

Article

The Effectiveness of Synthetic and Inorganic Substances in Different Apple Scab Control Strategies

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Abstract: A two-year trial (2021 and 2022) was performed with five different fungicide and foliar fertiliser application strategies to control apple scab (*Venturia inaequalis*) in integrated apple orchards in Latvia. A strategy of using inorganic fungicides or combining them with synthetic fungicides was compared to a strategy of applications with only synthetic fungicides and untreated control. Furthermore, two strategies included foliar fertilisers to determine whether they may affect apple scab used alone or combined with synthetic fungicides. The timing of the fungicide applications was based on the risk forecasted by the decision support system RIMpro, and fertilisers were used at certain growth stages of the crop. The disease incidence on untreated fruits on cv. Auksis ranged from 38.3% to 59.6%, and on cv. Ligol from 99.3% to 99.5%. Strategies including synthetic fungicides were the most effective against scab on shoot leaves and fruits. The strategy using only inorganic fungicides was effective for low-inoculum orchards. Combining synthetic and inorganic fungicides provided the best apple scab control strategy on fruits, likely helping reduce the resistance selection pressure and residues of synthetic fungicides. Foliar fertilisers were insufficient to control apple scab; they would supplement existing scab fungicide programs.



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Keywords: fungicides; fertilisers; *Venturia inaequalis*; decision support system RIMpro

1. Introduction

Apple scab, caused by the pathogen *Venturia inaequalis* (Cooke) G. Wint., causes economic losses in apple production areas worldwide, and intensive fungicide usage is necessary for commercial apple production [1]. With the cultivation of susceptible apple cultivars, disease control becomes more complex, and losses may amount to more than 70% if no control measures are applied [2]. There is a growing concern over the continuous use of synthetic pesticides on food crops because of their potential effects on human health and the environment [2]. To make agriculture more sustainable and reduce further loss of biodiversity, the European Union has developed the “farm-to-fork strategy” aiming to reduce the amounts and risks of pesticides by 50% by 2030 (based on use in 2015–2017) [3]. Fungicide resistance is another factor complicating the continuous use of synthetic fungicides [4–6]. Synthetic fungicides used to control apple scab in Latvia primarily come from four groups: quinone outside inhibitors with high resistance risk, aniline-pyrimidines, demethylation inhibitors, and guanidines associated with high to medium resistance risk [7,8]. There is a worldwide trend to investigate the efficacy of alternatives to synthetic fungicides in managing plant diseases, and farmers are advised to adjust their spray programs accordingly, especially during the season for secondary dissemination of inoculum [9,10].

One possible adaptation in the season's second part is that the frequent use of inorganic substances is allowed in organic apple production [11]. This approach is introduced in so-called zero residue fruit production systems [12,13]. Alternatives to synthetic fungicides may be inorganic substances like copper fungicides, lime sulphur, and wettable sulphur, commonly used in the early 1900s [14,15]. They are primarily associated with a protective effect against *V. inaequalis*; however, lime sulphur was tested and proved effective and to have a curative effect against apple scab [16]. Bicarbonate salts are one of the alternative control options widely tested in recent decades [2,17,18] but have been registered in Latvia only since 2022 [8]. Inorganic fungicides are characterised by multi-site contact activity and are typically considered to have no risk of developing fungicide resistance [7].

Foliar fertilisation of apple trees can complicate the management of pests, particularly diseases. Foliar urea applied between the advanced bud break and calyx stages to stimulate tree growth may also suppress apple scab [19,20]. Foliar calcium chloride, used to suppress calcium deficiency, will partially suppress scab on leaves and fruits [21]. In plant protection, boron has a recognised effect in inhibiting fungal infections, including apple scab, to the point where a foliar application of boron could replace a fungicide treatment [22]. There is a need to develop a strategy involving inorganic preparations and fertilisers to control apple scab, considering local seasonal conditions and local cultivars.

This study aimed to establish a treatment strategy, including using inorganic fungicides and foliar fertilisers to control apple scab and reduce fungicide residues and the risk of developing fungicide resistance.

2. Materials and Methods

2.1. Experimental Design

A two-year trial (2021 and 2022) was performed in Latvia in integrated apple orchards with apple cvs. Ligol and Auksis in Jelgava and Smiltene, respectively. The orchard with cv. Ligol had a high inoculum potential; it had been sprayed intensively over several years, and a decrease in sensitivity to cyprodinil and difenoconazole was detected in the *V. inaequalis* population in 2020 [6]. In the orchard with cv. Auksis, no fungicides had been applied before. Both cultivars were on rootstock B 396, were planted in 2014 and pruned to a pyramidal shape to an average height of 2.5 m. The planting distance in the cv. Ligol orchard was 5×1.2 m and in cv. Auksis it was 5×3.0 m. In the former planting, the soil was a sandy loam containing 3.2% organic matter, with a pH of 7.1, and the latter planting had a sandy clay soil with 2.8% organic matter and a pH of 5.5. Weeds were controlled mechanically using a mower in cv. Ligol and geotextile covering the soil in cv. Auksis. Applications against insects and mites were performed in all plots, including the non-fungicide-treated controls. None of the trial sites received additional fertilisation maintenance during the two-year experimental period. The trials were organised in a randomised complete block design with four replicates in cv. Ligol and three in cv. Auksis. Each plot consisted of 6 trees in a row, and the plot size was 36 m² in cv. Ligol and 45 m² in cv. Auksis.

2.2. Fungicide and Fertiliser Strategies

Five different fungicide and foliar fertiliser strategies were applied to control apple scab (Table 1). The strategy using inorganic fungicides (InFu) or combining them with synthetic fungicides (SyInFu) were compared to a strategy of applications with only synthetic fungicides (SyFu) and an untreated control (UC). Two strategies included foliar fertilisers to determine whether they may affect apple scab used alone or combined with synthetic fungicides. Fertilisers were applied separately in one strategy (Fer) or used in a tank mix with fungicides (SyFuFer). Foliar fertilisation with sulphur, intended to have a fungicidal effect, was used only in the InFu and SyInFu strategies in a tank mix with potassium bicarbonate (Table 1). Dosage and timing of synthetic and inorganic fungicides and foliar fertilisers used in the experiments is shown in Table 2.

Table 1. Synthetic and inorganic fungicides and foliar fertilisers used in different apple scab control strategies.

Type of Product	Strategy				
	Fer	SyFu	InFu	SyInFu	SyFuFer
Synthetic	x	captan ¹	x	captan	captan
	x	cyprodinil	x	cyprodinil	cyprodinil
	x	dodine	x	dodine	dodine
	x	difenoconazole	x	difenoconazole	difenoconazole
Inorganic	x	x	copper (II) hydroxide	copper (II) hydroxide	x
	x	x	sulphur	sulphur	x
	x	x	potassium bicarbonate	potassium bicarbonate	x
	x	x	lime sulphur	lime sulphur	x
Foliar fertilisers	nitrogen ²	x	x	x	nitrogen
	calcium	x	x	x	calcium
	boron	x	x	x	boron

¹ The fungicide formulations used and the registered rates applied were: cyprodinil as Chorus 50 WG at 450 g ha⁻¹; dodine as Syllit 544 SC at 1250 mL ha⁻¹; captan as Merpan 80 WG at 1800 g ha⁻¹; difenoconazole as Score 25 EC at 200 mL ha⁻¹; copper (II) hydroxide as Champion 50 WG at 1000 g ha⁻¹, potassium bicarbonate as VitiSan at 5000 g ha⁻¹, lime sulphur as Curatio at 5000–12,000 mL ha⁻¹. ² The fertiliser formulations used and rates applied were: sulphur as Kingfol S 72% at 4000 mL ha⁻¹, nitrogen as Urea 46% at 3000 g ha⁻¹, calcium as YaraVita Stopit at 7200 mL ha⁻¹, boron as Borax 11.3% at 1200 g ha⁻¹.

Table 2. Dosage and timing of synthetic and inorganic fungicides and foliar fertilisers used in the experiments.

Type of Product	Active Substance	Dosage, kg or L ha ⁻¹	Timing
Synthetic	captan	1.80	preventive ¹ /germination window ² , BBCH 51-85
	dodine	1.25	preventive/germination window, BBCH 53-77
	difenoconazole	0.20	curative ³ , BBCH 61-84
	cyprodinil	0.45	curative, BBCH 55-85
Inorganic	copper (II) hydroxide	1.00	preventive, BBCH 51-53
	potassium bicarbonate	5.00	germination window/curative, BBCH 53-83
	lime sulphur	5.00/12.0	germination window/curative, BBCH 53-83
Foliar fertilisers	sulphur	4.00	preventive/germination window, BBCH 53-83
	nitrogen	3.00	BBCH 53-69
	boron	1.20	BBCH 59-73
	calcium	7.20	BBCH 69-85

¹ preventive: treatment shortly before the rain; ² germination window: treatment during ascospore germination; ³ curative: treatment after infection.

All sprays were applied with a motorised backpack sprayer (STIHL SR-430, Waiblingen, Germany). Tree-Row-Volume (TRV) was calculated to determine foliage volume and the amount of required water; 426 L ha⁻¹ in cv. Ligol and 526 L ha⁻¹ in cv. Auksis. Fungicide rates and growth stages followed the list of plant protection products registered in Latvia [8].

2.3. Decision Criteria for Fungicide and Fertiliser Usage

The decision of the exact time for applications with inorganic and synthetic fungicides during the primary infection period (period of ascospore release of *V. inaequalis*) was supported by the decision support system (DSS) RIMpro [23,24]. RIMpro predicts apple scab infection risks based on biological information about the pathogen and weather data (Figure 1). Weather stations equipped with air and soil temperature, precipitation, leaf wetness, relative humidity, and solar radiation sensors were placed in each orchard. In cv. Auksis, it was an iMETOS IMT 300 (Pessl Instruments, Weiz, Austria), and in cv. Ligol, the weather station was a Davis Vantage Pro2 (Davis Instruments, Hayward, CA, USA).

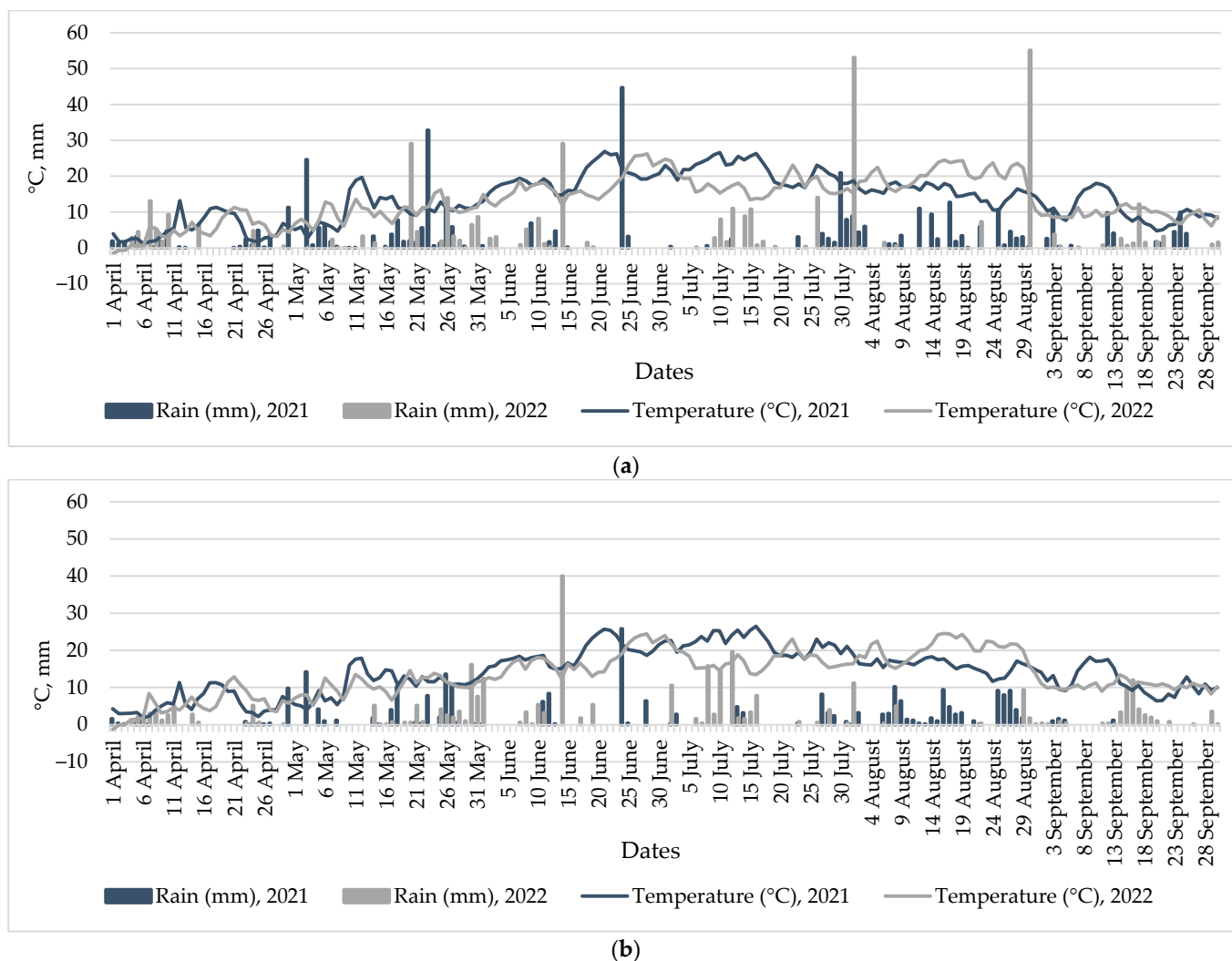


Figure 1. Weather data: (a) daily weather data in 2021 and 2022 in cv. Auksis; (b) daily weather data in 2021 and 2022 in cv. Ligol.

Preventive treatments were applied shortly before rain and a predicted infection or preferably during the germination window, i.e., on wet leaves after a significant release of ascospores had ceased in the daytime but before the infection occurred in the evening. Curative treatments were carried out on dry leaves within 24 h after infection [24].

After the primary infection period had ended, the decision on the need for fungicide applications was made depending on scab monitoring at specific intervals. Inorganic fungicides in the SyInFu strategy were preferred during the secondary infection period (period of conidia dissemination). The exception was in 2022, when all treatments were applied with cyprodinil in cv. Ligol at the very end of the season due to the high prevalence of scab. Fertilisers were applied at key phenological stages of the crop [25]. Nitrogen was used five times, every five to ten days from bud burst (BBCH 53) to the end of flowering (BBCH 69). Calcium was applied starting from the end of flowering. This treatment was repeated every ten days for the first month and later at a more extended frequency based on potential rain wash-off; altogether, it was applied five times. Boron was applied at the pink bud stage (BBCH 59), at the end of flowering, in early June and at mid or end of June; altogether, it was applied four times.

2.4. Disease Incidence and Severity on Leaves and Fruits

For leaf incidence assessments, leaves on 10 terminal shoots per replicate were assessed on 14 and 13 July in 2021 and 2022, respectively, in cv. Auksis, and 29 and 30 June in 2021 and 2022, respectively, in cv. Ligol. Observations were made on 10 older, fully developed leaves close to the shoot base for each terminal shoot. Incidence and severity assessments of fruit were recorded every three weeks by counting the number of infected fruits and visually estimating their percentage of diseased areas. Leaf and fruit incidence was calculated as the proportion of infected leaves with at least one scab lesion. Scab severity on fruits was assessed using a percentage scale: 0, 5, 15, 30, 50, 75, 90, 100. At the last assessment at harvest, the area under the disease progress curve (AUDPC) was calculated [26]. Incidence and AUDPC values using severity data of scab were calculated using ARM software version 2022.3 (GDM Solutions, Inc., Brookings, SD, USA).

2.5. Yield Evaluation

Fruits were harvested on 30 August 2021 and 19 September 2022 in cv. Auksis, and 11 October 2021 and 7 October 2022 in cv. Ligol. The yield was characterised by the weight of all harvested fruits from four trees in each replicate and was divided into standard and non-standard. In our experiment, the standard category, including extra, I and II classes, was defined as fruits with a scab severity of $<1 \text{ cm}^2$, russet $< 30\%$, no insect damages and fruit size $> 60 \text{ mm}$ [27]. Fruit russeting was evaluated on 100 fruits per replicate, using a scale of 1 to 3, where 1 = no russeting; 2 = $<30\%$ slight russeting; and 3 = 30–100% severe russeting on the fruit surface area [28].

2.6. Fungicide Residues

At harvest, fruit samples, i.e., 1000 g each, were taken from treatment strategies UC, SyFu and SyInFu in both trial years to detect fungicide residues. Fruit samples were packed and sent immediately to the laboratory after harvest. Fruit samples were analysed by Water & Life Lab (Entratico, Italy) for identification of pesticide residues via susceptible analytical methods based on liquid or gas chromatography, coupled with mass spectrometry by 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” [29]. Data on a maximum residue level (MRL) were taken from the EU Pesticide Database [30].

2.7. Statistical Analysis

The data were analysed using ARM software version 2022.3 (GDM Solutions, Inc., Brookings, SD, USA), and the Student–Newman–Keuls multiple range test was applied to determine significant differences between treatments ($p \leq 0.05$). Years and cultivars were analysed separately for each variable.

3. Results

3.1. Evaluation of the Fungicide and Fertiliser Treatment Strategies

During the experimental periods in 2021 and 2022, there were several primary infection risks (Tables A1–A4). The first scab symptoms on leaves in untreated plots appeared in the last week of May during flowering in cv. Ligol and in the first week of June after the flowering in cv. Auksis. The incidence of scab was considerably higher on cv. Ligol than on cv. Auksis (Tables 3 and 4).

Treatments with synthetic fungicides alone, combined with inorganic substances and fertilisers, significantly decreased leaf disease incidence compared with the untreated control on cv. Auksis in 2021. There was no significant difference in leaf disease incidence between untreated control, fertilisers and inorganic substances alone. All treatments, except for the fertiliser strategy, significantly decreased disease incidence on fruits compared to untreated plots in 2021. The AUDPC values of the treated plots were significantly lower than the untreated control, except for the fertiliser strategy in 2021 (Table 3). There was a tendency for better results for all treatments, except the fertiliser strategy, in comparison

with the untreated control in 2022, both for incidence and AUDPC values on fruits, but without significant difference due to high data dispersion. In 2021, yield was low due to cool weather conditions during spring, without significant differences between treatments. In 2022, the reference treatment with synthetic fungicides and fertilisers had the highest yield, but there was no significant difference from the other treatments (Table 3). The non-standard yield in the untreated control was significantly higher than that of all the treatment strategies.

Table 3. Effect of different fungicide treatment strategies on the incidence of apple scab on leaves and fruits, the area under the scab progress curve (AUDPC), and standard and non-standard yield in cv. Auksis, 2021–2022.

Strategy	Year									
	2021					2022				
	Shoots Leaves	Fruits		Yield, t ha ⁻¹		Shoots Leaves	Fruits		Yield, t ha ⁻¹	
Incidence (%)	Incidence ³ (%)	AUDPC ⁴	Standard	Non-Standard	Incidence (%)	Incidence (%)	AUDPC	Standard	Non-Standard	
UC ¹	27.7 a ²	59.6 a	690.0 a	0.2 a	0.2 a	12.7 a	38.3 a	126.8 a	6.1 a	0.7 a
Fer	30.0 a	37.7 ab	437.0 ab	0.4 a	0.1 a	15.3 a	19.7 a	54.6 a	10.0 a	0.3 b
SyFu	0.3 b	0.00 c	0.9 b	0.9 a	0.3 a	0.7 a	0.0 a	0.0 a	10.6 a	0.3 b
InFu	17.7 ab	14.8 bc	133.1 b	0.6 a	0.1 a	1.7 a	3.0 a	23.8 a	9.1 a	0.3 b
SyInFu	2.7 b	0.7 c	2.3 b	1.0 a	0.2 a	1.7 a	0.3 a	0.0 a	10.3 a	0.2 b
SyFuFer	3.0 b	0.0 c	0.0 b	1.0 a	0.2 a	1.7 a	1.0 a	0.1 a	14.6 a	0.22 b
LSD $p \leq 0.05$	14.8	24.2	331.3	0.7	0.2	16.6	26.1	136.1	9.3	0.3
SD	8.1	13.3	182.1	0.4	0.1	9.1	14.4	74.8	5.1	0.2

¹ UC–untreated control; Fer–foliar fertilisers; SyFu–synthetic fungicides; InFu–inorganic fungicides; SyInFu–synthetic + inorganic fungicides; SyFuFer–synthetic fungicides + foliar fertilisers; ² means followed by the same letter do not differ significantly ($p \leq 0.05$, Student–Newman–Keuls method); ³ assessment during harvest; ⁴ the area under the scab progress curve consists of a quantitative summary of the disease severity on fruits, assessments were performed four times.

Table 4. Effects of different fungicide treatment strategies on incidence of apple scab on leaves and fruits, the area under the scab progress curve (AUDPC), and standard and non-standard yield in cv. Ligol, 2021–2022.

Strategy	Year									
	2021					2022				
	Shoots Leaves	Fruits		Yield, t ha ⁻¹		Shoots Leaves	Fruits		Yield, t ha ⁻¹	
Incidence (%)	Incidence ³ (%)	AUDPC ⁴	Standard	Non-Standard	Incidence (%)	Incidence (%)	AUDPC	Standard	Non-Standard	
UC ¹	71.5 a ²	99.5 a	2458.5 a	2.3 a	3.1 a	83.0 a	99.3 a	3134.7 a	2.9 c	13.7 a
Fer	75.8 a	98.6 a	2629.8 a	2.1 a	2.8 a	77.3 a	94.0 a	2607.4 a	7.5 c	13.6 a
SyFu	24.5 bc	60.7 b	634.9 b	5.1 a	1.3 a	41.5 b	62.0 b	555.5 b	30.7 a	12.5 a
InFu	31.3 b	79.1 ab	921.2 b	4.0 a	1.1 a	43.0 b	66.5 b	942.7 b	17.2 b	13.8 a
SyInFu	10.3 bc	27.4 c	340.7 b	11.1 a	1.0 a	33.0 b	59.3 b	522.8 b	19.7 b	9.6 a
SyFuFer	3.8 c	35.1 c	579.6 b	9.5 a	1.1 a	38.0 b	64.0 b	791.8 b	25.5 ab	13.6 a
LSD $p \leq 0.05$	18.7	21.4	847.5	9.6	1.9	13.9	23.4	879.9	7.5	7.0
SD	12.4	14.1	554.8	6.4	1.2	9.2	15.6	583.8	5.0	4.6

¹ UC–untreated control; Fer–foliar fertilisers; SyFu–synthetic fungicides; InFu–inorganic fungicides; SyInFu–synthetic + inorganic fungicides; SyFuFer–synthetic fungicides + foliar fertilisers; ² means followed by the same letter do not differ significantly ($p \leq 0.05$, Student–Newman–Keuls method); ³ assessment during harvest; ⁴ the area under the scab progress curve consists of a quantitative summary of the disease severity on fruits, assessments were done six times.

For cv. Ligol, all treatments significantly decreased disease incidence on leaves and fruits compared to untreated plots (Table 4), except the treatment with fertilisers only. Combinations of synthetic and inorganic substances or fertilisers gave lower disease incidence and lower AUDPC values on fruits on cv. Ligol in 2021 in comparison with the other

treatments and the untreated. Treatments with inorganic substances applied alone were generally less effective than those including synthetic fungicides in both years (Table 4).

In 2021, the yield on cv. Ligol was low due to cool weather conditions during spring, without significant differences between treatments. There was a tendency for higher yield in strategies with synthetic fungicides combined with inorganic substances and fertilisers. In 2022, all strategies except fertilisers resulted in significantly higher yields in cv. Ligol compared to the untreated control (Table 4). The best results showed strategies with synthetic fungicides and synthetic fungicides combined with fertilisers.

3.2. Fruit Russetting

Fruit russetting was observed on both cvs. Auksis and Ligol in 2022, but it was not assessed in 2021. In cv. Auksis, a higher proportion of apples had slight and severe russetting symptoms than cv. Ligol (Figure 2). Inorganic substances are known to induce russetting, which was observed in both trials. In cv. Auksis, the proportion of apples with severe russetting symptoms (Figure 3) was significantly higher in the strategies with inorganic substances included. In cv. Ligol, strategies using inorganic substances significantly increased the number of apples with slight russetting symptoms.

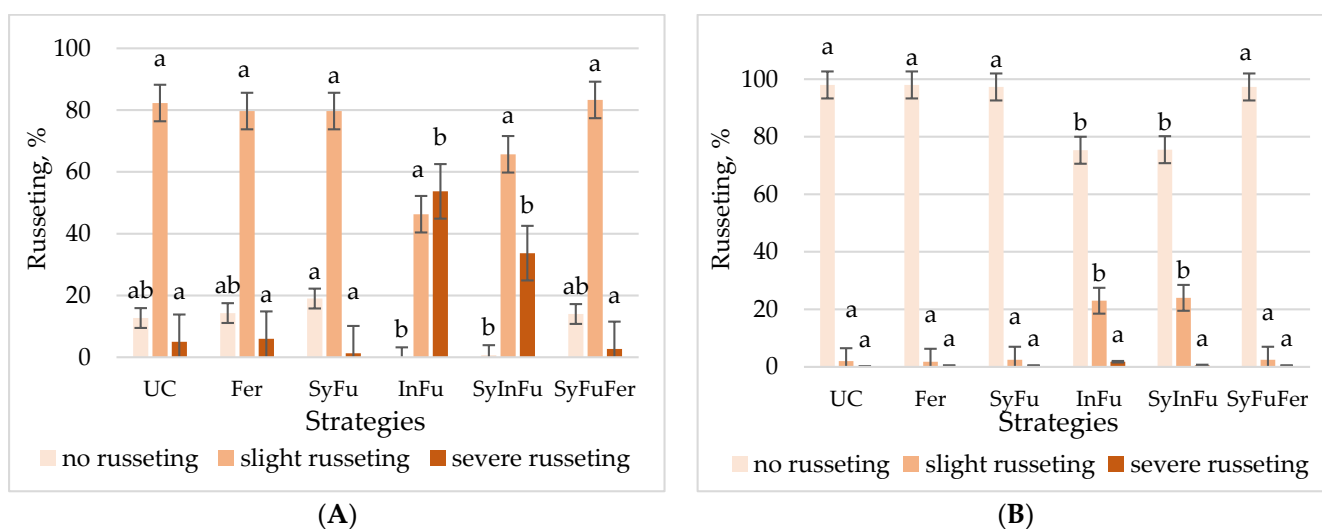


Figure 2. The apple russetting in fungicide treatment strategies on fruits of cv. Auksis in 2022 (A). The apple russetting in fungicide treatment strategies on fruits of cv. Ligol in 2022 (B). UC—untreated control; Fer—foliar fertilisers; SyFu—synthetic fungicides; InFu—inorganic fungicides; SyInFu—synthetic + inorganic fungicides; SyFuFer—synthetic fungicides + foliar fertilisers. Means followed by the same letter do not differ significantly ($p \leq 0.05$, Student–Newman–Keuls method).

3.3. Fungicide Residues

Residues of captan (captan sum and THPI, expressed as captan) were found in fruits of both cv. Auksis and cv. Ligol in 2021, and cyprodinil was found on the fruit of cv. Ligol in 2022 (Table 5). The highest concentration of captan, 0.560 mg kg^{-1} , was detected in cv. Auksis in the strategy with synthetic fungicides, 34 days after the last treatment. In cv. Ligol in 2021, captan was detected in the strategy with synthetic fungicides and these were combined with inorganic substances; respectively, 0.100 and 0.018 mg kg^{-1} , 81 and 132 days after the last treatment. Cyprodinil was detected in the strategy with synthetic fungicides and combined with inorganic substances, 0.100 and 0.040 mg kg^{-1} , respectively, 32 days after the last treatment in 2022.



Figure 3. The negative aspects of inorganic fungicide treatment strategies on cv. Auksis in 2022: severe russetting on fruit.

Table 5. The types and levels of the fungicide residues in apple samples (mg kg^{-1}), days from the last treatment to harvest, and the amount of active substance used in the strategy.

Year	Cultivar	Strategy	Detected Fungicide Residues	Amount (mg kg^{-1})	LOQ ² (mg kg^{-1})	MRL ³ (mg kg^{-1})	Days from the Last Treatment to Harvest	Amount of Active Substance Used (kg ha^{-1})
2021	Auksis	SyFu ¹	captan	0.560	0.01	10	34	5.76
			SyInFu	captan	0.042	0.01	10	79
2021	Ligol	SyFu	captan	0.100	0.01	10	81	4.32
			SyInFu	captan	0.018	0.01	10	132
2022	Ligol	SyFu	cyprodinil	0.100	0.01	2	32	0.68
			SyInFu	cyprodinil	0.040	0.01	2	32

¹ SyFu—synthetic fungicides; SyInFu—synthetic + inorganic fungicides; ² LOQ—limit of quantification; ³ MRL—maximum residue level.

4. Discussion

The present study demonstrated the efficacy of five fungicide and foliar fertiliser application strategies with commonly used synthetic and inorganic substances at key infection risk periods and crop phenological stages. The overall incidence of scab was much higher in cv. Ligol, possibly because of three factors: (1) cv. Ligol is more susceptible to scab than cv. Auksis [31]; (2) there was a high inoculum potential from the previous seasons; and (3) a reduction in sensitivity to cyprodinil and difenoconazole was detected in the *V. inaequalis* population in 2020 [6]. In both years in both trials, the strategies, including synthetic fungicides, were the most effective against scab on shoot leaves and fruits. In the trial on cv. Auksis, the strategy with only inorganic fungicides used seven times showed sufficient activity against apple scab, but eight to ten treatments did not provide acceptable control in cv. Ligol in 2021. Most likely, applications of inorganic substances should be more intensive in orchards with susceptible cultivars and high inoculum potential. In organic apple orchards, 10–26 sprays with inorganic substances may be applied in each season, depending on cultivar susceptibility, weather conditions and inoculum pressure [32], while synthetic fungicides may be used 6–20 times [31,33,34]. Although inorganic fungicides showed activity against apple scab in both cultivars, they caused notable fruit russetting only in cv. Auksis, which is known as a russet-susceptible cultivar. Lime sulphur-based fungicides are highly caustic and can injure the tree, causing phytotoxic burning and russetting of the fruit [35]. Depending on the climatic conditions during application, copper-

and sulphur-based products can also cause severe damage to leaves and fruit. A previous study in South Tirol, Italy, found that potassium bicarbonate also increased percent of severe fruit russeting [36]. In our study of combining synthetic and inorganic fungicides, the first treatment was applied with copper; synthetic fungicides were used during the primary infection period, followed by inorganic substances during the season for secondary dissemination of inoculum. The average number of treatments of synthetic and inorganic substances in cv. Auksis was 3.5 each; in cv. Ligol the numbers were 4 and 5.5, respectively. In both years in cv. Ligol, combining synthetic and inorganic fungicides resulted in less fruit scab at harvest compared to synthetic fungicides alone. In a field experiment conducted in the Trentino region of Italy, it was also concluded that a strategy that integrates inorganic fungicides with synthetic fungicides is possible, and it will permit a reduction of the dependence as well as the resistance selection pressure of synthetic fungicides [37]. A positive aspect should be mentioned: fungicide residues found in this study were in lower concentrations in the combined strategy than if only synthetic fungicides were used. Furthermore, synthetic fungicides were not significantly better than other treatments, except for fertilisers used alone, which may be explained by reduced sensitivity to systemic fungicides in this orchard. Our results showed that the strategy using only foliar fertilisers eight to ten times provided slight control of apple scab on fruits in some cases compared to untreated control; however, without an economically acceptable outcome. These research findings confirm that calcium-based fertilisers suppress scab. A previous UK study found that calcium-based fertilisers suppress scab, but calcium alone should not be used as a replacement for synthetic fungicides [21]. Although boron fertiliser was also included in the fertilisers strategy, the application schedule may not have been intense enough to reach sufficient results. Boric acid applications at 10 day intervals from 90% petal fall until harvest reduced scab on leaves and fruit [22]; however, in our study, boron fertiliser was used only four times per season. As a disadvantage of boron, limitations are using it during full bloom, which is often a key stage of apple scab control [22]; this means that other substances would be essential at this time. In our study, we used foliar application with urea within this period. Urea applications to the orchard floor in the fall are a well-known scab reduction strategy [38,39], mainly from older studies that foliar urea applied early in the season can help suppress scab inoculum in spring [19,20]. It should be noted that since urea was one of several foliar fertilisers included in the strategy, it was impossible to evaluate their effectiveness alone. Apple scab incidence and AUDPC values were higher using only foliar fertilisers compared to other strategies, likely requiring more frequent applications and higher dosages, but still considering that severe infection periods require fungicides. Although the strategy with synthetic fungicides combined with foliar fertilisers did not show a clear significant difference compared to the strategy with only synthetic fungicides, we would see more potential to use foliar fertilisers in rotation with synthetic fungicides as part of integrated pest management (IPM) than to rely only on them.

5. Conclusions

This research shows that strategies, including synthetic fungicides, were the most effective against scab on the leaves and fruits of apples. Using only inorganic fungicides would be suitable for low-inoculum orchards and apple cultivars that are not sensitive to russeting. Combining synthetic and inorganic fungicides provides the best apple scab control on fruits and helps reduce the resistance selection pressure and potential residues of synthetic fungicides. Foliar fertilisers are insufficient to control apple scab; however, if further investigated they may be a useful supplement in existing scab fungicide programs.

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Appendix A

Table A1. Treatment dates of synthetic and inorganic fungicides and foliar fertilisers used in different apple scab control strategies at certain growth stages and infection periods in cv. Auksis in 2021.

Treatment Date	Growth Stage *	Infection Period	Infection Severity	Treatment	Fungicides/Fertilisers				
					Fer	SyFu	InFu	SyInFu	SyFuFer
1 May	54	5–7.05	L	Prev.	N	Dodine	Copper	Copper	Dodine + N
15 May	57	14–29.05	S	Germ.	N	Dodine	Bicarb. + S	Dodine	Dodine + N
20 May	59	14–29.05	S	Cur.	N + B	Cyp.	L. sulph.	Cyp.	Cyp. + N + B
28 May	67	14–29.05	S	Cur./Prev.	N + Ca + B	Dif. + Capt.	Bicarb. + S	Dif. + Capt.	Dif. + Capt. + N + Ca + B
4 June	69	x	x	Fert.	N + Ca + B	x	x	x	N + Ca + B
12 June	70	10–11.06; 13.06–14.06	S; M	Cur./Prev.	Ca + B	Cyp. + Capt.	L. sulph.	Cyp. + Capt.	Cyp. + Capt. + Ca + B
3 July	74	sec. infec.	S	Prev.	Ca	Capt.	L. sulph.	L. sulph.	Capt. + Ca
27 July	76	sec. infec.	S	Prev.	Ca	Capt.	Bicarb. + S	Bicarb. + S	Capt. + Ca

* Growth stages: green tip stage—20 April; full bloom—26 May. Primary infection period and secondary infection (sec. infec.) forecasted by RIMpro. Infection severity: L—light infection risk < 100 RIM; M—medium infection risk 100–300 RIM; S—severe infection risk > 300 RIM. Treatments: prev.—preventive; cur.—curative; germ.—germination window. Fungicides: cyp.—cyprodinil; dif.—difenoconazole; capt.—captan; bicarb.—potassium bicarbonate; l. sulph.—lime sulphur. Fertilisers: N—nitrogen; B—boron; Ca—calcium; S—sulphur.

Table A2. Treatment dates of synthetic and inorganic fungicides and foliar fertilisers used in different apple scab control strategies at certain growth stages and infection periods in cv. Auksis in 2022.

Treatment Date	Growth Stage *	Infection Period	Infection Severity	Treatment	Fungicides/Fertilisers				
					Fer	SyFu	InFu	SyInFu	SyFuFer
29 April	54	x	x	Fert.	N	x	x	x	N
15 May	57	16–17.05	L	Prev.	N	Dodine	Copper	Copper	Dodine + N
19 May	59	20–23.05	S	Prev.	N + B	Dodine	Copper	Copper	Dodine + N + B
23 May	65	20–23.05	S	Germ.	N	Cyp.	L. sulph.	Cyp.	Cyp. + N
28 May	69	26.05–5.06	S	Cur./Prev.	N + B	Dif. + Capt.	Bicarb. + S	Dif. + Cap	Dif. + Capt. + N + B
4 June	72	26.05–5.06	S	Cur.	Ca + B	Cyp.	L. sulph.	Cyp.	Cyp. + Ca + B
11 June	74	8–11.06; 14–15.06	S; L	Cur./Prev.	Ca + B	Dif. + Capt.	L. sulph.	L. sulph.	Dif. + Capt. + Ca + B
21 June	74	x	x	Fert.	Ca	x	x	x	Ca
9 July	76	sec. infec.	S	Prev.	Ca	Capt.	Bicarb. + S	Bicarb. + S	Capt. + Ca
3 August	79	x	x	Fert.	Ca	x	x	x	Ca

* Growth stages: green tip stage—20 April; full bloom—May 23. Primary infection period and secondary infection (sec. infec.) forecasted by RIMpro. Infection severity: L—light infection risk < 100 RIM; M—medium infection risk 100–300 RIM; S—severe infection risk > 300 RIM. Treatments: prev.—preventive; cur.—curative; germ.—germination window. Fungicides: cyp.—cyprodinil; dif.—difenoconazole; capt.—captan; bicarb.—potassium bicarbonate; l. sulph.—lime sulphur. Fertilisers: N—nitrogen; B—boron; Ca—calcium; S—sulphur.

Table A3. Treatment dates of synthetic and inorganic fungicides, and foliar fertilisers used in different apple scab control strategies at certain growth stages and infection periods in cv. Ligol in 2021.

Treatment Date	Growth Stage *	Infection Period	Infection Severity	Treatment	Fungicides/Fertilisers				
					Fer	SyFu	InFu	SyInFu	SyFuFer
29 April	54	29–30.04	M	Prev.	N	Dodine	Copper	Copper	Dodine + N
14 May	58	15–17.05	L	Prev.	N	Dodine	Bicarb. + S	Dodine	Dodine + N
19 May	60	20–22.05	L	Prev.	N + B	Cyp.	L. sulph.	Cyp.	Cyp. + N + B
28 May	67	26.05–2.06	S	Cur./Prev.	N	Dif. + Capt.	Bicarb. + S	Dif. + Cap	Dif. + Capt. + N

Table A3. Cont.

Treatment Date	Growth Stage *	Infection Period	Infection Severity	Treatment	Fungicides/Fertilisers				
					Fer	SyFu	InFu	SyInFu	SyFuFer
4 June	69	x	x	Fert.	N + Ca + B	x	x	x	N + Ca + B
11 June	71	8–11.06	M	Germ.	Ca + B	Capt.	Bicarb. + S	Capt.	Capt. + Ca + B
28 June	72	26–27.06	L	Cur.	Ca + B	Cyp.	L. sulph.	L. sulph.	Cyp. + Ca + B
22 July	76	sec. infec.	S	Prev.	Ca	Capt.	Bicarb. + S	Bicarb. + S	Capt. + Ca
3 August	77	sec. infec.	S	Cur.	Ca	Cyp.	L. sulph.	L. sulph.	Cyp. + Ca

* Growth stages: green tip stage—19 April; full bloom—25 May. Primary infection period and secondary infection (sec. infec.) forecasted by RIMpro. Infection severity: L—light infection risk < 100 RIM; M—medium infection risk 100–300 RIM; S—severe infection risk > 300 RIM. Treatments: prev.—preventive; cur.—curative; germ.—germination window. Fungicides: cyp.—cyprodinil; dif.—difenoconazole; capt.—captan; bicarb.—potassium bicarbonate; l. sulph.—lime sulphur. Fertilisers: N—nitrogen; B—boron; Ca—calcium; S—sulphur.

Table A4. Treatment dates of synthetic and inorganic fungicides and foliar fertilisers used in different apple scab control strategies at certain growth stages and infection periods in cv. Ligol in 2022.

Treatment Date	Growth Stage *	Infection Period	Infection Severity	Treatment	Fungicides/Fertilisers				
					Fer	SyFu	InFu	SyInFu	SyFuFer
22 April	54	24–26.04	M	Prev.	N	Dodine	Copper	Copper	Dodine + N
11 May	57	15–17.05	L	Prev.	N	Dodine	Copper	Copper	Dodine + N
16 May	58	15–17.05	L	Germ.	N + B	Cyp.	L. sulph.	Cyp.	Cyp. + N + B
23 May	65	26.05–3.06	S	Prev.	N	Capt.	Bicarb. + S	Capt.	Capt. + N
30 May	69	26.05–3.06	S	Cur./Prev.	N + Ca + B	Dif. + Capt.	L. sulph.	Dif. + Capt.	Dif. + Capt. + N + Ca + B
3 June	70	26.05–3.06	S	Cur.	x	Cyp.	L. sulph.	L. sulph.	Cyp.
11 June	72	8–11.06	M	Germ.	Ca + B	Capt.	Bicarb. + S	Bicarb. + S	Capt. + Ca + B
15 June	73	14–15.06	L	Germ.	x	Capt.	L. sulph.	L. sulph.	Capt.
22 June	74	x	x	Fert.	Ca + B	x	x	x	Ca + B
13 July	78	sec. infec.	S	Prev.	Ca	Capt.	L. sulph.	L. sulph.	Capt. + Ca
1 August	79	sec. infec.	S	Prev.	Ca	Capt.	L. sulph.	L. sulph.	Capt. + Ca
5 September	81	sec. infec.	S	Cur.	Cyp.	Cyp.	Cyp.	Cyp.	Cyp.

* Growth stages: green tip stage—29 March; full bloom—23 May. Primary infection period and secondary infection (sec. infec.) forecasted by RIMpro. Infection severity: L—light infection risk < 100 RIM; M—medium infection risk 100–300 RIM; S—severe infection risk > 300 RIM. Treatments: prev.—preventive; cur.—curative; germ.—germination window. Fungicides: cyp.—cyprodinil; dif.—difenoconazol; capt.—captan; bicarb.—potassium bicarbonate; l. sulph.—lime sulphur. Fertilisers: N—nitrogen; B—boron; Ca—calcium; S—sulphur.

References

- Chatzidimopoulos, M.; Lioliopoulou, F.; Sotiropoulos, T.; Vellios, E. Efficient Control of Apple Scab with Targeted Spray Applications. *Agronomy* **2020**, *10*, 217. [CrossRef]
- Jamar, L.; Lefrancq, B.; Lateur, M. Control of apple scab (*Venturia inaequalis*) with bicarbonate salts under controlled environment. *J. Plant Dis. Prot.* **2007**, *114*, 221–227. [CrossRef]
- Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions—A Farm to Fork Strategy for a Fair, Healthy and Environmentally-Friendly Food System. COM(2020) 381 Final. Available online: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52020DC0381> (accessed on 30 December 2023).
- Cox, K.D. Fungicide Resistance in *Venturia inaequalis*, the Causal Agent of Apple Scab, in the United States. In *Fungicide Resistance in Plant Pathogens*; Ishii, H., Hollomon, D., Eds.; Springer: Tokyo, Japan, 2015; pp. 433–447.
- Stević, M.; Vukša, P.; Elezović, I. Resistance of *Venturia inaequalis* to demethylation inhibiting (DMI) fungicides. *Žemdirb. Agric.* **2010**, *97*, 65–72.
- Rancāne, R.; Valiūškaitē, A.; Zagorska, V.; Komašilovs, V.; Rasiukevičiūtē, N. The Overall Environmental Load and Resistance Risk Caused by Long-Term Fungicide Use to Control *Venturia inaequalis* in Apple Orchards in Latvia. *Plants* **2023**, *12*, 450. [CrossRef]
- FRAC Code List ©*2023. Available online: <https://www.frac.info/docs/default-source/publications/frac-code-list/frac-code-list-2023---final.pdf> (accessed on 30 December 2023).
- List of Plant Protection Products Registered in Latvia. Available online: http://registri.vaad.gov.lv/reg/aal_saraksts.aspx (accessed on 30 December 2023).
- Kowalska, J.; Tyburski, J.; Krzywińska, J.; Jakubowska, M. Cinnamon powder: An in vitro and in vivo evaluation of antifungal and plant growth promoting activity. *Eur. J. Plant Pathol.* **2020**, *156*, 237–243. [CrossRef]

10. Paušič, A.; Roškarič, M.; Lešnik, M. 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. *Agronomy* **2023**, *13*, 1151. [CrossRef]
11. Commission Regulation (EC) No 889/2008 of 5 September 2008 Laying down Detailed Rules for the Implementation of Council Regulation (EC) No 834/2007 on Organic Production and Labelling of Organic Products with Regard to Organic Production, Labelling and Control. Available online: <https://eur-lex.europa.eu/eli/reg/2008/889/oj> (accessed on 30 December 2023).
12. *Apple Best Practice Guide*; Agriculture and Horticulture Development Board: Kenilworth, UK, 2022; Available online: <https://apples.ahdb.org.uk/zero-residue-production/> (accessed on 30 December 2023).
13. *Clean Fruit—Standardisation of Innovative Pest Control Strategies to Produce Zero Residue Fruit for Baby Food and Other Fruit Produce*; EIT Food: Leuven, Belgium, 2022. Available online: <https://www.eitfood.eu/innovation/projects/cleanfruit/> (accessed on 30 December 2023).
14. Hamilton, J.M. Studies of fungicidal action of certain dust and sprays in the control of apple scab. *Phytopathology* **1931**, *21*, 445–523.
15. MacHardy, W.E. *Apple Scab, Biology, Epidemiology and Management*; APS Press: St. Paul, MN, USA, 1996; pp. 511–517.
16. Montag, J.; Schreiber, L.; Schönherr, J. An in vitro study on the post infection activities of hydrated lime and lime sulphur against apple scab (*Venturia inaequalis*). *J. Phytopathol.* **2005**, *153*, 485–491. [CrossRef]
17. İlhan, K.; Arslan, U.; Karabulut, O. The effect of sodium bicarbonate alone or in combination with a reduced dose of tebuconazole on the control of apple scab. *Crop Prot.* **2006**, *25*, 963–967. [CrossRef]
18. Tamm, L.; Amsler, T.; Schärer, H.; Refardt, M. Efficacy of Armicarb (potassium bicarbonate) against scab and sooty blotch on apples. In Proceedings of the 12th International Conference on Cultivation Technique and Phytopathological Problems in Organic Fruit-Growing, Weinsberg, Germany, 31 January–2 February 2006.
19. Stoddard, E.M. Fungicidal synergism between urea and sulfur. *Phytopathology* **1950**, *40*, 27.
20. Palmiter, D.H.; Hamilton, J.M. *Influence of Certain Nitrogen and Fungicide Applications on Yield and Quality of Apples*; New York State Agricultural Experiment Station: Geneva, NY, USA, 1954; Volume 766, p. 52.
21. Percival, G.C.; Haynes, I. The influence of calcium sprays to reduce fungicide inputs against apple scab (*Venturia inaequalis* (Cooke) G. Wint.). *Arboric. Urban For.* **2009**, *35*, 263–270. [CrossRef]
22. Arslan, U. Efficacy of Boric Acid, Monopotassium Phosphate and Sodium Metabisulfite on the Control of Apple Scab. *J. Phytopathol.* **2016**, *164*, 678–685. [CrossRef]
23. Apple Scab (*Venturia inaequalis*) Model. Available online: <https://rimpro.cloud/platform/apple-scab-venturia-inaequalis/> (accessed on 30 December 2023).
24. Trapman, M.C. Development and evaluation of a simulation model for ascospore infections of *Venturia inaequalis*. *Nor. J. Agric. Sci.* **1994**, *17*, 55–67.
25. Growth Stages of Mono- and Dicotyledonous Plants. BBCH Monograph. Available online: <https://www.politicheagricole.it/flex/AppData/WebLive/Agrometeo/MIPEFY800/BBCHengl2001.pdf> (accessed on 30 December 2023).
26. Jeger, M.; Viljanen-Rollinson, S. The use of the area under the disease-progress curve (AUDPC) to assess quantitative disease resistance in crop cultivars. *Theor. Appl. Genet.* **2001**, *102*, 32–40. [CrossRef]
27. UNECE Standard FFV-50 Concerning the Marketing and Commercial Quality Control of Apples. Available online: https://unece.org/sites/default/files/2020-12/50_Apples.pdf (accessed on 30 December 2023).
28. Khanal, B.P.; Shrestha, R.; Hückstädt, L.; Knoche, M. Russetting in Apple Seems Unrelated to the Mechanical Properties of the Cuticle at Maturity. *HortScience* **2013**, *48*, 1135–1138. [CrossRef]
29. *EN 15662:2018; Foods of Plant Origin—Multimethod for the Determination of Pesticide Residues Using GC-MS/MS and LC-MS/MS-Based Methods*. European Committee for Standardisation (CEN): Brussels, Belgium, 2018.
30. EU Pesticides Database. Available online: https://food.ec.europa.eu/plants/pesticides/eu-pesticides-database_en (accessed on 30 December 2023).
31. Valiuškaitė, A.; Raudonis, L.; Lanauskas, J.; Sasnauskas, A.; Survilienė, E. Disease incidence on different cultivars of apple tree for organic growing. *Agron. Res.* **2009**, *7*, 536–541.
32. Holb, I.J. Effect of six sanitation treatments on leaf litter density, ascospore production of *Venturia inaequalis* and scab incidence in integrated and organic apple orchards. *Eur. J. Plant Pathol.* **2006**, *115*, 293–307. [CrossRef]
33. Masny, S. Occurrence of *Venturia inaequalis* races in Poland able to overcome specific apple scab resistance genes. *Eur. J. Plant Pathol.* **2017**, *147*, 313–323. [CrossRef]
34. Rancane, R.; Eihe, M.; Jankovska, L. Adaption of simulation model RIMpro for primary apple scab control in Latvia. *Acta Hort.* **2008**, *803*, 69–75. [CrossRef]
35. Cromwell, M.L.; Berkett, L.P.; Darby, H.M.; Ashikaga, T. Alternative Organic Fungicides for Apple Scab Management and Their Non-target Effects. *HortScience* **2011**, *46*, 1254–1259. [CrossRef]
36. Kelderer, M.; Casera, C.; Lardschneider, E. Formulated and unformulated carbonates to control apple scab (*Venturia inaequalis*) on organic apple. In Proceedings of the Eco-Fruit 13th International Conference on Cultivation Technique and Phytopathological Problems in Organic Fruit Growing, Weinsberg, Germany, 18–20 February 2008; Volume 13641, pp. 47–53.
37. Profaizer, D.; Baldessari, M.; Giuliani, G.; Angeli, G. The use of inorganic compounds to control apple scab in integrated fruit production. *IOBC-WPRS Bull.* **2013**, *91*, 73–79.

38. Ciecierski, W.; Cimanowski, J.; Bielenin, A. Effect of urea application on ascospore production of *Venturia inaequalis*. *Acta Hort.* **1996**, *422*, 395–396. [[CrossRef](#)]
39. Sutton, D.K.; MacHardy, W.E.; Lord, W.G. Effects of shredding or treating apple leaf litter with urea on ascospore dose of *Venturia inaequalis* and disease buildup. *Plant Dis.* **2000**, *84*, 1319–1326. [[CrossRef](#)] [[PubMed](#)]

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