meet the requirements of supermarket chains much more successfully. The demonstrated approach could also be helpful for those fruit producers who want to market their fruit as having lower residue levels than the existing requirements of supermarket chains and who are developing new strategies for branding 0.0-residue fruit. The levels of residue reduction and the lowering of the ∑% MRL and ∑% ARFD parameters are significant enough for us to consider the tested approach to be a contribution to lowering consumer exposure. Fruit production can move closer to consumer requirements, keeping in mind that a certain, mostly acceptable, risk of yield losses remains. However, with the help of such preparations, we are supporting the sustainable use of conventional pesticides, which are still the backbone of food security, despite the public's great desire to stop using them. The problem of residues on fruit has the most powerful effect on the development of strong public rejection of pesticide use. By using our approach, we do not need to reduce plant protection product application too much during the primary pest control season, because at the end of the season, we have a tool to remove a significant portion of residues in order to meet the requirements of the ESC. We believe that the presented approach deserves further study and development. Maybe producers of plant protection products themselves can provide preparations for the safe removal of residues at the end of the season, or they can develop special product formulations for usage in the second part of the growing season, which have different dissipation kinetics than the formulations of the same a.s. intended for use in the first part of the season. For example, in certain fungicides, we have additives that enable a strong binding of a.s. in order to peel waxes and to obtain the required resistance of fungicide deposit against rain washing. This kind of additive is useful for the first part of the season, but it is not suitable for treatments in the last part of the season for fruits that will not be stored for a long time.

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