agronomy

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Inorganic Fungicides (Phosphites) Instead of Organic Fungicides in Winter Wheat—Consequences for Nitrogen Fertilizer Productivity

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Abstract: Substitution of organic with inorganic fungicides (phosphites, Phi) does not change the efficiency of fertilizer nitrogen (N_f) in winter wheat. This hypothesis was tested in the 2016/2017 and 2017/2018 growing seasons. A two-factorial experiment with three phosphite variants (Cu–Phi, Mg–Phi, and Cu/Mg) and six plant protection methods (fungicides + Phi $\longrightarrow$ reduced fungicide frequency + phosphite $\longrightarrow$ phosphite). Grain yield decreased with increasing frequency of phosphites instead of fungicides. The decrease in yields was 3.6 t ha^{-1} in the favorable 2016/2017 and 1.1 t ha^{-1} in the dry 2017/2018. The primary reason for yield decrease in a given growing season was increased wheat infestation by pathogens. The direct cause was disturbances in the nitrogen status of wheat after flowering on treatments with a predominance of phosphites. The thousand grain weight (TGW) responded negatively to reduced fungicide application frequency. The critical stage in the assessment of pathogen pressure on wheat was the medium milk phase (BBCH 75). At this stage, indices of SPAD and leaf greenness together with indices of wheat infestation with pathogens allowed for a reliable prediction of both TGW and grain yield. It can be concluded that phosphites do not substitute organic fungicides in limiting pathogen pressure in winter wheat. Moreover, increased pressure of pathogens significantly reduces N_f productivity.

Keywords: pathogens; yield gap; SPAD index; leaf greenness; nitrogen accumulation; nitrogen productivity; nitrogen gap

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Citation: Grzebisz, W.; Łączny, S.; Szczepaniak, W.; Potarzycki, J. Inorganic Fungicides (Phosphites) Instead of Organic Fungicides in Winter Wheat—Consequences for Nitrogen Fertilizer Productivity. *Agronomy* **2023**, *13*, 627. https://tdoi.org/10.3390/agronomy13030627

Academic Editors: Claudio Ciavatta and Victor Galea

Received: 30 December 2022
Revised: 13 February 2023
Accepted: 21 February 2023
Published: 22 February 2023

1. Introduction

Modern agriculture is based on three pillars rooted in the Green Revolution. These are (i) high-yielding plant varieties, (ii) high doses of nitrogen fertilizer (N_f), and (iii) full protection of the crop canopy during the growing season with pesticides, including fungicides [1]. Currently cultivated varieties require large doses of fertilizer nitrogen (N_f), but taking into account world agriculture, its efficiency is low. This means that most of the applied N_f is not used by plants, which in turn creates serious problems for the environment [2]. The risks of using pesticides to the environment and human health have been recognized and extensively documented [3]. In the European Union, the use of pesticides in agriculture is based on two legal acts. The first is Directive 128/EC on the sustainable use of plant protection measures in agriculture, supported by Regulation EC, No 1107/2009) [4]. The essence of the directive is to eliminate the use of those pesticides that pose a real and potential threat to the environment and human health. In Poland, following the directive, the use of organic pesticides is regulated by the Plant Protection Act (8 March 2013) [5]. Today, efforts to decrease the use of pesticides have accelerated. The main goals of the EU initiative by 2030, called the Green Deal, are to reduce the total use of chemical pesticides by 50%, and hazardous ones also by 50% [3].

At this point, a question should be asked about the production effects of a considerable reduction in the use of organic pesticides. It is well documented, regardless of the country, that without the use of pesticides, the yield losses are substantial. Studies carried out to reduce the dose of pesticides used in wheat by 50% have shown yield losses in France in the range of 2 to 3 million tons per year [6]. In Poland, yield losses caused by pathogens in winter wheat can reach 20–30% and even 50% [7]. In the light of such strong controversy, there are several key issues to consider regarding the use of fungicides:

(1) Have new chemicals been developed that are able to substitute classic, i.e., organic fungicides?
(2) Can inorganic fungicides effectively replace organic fungicides?
(3) Are inorganic fungicides able to maintain the effectiveness of N_f at the level provided by classic ones?

The second and third questions formulated above are the essence of this article. Based on the present knowledge on the possibility of substitution of organic fungicides with inorganic ones, it cannot be clearly stated that both groups have the same anti-pathogen effectiveness [8,9]. Inorganic fungicides are classified into six groups such as carbonates, orthophosphates V (Pi), silicates, chlorides, orthophosphates III (Phi), and mixed [9]. One of the above-mentioned groups, which has been of interest in crop protection since the 1930s, is the salts of orthophosphoric III acid ($H_2PO_3^-$), known as phosphites (Phi) [8]. Salts of this acid, applied to the soil or to plant foliage, have a very wide spectrum of activities and measurable effects, including [10–12]:

(1) Herbicide—increases the effect of applied herbicides;
(2) Fungicide—protection of the plant canopy against pathogens;
(3) Biostimulating—accelerating plant growth; increasing yield; improving yield quality; increasing plant resistance to abiotic stresses;
(4) Nutritional—source of phosphorus.

Phosphorus is the essential nutrient for all living organisms. In nature, P does not occur as a free element because it binds immediately to oxygen (O) and hydrogen (H). Fully oxidized P combines with four O atoms to form an orthophosphate ion (PO_4^{3-}, Pi). The charge of the Pi ion is evenly distributed between the four O atoms, creating a completely symmetrical construct. In partially oxidized P, one of the O atoms is replaced by an H atom, forming a phosphite molecule (Phi). In the Phi ion, the P atom is also in the center of the tetrahedron, but the perfect symmetry does not exist [8,13]. Phosphite salts are more soluble in water that orthophosphate ones, resulting in a more effective uptake by plant roots or leaves [14]. However, the nutritional role of phosphorus from phosphites, despite the observed positive response of some crops (avocado, onion, cotton, celery, potatoes, and tomato), is disputed [13,14]. Phi compounds used in high doses, especially on P-deficient plants, may inhibit the growth of both roots and shoots [12]. The action of phosphites as fungicides has been reported for many pathogenic fungi, such as *Phytophtora* spp., (broad set of diseases) for example, late blight in potato, *Venturia inaequalis* (apple scab), *Plasmodiophora brassicae* (clubroot, cabbage). However, despite the quasi-fungicidal effect of phosphites on some pathogens, the mechanisms of their action are not known [11,12,15]. The most commonly used phosphite salts are potassium, (potassium phosphite, Nutrol acts as a fertilizer and fungicide; Fosphite, acts as a fungicide), aluminium phosphite (Aliette, acts as a fungicide), phosphorous acid (Ele-Mac, acts as a fertilizer) [14].

Plant nutrients, by affecting the metabolic and physiological processes of the plant, directly or indirectly affect its resistance to the pressure of pathogens. The group of nutrients that directly improve plant crop resistance to pathogens includes copper, manganese, zinc, and sulfur [16–18]. Attention is also drawn to the fact that any nutrient that effectively balances N indirectly reduces the pressure of pathogens [17,19]. One of the most recognized elements, acting as a nutrient and fungicide, is copper. The nutritional functions of Cu in crop plants are well studied and widely presented in scientific books and articles [18] The fungistatic (biocidal) effect of Cu was noted for the first time in the second half of the

19th century when the lime–copper sulfate liquid called *Bordeaux Mixture* was applied to protect grapevines against *Plasmopara viticola* (downy mildew) [20]. However, excessive application of Cu, which was the strategy of plant protection, mainly for viticulture in the past, created a health hazard for both humans, animals, and the environment [20,21]. However, studies on foliar Cu application to wheat indicate its interaction with N, leading to a grain yield increase [22–24].

Wheat yield is a function of two yield components. The first one is grain density, which is an aggregated indicator, consisting of the number of ears per unit area and the number of grains per ear [25]. The first component is formed over a long period, extending from the beginning of stem elongation to the end of heading [26,27]. Grain density, strictly related to the number of fertile flowers, is a yield component which is very sensitive to both the state of environmental factors and the nutritional status of wheat before flowering. The decisive nutritional factor affecting its development is nitrogen [28]. The second basic yield component is grain weight, expressed as the thousand grain weight (TGW) [25]. The critical period of grain growth is the beginning of the milk phase. Its growth rate may be interrupted by unfavorable environmental conditions, such as extreme temperatures or drought [29,30]. Grain growth is driven by temperature during the grain filling period (GFP). Its effect on the rate of grain growth is contradictory. On the one hand, temperature determines both the rate of sugars production and their further transportation to the grains. On the other hand, temperature affects the length of the photosynthetic activity of leaves, thus influencing the production of assimilates [31]. The longevity of wheat leaves also depends on the content of N and pressure of pathogens [32]. Both factors are significantly but negatively interrelated. Globally, wheat diseases cause yield losses of 10–28% [33].

The greatest losses in wheat yields are caused by diseases that attack the leaves. A high content of N in wheat leaves creates an excellent environment for biotrophic pathogens, such as *Zymoseptoria tritici* (Roberge ex Desm.) and *Puccinia recondite* (Roberge ex Desm), for example [34,35]. In Poland, wheat infestation by the first of these pathogens increases in years favorable to the yield formation by this crop [36]. The health of the upper leaves, especially during GFP, is a prerequisite for higher wheat yields [37]. Infection of wheat after flowering, which mainly concerns the flag leaf and ears, shortens their photosynthetic activity and longevity, and thus reduces the yield [38,39]. The use of fungicides, limiting wheat infestation by leaf diseases, results in a grain yield increase. A positive impact of these treatments on TGW was reported in Poland by Kaniuczak and Noworolnik [40].

The key question in the current concept of the EU, known as the Green Deal, is to what extent inorganic fungicides, for example, Cu-, and Mg-phosphites, can replace organic fungicides in maintaining winter wheat resistant to pathogen pressure. Crop plant infestation by pathogens is an important factor for the production of food globally. Therefore, the main objective of the study was to assess the impact of the substitution of organic fungicides with phosphites in winter wheat on nitrogen fertilizer productivity.

2. Materials and Methods

2.1. Experimental Setup

Studies on the productivity of nitrogen fertilizer in winter wheat in response to the substitution of organic fungicides with phosphites was carried out in the 2016/2017 and 2017/2018 seasons in Jarosławiec/Pamiątkowo (52°33′ N; 16°40′ E), Poland. The field experiment was conducted on soil formed from sandy loam over loam, classified as Albic Luvisol. The organic carbon (C_{org}) content and pH values were optimal for winter wheat. The content of available nutrients in the soil, determined before wheat sowing, i.e., before applying fertilizers, was variable, especially for P, which was very high in 2016/2017 but low in 2017/2018. The content of available K was high; Mg was in the medium and Cu in the low class. The amount of mineral N (N_{min}), determined just before the spring regrowth of winter wheat in a 0.0–0.9 m soil layer, was generally high or very high, as in 2018 (Table 1).

Table 1. Agrochemical properties of the soil in subsequent growing seasons.

Growing Seasons	Soil Layer, cm	pH [1]	C_{org} [2]	Phosphorus [3]	Potassium	Magnesium	Copper	N_{min} [4]
			%	mg kg^{-1}				kg ha^{-1}
2016/2017	0–30	6.8	1.4	140 ± 16 **VH** [5]	219 ± 26 **H**	105 ± 13 **M**	1.2 ± 0.1 **L**	31 ± 19
	30–60	6.9	1.2	106 ± 36	111 ± 24	98 ± 15	1.2 ± 0.2	20 ± 6
	60–90	6.9	1.1	57 ± 23	88 ± 27	98 ± 22	1.1 ± 0.2	28 ± 11
2017/2018	0–30	6.5	1.9	52 ± 16 **L**	235 ± 19 **H**	83 ± 25 **M**	3.9 ± 0.2 **L**	41 ± 27
	30–60	6.7	2.3	26 ± 18	147 ± 31	108 ± 24	3.2 ± 0.8	40 ± 30
	60–90	6.9	1.7	15 ± 14	117 ± 28	134 ± 52	2.1 ± 0.9	35 ± 19

[1] 1.0 M KCl soil/solution ratio 1:2.5; *m*/*v*; [2] loss on ignition; [3] Mehlich 3 [41]; [4] 0.01 dm^{-3} $CaCl_2$, soil/solution ratio 1:5; *m*/*v*; [5] availability classes: VL—very low; L—low; M—medium; H—high; VH—very high [42,43].

2.2. Meteorological Conditions

The climate in the field study region, classified as intermediate between Atlantic and Continental, is characterized by seasonality, especially in Summer. Basic meteorological data are shown in Figure 1. In the 2016/2017 growing season, the average temperature was 9.4 °C; it was higher than the long-term average by 0.5 °C. In the 2017/2018 growing season, the average temperature was 10.3 °C, and the difference compared to the long-term reached +1.4 °C. The long-term sum of precipitation for the region is 524 mm. It was by 243 mm (+46%) and by 111 mm (+21%) higher in both growing seasons. The 2016/2017 season was very favorable for wheat growth, as indicated by the predominance of wet conditions, especially in June. In contrast, the 2017/2018 growing season was unfavorable for wheat, because of the predominance of dry conditions. The beginning of the 2018 growing season was dry and cold, while May was semi-dry, and June very dry. These two months are critical for yield formation by winter wheat in Poland [24].

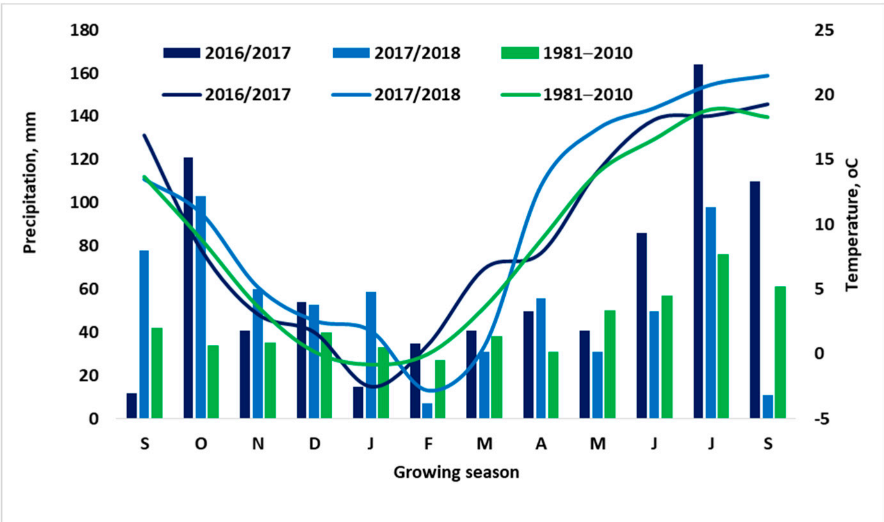

Figure 1. Meteorological conditions during the growing season of winter wheat. Source of data: Competence Center weather station BASF Jarosławiec and Pamiątkowo, http://www.pogodynka.pl/polska/daneklimatyczne/ (accessed on 20 December 2022).

2.3. Experimental Design

The field experiment, arranged in a two-factor split-plot design, replicated four times, included:

1. Three variants of foliar applied phosphites to winter wheat during the growing season (Phi)—main plot:

1.1 Cu–Phi;
1.2 Mg–Phi;
1.3 Cu/Mg–Phi (mixed Phi application, Cu–Phi at BBCH 21 (autumn); Mg–Phi in spring).

2. Six plant protection methods (plots, PPMs), including both organic fungicides (OF) and phosphites (Phi) (dates of fungicide application are specified in Table 2)—subplots:

Table 2. Specification of organic fungicide composition and application dates.

Fungicide	Active Compounds $g\ dm^{-3}$	Dosis $dm^3\ ha^{-1}$	Growth Stage of Winter Wheat
Capalo 337.5 SE	Epoksykonazol 62.5 Fenpropimorf 200 Metrafenon 75	1.5	BBCH 30
Adexar Plus	Epoksykonazol 41.6 Fluksapyroksad 41.6 Piraklostrobina 66.6	1.25	BBCH 39–45
Osiris 65 EC	Epoksykonazol 37.5 Metkonazol 27.5	1.5 l	BBCH 65

2.1 A—full fungicide protection + 3 × phoshite application (as in F plot of PPM, excluding BBCH 21);
2.2 B—full fungicide protection + 4 × phoshite application (as in F plot);
2.3 C—full fungicide protection + phosphite applied at BBCH 21;
2.4 D—fungicide protection at BBCH 30 and BBCH 39–45 + phosphite at BBCH 21 and BBCH 55;
2.5 E—fungicide protection at BBCH 30 + phosphite at BBCH 21, BBCH 32, BBCH 55;
2.6 F—phosphite applied alone at BBCH 21, BBCH 29, BBCH 32, BBCH 55.

Mg phosphite with 3% N, 39.5% P_2O_5, 9.9% MgO and Cu phosphite with 10.5% N, 24% P_2O_5, 4% Cu were used in the experiment. On the variant with a mixed application of Cu and Mg phosphites, Cu–Phi was applied in autumn, and Mg–Phi in spring. The one-time dose of phosphite was 2 $dm^3\ ha^{-1}$. The total amount of MgO and Cu in one single spray was 0.29 and 0.1 kg ha^{-1}, respectively.

The total area of a single plot was 13.5 m^2 (3 × 4.5 m). The winter wheat cv. *Princes* was sown annually in the fourth week of September at the rate of 350 grains m^{-2}. Winter oilseed rape was the fore-crop for winter wheat. The crop was harvested the following year at the end of July from an area of 9.0 m^{-2}. Nitrogen was applied in the form of ammonium nitrate (34:0:0) in accordance with the experimental schedule:

(1) 102 kg N ha^{-1}—at the end of tillering/beginning of shoot elongation (BBCH 29/30);
(2) 78 kg N ha^{-1}—at the stage of a flag leaf visible (BBCH 39).

Phosphorus was applied at the rate of 69 kg P_2O_5 ha^{-1} in the form of triple superphosphate (46% P_2O_5). Potassium was applied at the rate of 120 kg K_2O ha^{-1} as Korn-Kali (K-MgO-Na_2O-SO_3 $\longrightarrow$ 40-6-3-12.5). Both fertilizers were applied two weeks before wheat sowing. Foliar application of fungicides was carried out in accordance with the experimental schedule, as shown in Table 2. Foliar application of phosphites was carried out in accordance with the experimental schedule, as shown for the method F.

2.4. Plant Measurements and Sampling

The plant material for the determination of dry matter and the N content was collected at four stages of winter wheat growth: (i) the beginning of stem elongation (BBCH 31), (ii) the end of heading (BBCH 59), (iii) the full milk phase (BBCH 75), (iv) at wheat maturity (BBCH 89) [44]. The chlorophyll meter SPAD-502Plus was used to measure the absorbance of the flag leaf. This index expresses the relative amount of chlorophyll in a plant leaf [45]. The assessment of wheat infestation by fungal diseases and the GREENT test were carried out with EPPO methodology [46]. A single plant sample, depending on the stage of winter wheat growth, was divided into leaves, stems, ears, chaffs, and grain. The N content was determined in plant parts using the standard macro-Kjeldahl procedure [47]. N content is expressed on the dry weight basis.

2.5. Calculated Parameters

Based on the primary data concerning the plant biomass, grain yield, nitrogen fertilizer dose, and the content of N in the plant, the specific set of N indicators was calculated:

$$\text{Partial Factor Productivity of } N_f: \ PFP_{Nf} = \frac{Y}{N_f} \left(\text{kg kg}^{-1}\ N_f\right) \tag{1}$$

$$\text{Attainable maximum yield}: \ Y_{attmax} = \ cPFP_{Nf} \cdot N_f\left(\text{t, kg ha}^{-1}\right) \tag{2}$$

$$\text{Yield Gap}: \ YG = \ Y_{attmax} - \ Y_a \left(\text{t ha}^{-1}\right) \tag{3}$$

$$\text{Nitrogen Gap } (N_{uw}): \ NG = \frac{YG}{cPFP_{Nf}}\left(\text{kg N ha}^{-1}\right) \tag{4}$$

where:

N_f is the amount of applied fertilizer N (kg ha^{-1});

PFP-N_f is the partial factor productivity of N_f (kg grain per kg N_f);

Y_{attmax} is the maximum attainable yield (t ha^{-1}); *c*PFP-N_f is the average of the third quartile (Q3) set of PFP_{Nf} indices, arranged in ascending order (kg grain per kg N_f);

YG is the yield gap (t ha^{-1});

NG is the nitrogen gap (kg N ha^{-1}).

2.6. Statistical Analysis

The impact of experimental factors (year, phosphite variants, plant protection methods) and their mutual interactions on grain yield and nitrogen productivity indices were assessed by analysis of variance. Means were separated by honest significant difference (HSD) using the Tukey method when the F-test showed significant factor effects at $p < 0.05$. Relationships between the examined characteristics were analyzed using Pearson correlation and linear regression. The stepwise regression analysis was used to determine the optimal set of variables for a given plant trait. The best regression model was selected based on the highest *F*-value for the entire model. STATISTICA 12 software was used for all statistical analyses (StatSoft Inc., Tulsa, OK, USA, 2013).

3. Results

3.1. Grain Yield and Yield Components

The grain yield (GY) of winter wheat significantly depended on the total crop biomass (B89) at harvest (Table A1). This relationship was clearly supported by the stepwise regression analysis, which showed that the wheat biomass and the harvest index (HI) were two decisive plant factors, defining grain yield:

$$GY = -9.71 + 0.46B89 + 0.21HI \text{ for } n = 36, R^2 = 0.99 \text{ and } p \leq 0.001 \tag{5}$$

It should be clearly emphasized that wheat biomass responded to all studied factors. However, this was the result of the interaction of plant protection methods (PPMs) and years (Table 3). In contrast, the HI responded only to years and PPMs. A higher HI was recorded in 2018. Wheat fully protected with fungicides was characterized by a significantly higher HI compared to treatments with reduced frequency in their use.

Table 3. Grain yield, yield components response to the method of winter wheat canopy foliar protection against pathogens.

Factor	Level of Factor	GY [1]	ED	GNE	GD	TGW	B89	HI
		t ha^{-1}	Number m^{-2}	Number ear^{-2}	Number m^{-2} × 1000	g	t ha^{-1}	%
Year (Y)	2017	10.5 a	667.8 a	43.0 a	1.858 a	47.3 a	24.37 a	43.5
	2018	7.5 b	633.5 b	39.4 b	1.565 b	40.4 b	16.09 b	46.8
p		***	*	***	***	***	***	***
Phosphites (Phi)	Cu	9.2	674.6 a	41.3	1.718	43.2	20.55	45.1
	Mg	9.0	644.2 ab	41.2	1.708	44.1	20.16	45.1
	Cu/Mg	8.9	633.2 b	41.2	1.707	44.3	19.98	45.3
p		ns	*	ns	ns	ns	ns	ns
Plant Protection Methods (PPMs)	A	9.825 a	677.4	41.0	1.699	45.5 a	21.42 a	46.4 a
	B	9.894 a	661.5	41.8	1.762	46.0 a	21.72 a	46.1 a
	C	9.679 a	625.0	40.4	1.638	44.7 a	20.77 ab	46.9 a
	D	8.971 b	632.6	42.2	1.791	44.5 a	20.59 ab	44.2 ab
	E	8.252 c	659.7	41.4	1.724	41.5 b	19.34 bc	43.5 b
	F	7.591 d	647.6	40.5	1.652	41.0 b	17.52 c	43.9 b
p		***	ns	ns	ns	***	***	**
Source of variation for the studied interactions								
Y × Phi		ns	ns	ns	ns	ns	ns	ns
Y × PPMs		***	ns	ns	ns	***	***	ns
Phi × PPMs		ns	ns	ns	ns	ns	ns	ns
Y × Phi × PPMs		ns	ns	ns	ns	ns	ns	ns

Similar letters in the column indicate a lack of significant differences between experimental treatments using Tukey's test; ***, **, * indicate significant differences at $p < 0.001$, $p < 0.01$, and $p < 0.05$, respectively; ns—non significant; Legend: A—full fungicide protection + 3 × phosphite application; B—full fungicide protection + 4 × phosphite application; C—full fungicide protection + phosphite at BBCH 21; D—fungicide protection at BBCH 30 and BBCH 39–45 + phosphite at BBCH 21 and BBCH 55; E—fungicide protection at BBCH 30 + phosphite at BBCH 21, BBCH 32, BBCH 55; F—phosphite alone at BBCH 21, BBCH 29, BBCH 32, and BBCH 55; [1] GY—grain yield; ED—number of ears; GNE—grains number per ear; GD—grain density; TGW—thousand grain weight; B89—crop biomass at BBCH 89; HI—harvest index.

The analysis of the impact of yield components on GY clearly showed the dominant role of thousand grain weight (TGW, Table 3). Moreover, TGW was significantly and strongly affected by wheat biomass at BBCH 89. At the same time, it showed a positive relationship with the number of grains per ear and grain density. The obtained stepwise regression model is as follows:

$$GY = -8.402 + 0.4TGW \text{ for } n = 36, R^2 = 0.88 \text{ and } p \leq 0.001 \quad (6)$$

All these three traits of winter wheat showed a significant dependence on the Y × Phi interaction (Table 3). The grain yield was both significantly higher in 2017 and at the same time showed a stronger response to the method of plant protection (Figure 2).

The highest yields of wheat were recorded on plots fully protected with organic fungicides and simultaneously treated with phosphites. The yield gap (Ygap) for these treatments in relation to the maximum attainable yield of 11.854 t ha^{-1} was negligible (<2%). The Ygap increased in treatments with a progressively increasing frequency of applied phosphites instead of fungicides. The lowest yield combined with the highest Ygap was found in the plot protected with phosphites alone (method F). In 2018, grain yield of wheat was lower, on average by 3 t ha^{-1}. The reason was a long-term drought (Figure 1). Despite this, the Ygap trend was the same as in favorable 2017, which was favorable for wheat, but the differences between methods were much smaller.

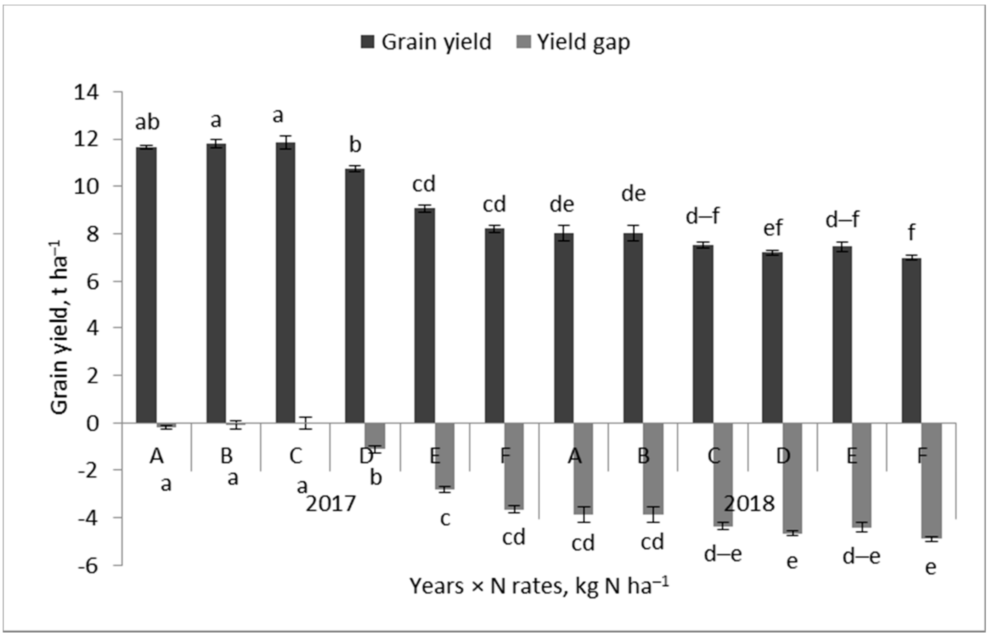

Figure 2. Effect of plant protection methods on the grain yield and yield gap of winter wheat. Similar letters indicate a lack of significant differences between experimental treatments using Tukey's test. The vertical bar in the column is the standard error of the mean.

The general trend of TGW corresponds to the pattern determined for grain yield (Figure 3). Significant differences between the methods of plant protection were only revealed in 2017. A significantly lower TGW was recorded in plots with a predominance of phosphites. In 2018, this wheat trait was both much lower and there was no difference between PPMs. TGW was strongly dependent on wheat biomass at harvest (Table A1). The response of wheat biomass to PPMs was almost the same as discussed for grain yield (Figure A1). In 2018, it was by $^1/_3$ lower compared to 2017. In both years, the most stable biomass was produced by plants fully protected with both fungicides and phosphites (methods A–C). Any reduction in the use of fungicides resulted in a decrease in biomass, which was more pronounced in 2017. Moreover, wheat biomass showed a significant, positive impact on all yield components (Table A1). However, apart from TGW, other yield components did not respond to the interaction of experimental factors and years (Table 3). The chemical form of phosphite used, apart from years, had a significant effect on the density of ears. Wheat treated with Mg-phosphite or sequentially with Cu and Mg produced a significantly lower number of ears compared to those treated with Cu-phosphite. The number of grains per ears and grain density was significantly lower (−15.8%) in 2018 compared to 2017.

3.2. Nitrogen Content in Leaves and Infestation of Plants by Pathogens

The leaves were used as an in-season indicator of winter wheat's nutritional status and sensitivity to pathogen pressure. The highest correlation coefficient of GY with this set of characteristics was recorded for the content of N in leaves at BBCH 75. The same value of the correlation coefficient (r) was obtained for the SPAD index, also determined at BBCH 75. A slightly lower strength of this relationship was noted for the "leaves greenness" (GREENT) index. The effect of the degree of wheat infestation by pathogens on grain yield was negative, but significant only for *Zymoseptoria tritici* (SEPTTR) (Table A2). Using the stepwise regression analysis, it was documented that the grain yield in 96% depended on the variability in two wheat traits, i.e., SPAD 75 and SEPTTR, while TGW depended on SPAD 75 and GREEENT. The obtained regression models are as follows:

$$GY = 6.387 + 0.0075SPAD75 - 0.105SEPTTR \text{ for n} = 36.\ R^2 = 0.96 \text{ and } p \leq 0.001 \quad (7)$$

$$TGW = 23.35 + 0.015SPAD75 + 0.19GREENT \text{ for } n = 36.\ R^2 = 0.87 \text{ and } p \le 0.001 \quad (8)$$

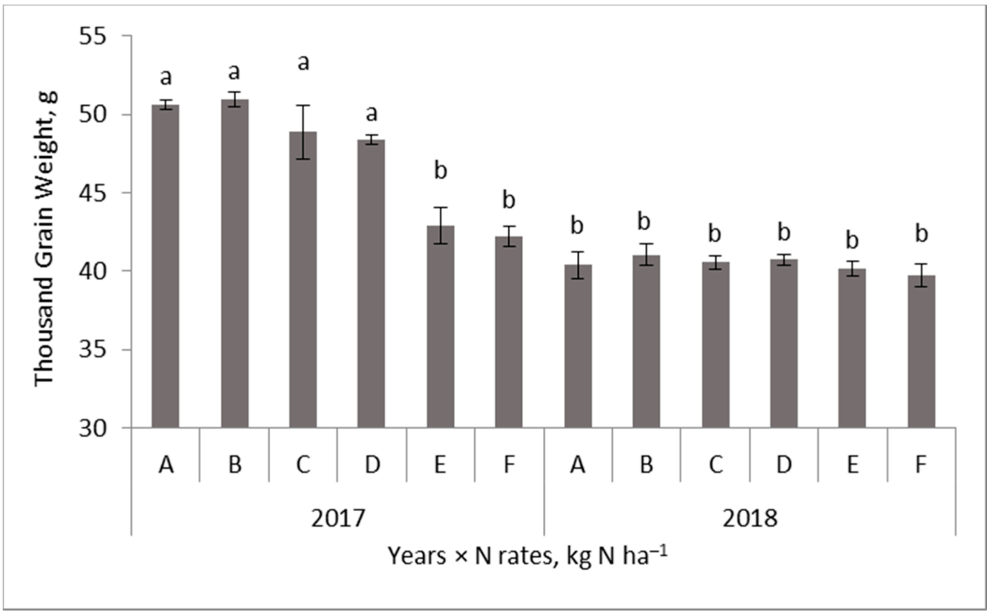

Figure 3. Effect of plant protection methods on thousand grain weight of winter wheat. Similar letters indicate a lack of significant differences between experimental treatments using Tukey's test. The vertical bar in the column is to the standard error of the mean.

All three traits of winter wheat and the content of N in leaves at BBCH 75 were sensitive to the interaction of Y × Phi × PPMs (Table 4). However, taking into account the factors determining grain yield and TGW, the interaction of Y × PPMs is further discussed. The average value of the SPAD index at BBCH 75 in 2018 was only 37% of that recorded in the 2017 value (Figure 4). In 2017, the SPAD indices amounted to over 700 on plots with full application of fungicides and simultaneous application of phosphites during the growing season. A sharp decrease (>100 units) was recorded on plots with increasing frequency of phosphite application. A very similar pattern of SPAD index response to wheat protection methods, despite a much lower values, was observed in 2018. The application of phosphite alone compared to full fungicide protection resulted in a 50% drop in the SPAD index. In addition, high variability between PPMs was noted as indicated by the standard error. The SPAD index was strongly associated with the N content in wheat leaves at BBCH 75 (Table A2). The main difference between the obtained patterns results from the fact that in each of the growing seasons, the decrease in the content of N started earlier than the decrease in SPAD (Figure A2). It should be emphasized that until the BBCH 59 stage, no considerable differences were noted in the N content in the leaves and in the SPAD indices.

Leaf greenness (GREENT) index showed a significant but weaker relationship with grain yield, TGW, and the SPAD index at BBCH 75. At the same, it was much stronger, but negatively correlated with the indices of wheat infection by pathogens (Table A2). In 2017, the GREENT indices for treatments fully protected with fungicides were very high, exceeding 83% (Figure A3). A sharp decrease was first observed in the plot without fungicide application at BBCH 65 (method D). It fell to 54% on the plot treated with phosphites alone (method F). In 2018, trends in GREENT indices were slightly different. The index values on plots with predominant fungicide protection, was at the same level, but 10 p.p. lower compared to the same treatments in 2017. On the other hand, on plots with a predominance of phosphites, its values were significantly higher.

Table 4. Nitrogen content in leaves, SPAD indices, and winter wheat infestation by pathogens during the growing season.

Factor	Factor Level	N–L31	NL–59	NL–75	NL–89	SPAD31	SPAD59	SPAD75	SEPTTR	PUCCRT	GREENT
									%		
Year (Y)	2017	4.4 a	3.3	2.4 a	1.58 a	675.8 b	723.5 a	671.0 a	8.6 a	2.3 a	73.0 a
	2018	4.1 b	3.2	1.3 b	0.79 b	687.5 a	714.0 b	254.2 b	6.6 b	1.0 b	70.5 b
p		***	ns	***	***	**	**	***	***	***	***
Phosphirones (Phi)	Cu	4.2	3.2	1.9	1.20	687.6	718.2	470.1	7.3 b	1.3 b	72.9 a
	Mg	4.3	3.2	1.8	1.16	678.1	714.5	453.5	8.1 a	1.4 b	70.2 b
	Cu/Mg	4.2	3.3	1.2	1.20	679.1	723.5	464.3	7.5 b	2.3 a	72.2 a
p		ns	ns	ns	ns	ns	ns	ns	***	***	***
Plant protection Methods (PPMs)	A	4.3	3.3	2.0 a	1.06 d	686.7	718.8	508.7 a	2.4 e	0.0 e	76.8 a
	B	4.2	3.3	2.0 a	1.12 b–d	682.3	720.2	516.4 a	2.0 e	0.0 e	78.2 a
	C	4.2	3.3	2.1 a	1.08 cd	677.4	718.0	454.3 ab	3.1 d	0.6 d	77.6 a
	D	4.2	3.1	1.7 b	1.18 bc	677.5	712.9	494.3 b	9.7 c	2.2 c	73.0 b
	E	4.3	3.2	1.7 b	1.20 b	684.9	720.3	433.4 c	12.9 b	4.0 a	64.7 c
	F	4.2	3.3	1.6 b	1.49 a	681.1	722.2	368.5 a	15.8 a	3.2 b	60.1 d
p		n.s.	ns	***	***	ns	ns	***	***	***	***
Source of variation for the studied interactions											
Y × Phi		ns	ns	***	ns	ns	ns	ns	***	ns	ns
Y × PPMs		ns	ns	**	***	ns	ns	***	***	***	***
Phi × PPMs		ns	*	ns	***	ns	ns	***	***	***	***
Y × Phi × PPMs		ns	ns	*	***	ns	ns	***	***	***	***

Similar letters in the column indicate a lack of significant differences between experimental factors using Tukey's test; ***, **, * indicate significant differences at $p < 0.001$, $p < 0.01$, and $p < 0.05$. respectively; ns—non significant; Legend: A—full fungicide protection + 3 × phosphite application; B—full fungicide protection + 4 × phosphite application; C—full fungicide protection + phosphite at BBCH 21; D—fungicide protection at BBCH 30 and BBCH 39–45 + phosphite at BBCH 21 and BBCH 55; E—fungicide protection at BBCH 30 + phosphite at BBCH 21, BBCH 32 and BBCH 55; F—phosphite alone at BBCH 21, BBCH 29, BBCH 32 and BBCH 55; N–L, SPAD—nitrogen content in leaves and SPAD indices of winter wheat at respective BBCH stages; SEPTTR—*Zymoseptoria tritici*; PUCCRT—*Puccinia recondita*; GREENT—green test.

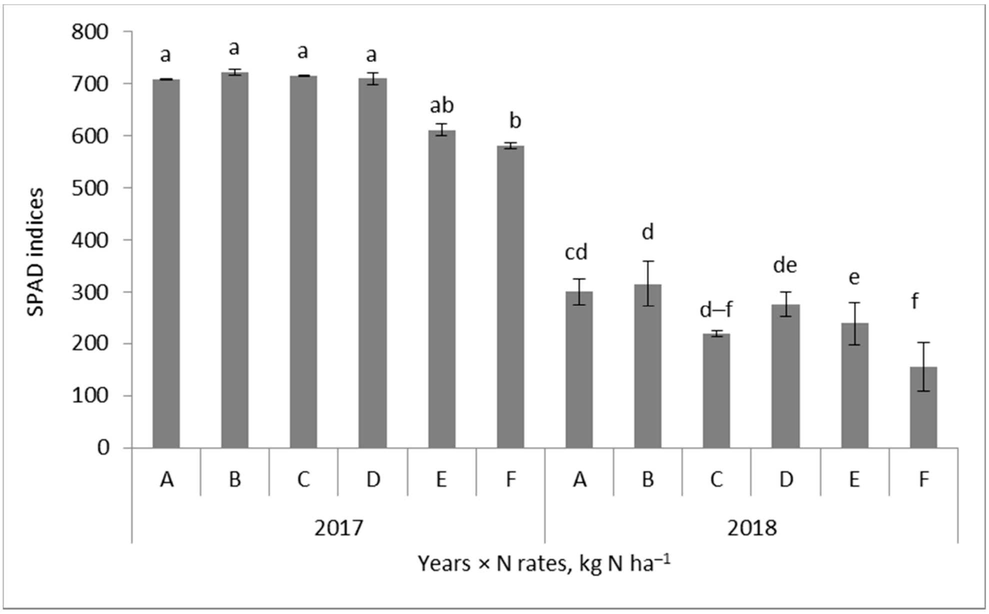

Figure 4. Effect of plant protection methods on the SPAD index of winter wheat. Similar letters indicate a lack of significant differences between experimental treatments using Tukey's test. The vertical bar in the column is the standard error of the mean.

Infestation of winter wheat by *Zymoseptoria tritici* was significantly stronger in 2017 than in 2018 (Table 4). In 2017, no infection of plants that were fully protected with fungicides was observed (Figure 5). On plots with a reduced frequency of applied fungicides, a linear increase in wheat infestations was observed. The highest value of 22% was found for plants treated with phosphites alone. In 2018, this pattern was slightly different. Firstly, all plants were attacked by the pathogen. Secondly, progressive pressure of the pathogen had already started on plot C, which was fully protected with fungicides and treated with phosphite in the fall (BBCH 21). Wheat infestation by *Puccinia recondita* (PUCCRT) was much lower compared to *Zymoseptoria tritici*. In 2017 this pattern was very similar to that recorded for *Zymoseptoria tritici*, but no further increase was observed in the plot treated with phosphite alone. In 2018, no infestation was recorded on plots fully protected with fungicides and simultaneously applied phosphites.

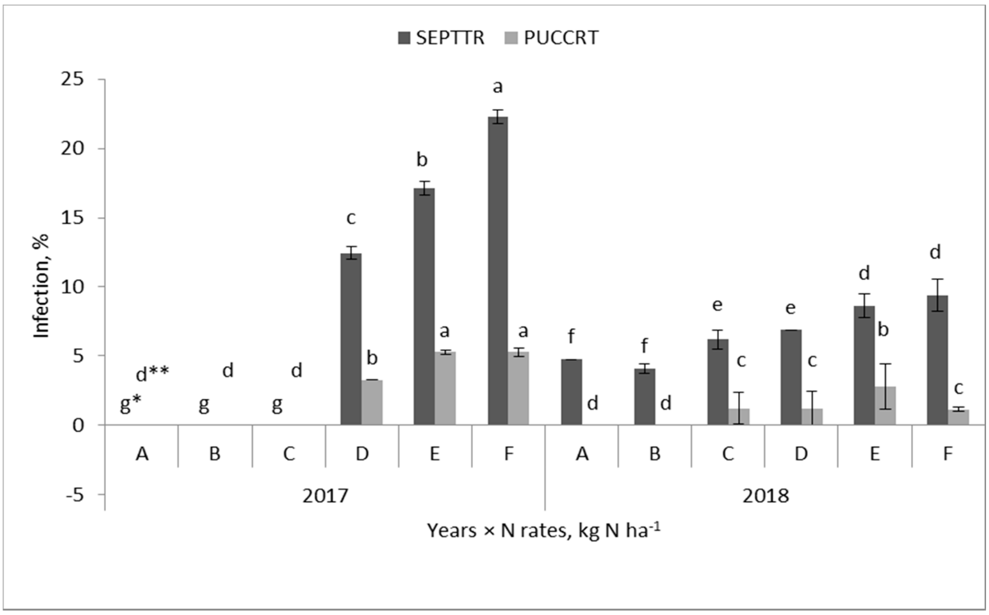

Figure 5. Effect of plant protection methods on infestation of winter wheat by pathogens. Similar letters indicate a lack of significant differences between experimental treatments using Tukey's test. The vertical bar in the column is the standard error of the mean. g*, d**—no infection for SEPTTR and PUCCTR, respectively.

3.3. *Indicators of N Economy*

The grain yield of winter wheat showed a strong correlation with the mass of N accumulated in the grain (Ngrain) (Table A3). Ngrain was positively and strongly correlated with the total N uptake by winter wheat and much weaker with indicators of N economy such as Ngap and NUE. At the same time, Ngrain showed a negative relationship with NHI (Table A3). The effect of the Y $\times$ PPMs interaction on Ngrain is shown in Figure 6. In 2017, a maximum value of Ngrain of above 235 kg ha^{-1} was achieved on plots fully protected with fungicides and simultaneously treated with phosphites. Its significant decrease began on plot D, where fungicides were not applied at BBCH 65. The reduction of Ngrain on the plot treated with phosphites alone (plot F, fungicide control) reached 28% (236 vs. 169 kg N ha^{-1}). In 2018, the same trends were recorded but the relative and absolute differences were much smaller (158 vs. 142 kg N ha^{-1}).

The basic indicator of winter wheat N economy, which is the partial factor productivity of fertilizer N (PFP-N$_f$), was 29% lower in 2018 compared to 2017 (Table 5). PFP-N$_f$ and its derivatives such as Ygap and Ngap also showed a significant response to the Y $\times$ PPMs interaction. In 2017, Ngap was almost negligible on plots fully protected with both fungicides and phosphites (Figure 6). A sharp decrease in the Ngap of -17 kg N ha^{-1} was first noted in the plot not treated with fungicides at BBCH 65 (method D). Its value increased to -55 kg N ha^{-1} on the plot treated with phosphites only (method F). In 2018, an Ngap was recorded for all treatments, but a significant decrease compared to 2017 (plot A) was found on plots treated with phosphites alone (plot F, -74 kg N ha^{-1}).

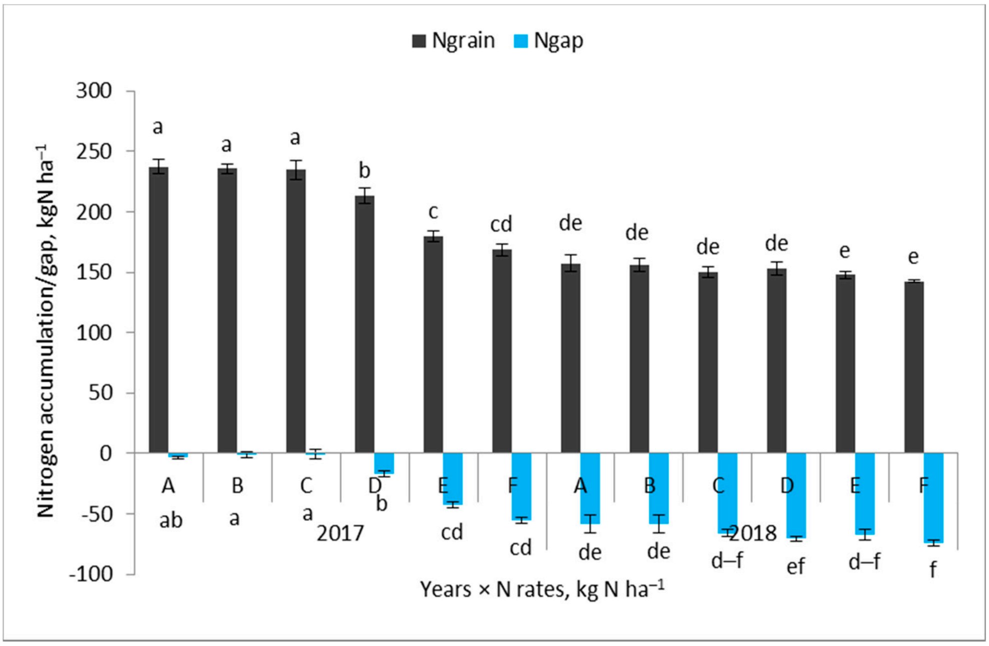

Figure 6. Effect of plant protection methods on nitrogen accumulation in grain and on nitrogen gap. Similar letters indicate a lack of significant differences between experimental treatments using Tukey's test. The vertical bar in the column is the standard error of the mean.

The nitrogen harvest index (NHI) of winter wheat, averaged over experimental treatments, reached 62% in 2017, while in 2018 it was 80% (Table 5). In 2017, NHI ranged from 66% to 68% on plots fully protected with fungicides and phosphites (Figure 7). A slight decrease was noted in the treatment, where fungicides were excluded at BBCH 65 (plot D). A dramatic decrease of about 10 p.p. was recorded for plants treated mainly or only with phosphites (plots E and F). In 2018, NHI ranged from 78% to 81%. The opposite trends were observed in the case of the Nitrogen Unit Accumulation (NUA) index. Any increase in NHI resulted in a linear decrease in NUA:

$$\mathrm{NUA} = 0.43\mathrm{NHI} + 59.5 \text{ for } n = 36.\ R^2 = 0.90 \text{ and } p \leq 0.001 \quad (9)$$

This index was positively, but weakly correlated with GY, TGW and most of the indicators of N economy in wheat (Table A3). The highest correlation coefficient (r = 0.76 ***) for NUA was found for N total. In 2017, its highest values were recorded for plots E and F, where mainly phosphites were used (Figure A4). Significantly lower values were recorded for plots protected with a predominance of fungicides. In 2018, this trend was also observed, but differences between treatments were less pronounced.

Table 5. Characteristics and indices of nitrogen economy of winter wheat at harvest.

Factor	Level of Factor	PFP–N_f	GYgap	Ngap	Ng89	Nt89	NHI	NUA
		kg Grain kg^{-1} N_f	t ha^{-1}		kg ha^{-1}		%	kg N t^{-1} Grain
Year (Y)	2017	58.6 a	−1.306 a	−19.8 a	211.5 a	339.5 a	62.4 b	32.6 a
	2018	41.8 b	−4.332 b	−65.8 b	151.2 b	189.3 b	79.9 a	25.2 b
p		***	***	***	***	***	***	***
Phosphirones (Phi)	Cu	51.1	−2.661	−40.4	183.0	266.9	70.9	28.6
	Mg	50.0	−2.857	−43.4	180.1	264.3	70.9	29.0
	Cu/Mg	49.5	−2.938	−44.6	181.0	262.0	71.6	28.9
p		ns	ns		ns	ns	ns	ns

Table 5. *Cont.*

Factor	Level of Factor	PFP–N_f	GYgap	Ngap	Ng89	Nt89	NHI	NUA
		kg Grain kg^{-1} N_f	t ha^{-1}		kg ha^{-1}		%	kg N t^{-1} Grain
Plant Protection Methods (PPMs)	A	54.6 a	−2.029 a	−30.8 a	197.4 a	279.4 a	73.3 a	27.8 b
	B	55.0 a	−1.960 a	−29.8 a	195.9 a	278.3 a	72.6 a	27.5 b
	C	53.8 a	−2.175 a	−33.0 a	192.5 ab	267.7 a	74.1 a	27.1 ab
	D	49.8 b	−2.883 b	−43.8 b	183.2 b	265.3 a	71.6 a	29.1 ab
	E	45.8 c	−3.602 c	−54.7 c	163.6 c	256.4 ab	67.6 b	30.6 a
	F	42.2 d	−4.263 d	−64.7 d	155.5 c	239.3 b	67.6 b	31.2 a
p		***	***	***	***	***	***	***
Source of variation for the studied interactions								
Y × Phi		ns	ns	ns	*	ns	ns	ns
Y × PPMs		***	***	***	***	***	***	***
Phi × PPMs		ns	ns	ns	*	ns	ns	ns
Y × Phi × PPMs		ns	ns	ns	ns	ns	ns	ns

Similar letters in the column indicate a lack of significant differences between experimental treatments using Tukey's test; ***, * indicate significant differences at $p < 0.001$ and $p < 0.05$, respectively; ns—non significant; Legend: A—full fungicide protection + 3 × phosphite application; B—full fungicide protection + 4 × phosphite application; C—full fungicide protection + phosphite at BBCH 21; D—fungicide protection at BBCH 30 and BBCH 39–45 + phosphite at BBCH 21 and BBCH 55; E—fungicide protection at BBCH 30 + phosphite at BBCH 21, BBCH 32 and BBCH 55; F—phosphite alone at BBCH 21, BBCH 29, BBCH 32 and BBCH 55; PFP-N_f—partial factor productivity of fertilizer N; GYgap—yield gap; Ngap—N gap; Ng89, Nt89—nitrogen accumulation by winter wheat at BBCH 89, grain total, respectively; HI—harvest index; NUA—N unit accumulation.

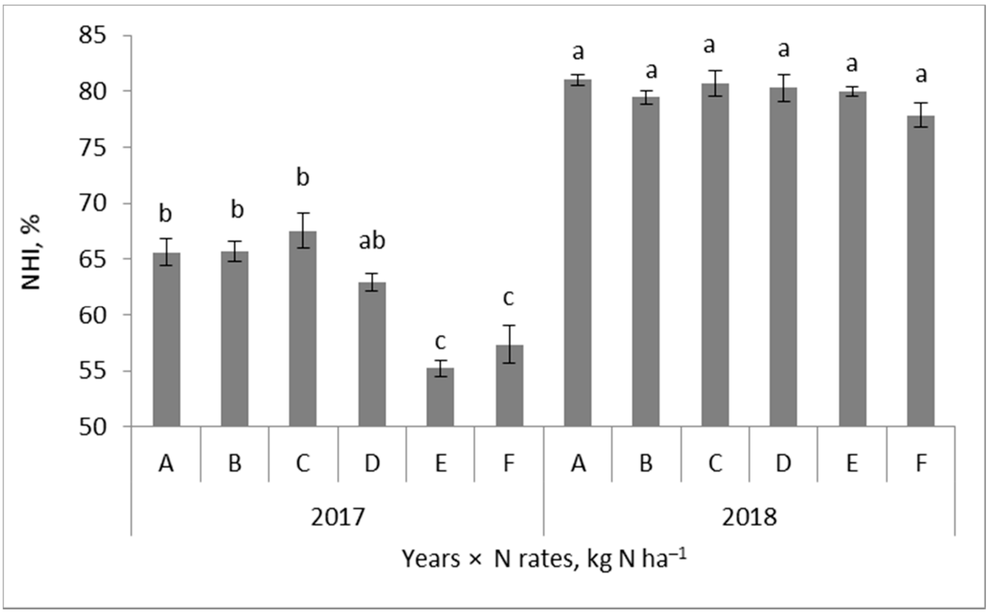

Figure 7. Effect of plant protection methods on nitrogen harvest index of winter wheat. Similar letters indicate a lack of significant differences between experimental treatments using Tukey's test. The vertical bar in the column is the standard error of the mean.

4. Discussion

The harvested yield of a given crop, independently of the weather during the growing season, is a basic criterion for selection of an effective method of plant protection against pathogens [6,35]. The highest grain yields, determining the maximum attainable yield of winter wheat for the environmental conditions and the applied rate of fertilizer nitrogen in the study, were obtained for experimental objects fully protected with organic fungicides and simultaneously applied phosphites (Table 3). The yield of 11.854 t ha^{-1} fully corroborates the results obtained for winter wheat in previous studies [48]. The use of phosphites instead of fungicides resulted in a significant grain yield reduction. It reached 3.6 t ha^{-1} in

2017, a year with favorable growth conditions for winter wheat (Table 3). In 2018, which was characterized by a deep drought during the spring, the maximum difference in yields due to reduction in organic fungicide use was of 1.1 t ha^{-1}. This result clearly indicates the need to protect wheat against pathogens even under water stress [36,37,40]. Moreover, these two figures clearly indicate that winter wheat protection against pathogens using phosphites was ineffective. It can be concluded that the tested phosphites were unable to fulfill the protective functions of organic fungicides [33]. The obtained results contradict both the expectations and some of the experimental evidence presented so far for using phosphites as fungicides [12]. The size of the recorded yield gap is explained by yield components such as (i) wheat biomass at harvest, (ii) harvest index, and (iii) thousand grain weight. All these three characteristics of winter wheat, regardless of the weather in the given growing season, deteriorated in the treatments where the use of organic fungicides was reduced. The decrease in wheat biomass, averaged over years and other treatments, on plots fully treated with phosphites, reached 20% in relation to plots fully protected with organic fungicides plus phosphites. Combined with a simultaneous decrease in TGW, the decrease in grain yield reached 23%. Such a large decrease in wheat biomass at harvest suggests a deep disturbance in yield formation by wheat in the pre-flowering period. It is well documented that wheat biomass in this particular period of its growth is a reliable tool of the grain yield prognosis [49].

The above considerations indicate at least two main reasons for the grain yield decrease. The first, dominant one was the weather during the spring part of winter wheat growth. The average yield decline in 2018 compared to 2017 was 3.0 t ha^{-1}. This resulted from a reduction of all yield components. The most noticeable was the decrease in grain density, which reached 16%. This aggregate yield component is considered as the main trait of the grain yield of wheat [38,50]. This wheat trait clearly explains the impact of weather on wheat biomass and yield [51]. The second yield component, TGW, decreased by 15%, and showed a significant dependence on the interaction of Y $\times$ PPMs (Figure 3). The lack of competition between the yield components, and especially between TGW and grain density, indicates that the weather during the grain filling period limited the increase in grain weight. In 2018, drought and high temperatures were the main reasons for yield decrease (Figure 1, Table 3). In fact, this factor significantly reduced the wheat biomass in the first place, consequently leading to a lower grain density. It is well documented that elevated temperatures (>30 °C) significantly reduce both photosynthesis and the growth rate of wheat grain [29,30,52]. The second reason that significantly reduced TGW, and thus, the yield, regardless of weather conditions in the studied seasons, was the pressure of pathogens. A higher infestation of wheat occurred in favorable 2017. The main factors contributing to the pressure of biotrophic pathogens on wheat, such as *Zymoseptoria tritici* and *Puccinia recondite*, are weather conditions and nitrogen nutrition [34,35]. In the grain filling period both the temperature and precipitation were high, which favors wheat infection by these pathogens [36,37]. As a consequence, a lower TGW was recorded in treatments with phosphites used as a dominant means of protecting the wheat canopy.

The impact of plant protection methods on yield was clearly emphasized by the response of three indicators, explaining the temporary production potential of winter wheat at BBCH 75. They were (i) SPAD index, (ii) N content in leaves, (iii) leaf greenness (GREENT). These indices indirectly emphasized the impact of the wheat protection method during the GFP on the yield, and actually, on TGW, as the main yield predictor [53]. This period is important for the grain growth rate, which depends on both the photosynthetic activity of wheat leaves and their activity during wheat post-flowering growth [30,54,55]. However, what is most important for agronomic practice is that these indicators can be used to evaluate the crop protection methods. The conducted assessment was based on the degree of winter leaf infestation by two pathogens, attacking leaves. Two pathogens, *Zymoseptoria tritici* and *Puccinia recondita*, which exhibit biotrophic feeding behavior, were used. It is assumed that plants well-fed with N are more sensitive to their attack [56]. The study clearly showed that wheat plants showed no difference in leaf nitrogen content until the beginning of flowering (Table 4). The attack of pathogens occurred in both years, but was significantly greater in the weather-favorable 2017 (Table 4, Figure 1). The greater infestation of wheat by *Zymoseptoria tritici* in 2017 can only be explained by the better, even luxurious, nitrogen nutrition of plants [39]. This state was recorded on plots with a reduced frequency of organic fungicide use. Substitution of fungicides with phosphites did not inhibit the pressure of either pathogens on wheat. This rule was observed in both years, independently on the prevailing type of weather. However, it should be emphasized that repeated application of phosphites to wheat may, at least partially, inhibit the pressure of *Puccinia recondite* (Figure 5).

The infestation of the flag leaf of wheat by pathogens results in a significant reduction of its green area, which can significantly disturb the physiological activity of the plant after flowering [57]. This study showed that simple diagnostic tools, such as the N-tester, GREENT test, and pathogen infestation tests used at BBCH 75, were very useful in making a reliable prediction of grain yield. The N-Tester is a widely applied diagnostic tool to assess the N status of plants within their growing season. In cereals, it is mainly used before flowering [45]. In this study, the SPAD index turned out to be an effective tool for forecasting the yield of winter wheat not in the diagnostically standard period, i.e., from BBCH 31 to BBCH 55, but in the middle of the grain filling period. Its diagnostic usefulness is emphasized by a very large, significant relationship with the N content in leaves at BBCH 75. Other visual tests of wheat health conditions applied in this period, despite their low relationship with the nutritional status of winter wheat, showed a high prognostic value for both grain yield and for the decisive yield component, which is TGW (Equations (7) and (8)).

Yield gap is calculated as the difference between the maximum yield achievable in a geographic region with defined climatic and soil conditions and the actual yield harvested by the farmer [58]. In rain-fed agriculture, the key factor driving the Ygap is the dominant course of weather in a given growing season [59]. The climatic yield gap in the studied case was the difference between the maximum attainable yield of 11.854 t ha^{-1} and the highest yield in the dry 2018, which was 3.848 t ha^{-1}. This value corresponds to a loss of 58 kg of N_f ha^{-1}. This amount of applied N_f was not converted into grain yield in 2018. The second reason of the total Ygap occurrence is the lack and/or inefficiency of agronomic factors [60]. In the case studied, it was the replacement of organic fungicides by phosphites. The most surprising fact is that due to use of phosphites instead of organic fungicides, the agronomic Ygap was much deeper in the favorable 2017 than in the dry 2018. The recorded Ygap in favorable growth conditions was 3.6 t ha^{-1}, while in unfavorable conditions it reached only 1.1 t ha^{-1}. The corresponding Ngap was -55 and -16 N_f ha^{-1}, but the total Ngap in the dry 2018 as compared to 2017 reached -74 N_f ha^{-1}. The key reason for this discrepancy was both weather and the ineffective control of the pathogen pressure due to the lack, or too low frequency of organic fungicide application. Phosphites, regardless of the frequency of application, were unable to stop the pressure of pathogens and thus replace organic fungicides.

Another indicator showing ineffective protection of the winter wheat canopy by phosphites was the nitrogen harvest index (NHI). Its values in favorable growing conditions, as in 2017, were highly sensitive to the used method of winter wheat canopy protection against pathogens. The lowest NHIs were recorded for plants protected just before flowering with phosphites. This situation strongly indicates a disturbance in the balance between the activity of the physiological source (leaf photosynthetic activity) and sink in winter wheat (TGW). The lower values of NHI for phosphite treated plants were due to both the excessive content of N in vegetative wheat organs, and a significantly lower weight of grains. The excessive accumulation of N at wheat harvest in phosphite treated plants is clearly expressed by the response of NUA indices to the examined protection methods. In the favorable 2016/2017 growing season this index for the fully fungicide protected plots reached 30 kg N t^{-1} grain, while for those treated with phosphite it increased up to

36 kg N t^{-1} grain. In the dry 2017/2018 season, the partitioning of N was not affected by the method of wheat canopy protection and ranged from 24 to 27 kg N t^{-1} grain.

5. Conclusions

Studies on the replacement of organic fungicides with inorganic ones, such as phosphites, in winter wheat protection against pathogens have clearly demonstrated the ineffectiveness of this strategy. A marked decrease in grain yield due to partial or full replacement of fungicides by phosphites was observed in both seasons, regardless of the weather. The pressure of pathogens caused a decrease in the thousand grain weight, which was significant in the favorable 2017/2017 growing season. This primary yield component was significantly dependent on the nitrogen nutritional status of wheat at BBCH 75 (nitrogen content in leaves). The main result of fungicide substitution with phosphites in winter wheat was a sharp decrease in the productivity of fertilizer nitrogen. The nitrogen gap, which quantified the ineffectiveness of the applied nitrogen fertilizer, was 55 and 16 kg N ha^{-1}, respectively, in favorable and unfavorable conditions for the grain yield development by winter wheat. The deterioration of wheat nitrogen nutritional status was clearly confirmed by indicators such as the SPAD and GREENT indices. These two N indicators together with the tests of wheat infestation by pathogens allowed us to carry out a highly significant prediction of both the thousand grain weight and the grain yield. These studies also showed that the medium milk stage of grain growth in winter wheat is an appropriate time to evaluate the effect of the applied fungicides on the nitrogen plant status and finally, the grain yield.

Author Contributions: Conceptualization, W.G. and S.Ł.; methodology, W.G. and S.Ł.; software, J.P.; validation, S.Ł., W.S. and J.P.; formal analysis, W.S.; investigation, S.Ł., W.S. and J.P.; resources, W.S.; data curation, S.Ł. and W.S.; writing—original draft preparation, S.Ł.; writing—review and editing, W.G.; visualization, W.S.; supervision, W.G.; project administration, J.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Correlation matrix of basic yield components and yield of winter wheat, n = 36.

Traits	EN [1]	GNE	GD	TGW	B89	HI
GY	0.33 *	0.64 ***	0.65 ***	0.94 ***	0.96 ***	−0.25
EN	1.00	0.21	0.22	0.23	0.41 *	−0.41 *
GNE		1.00	0.99 ***	0.61 ***	0.73 ***	−0.52 **
GD			1.00	0.63 ***	0.74 ***	−0.53 **
TGW				1.00	0.91 ***	−0.27
B89					1.00	−0.50 **

***, **, * indicate significant differences between wheat traits at $p < 0.001$, $p < 0.01$, and $p < 0.05$, respectively; ns—non-significant; Legend: [1] GY—grain yield; EN—number of ears; GNE—grains number per ear; GD—grain density; TGW—thousand grain weight; B89—wheat biomass at BBCH 89; HI—harvest index.

Table A2. Correlation matrix of the content of N, SPAD, and winter wheat infestation with pathogens, n = 36.

Traits	TGW	N–L31	N–L59	N–L75	N–L89	SPAD31	SPAD59	SPAD75	SEPTTR	PUCCRT	GREENT
GY	0.94 ***	0.42 *	0.08	0.90 ***	0.50 **	−0.39 *	0.29	0.90 ***	−0.41 *	−0.20	0.63 ***
TGW	1.00	0.33 *	−0.03	0.85 ***	0.48 **	−0.49 **	0.22	0.87 ***	−0.39 *	−0.17	0.61 ***
N–L31		1.00	0.18	0.51 **	0.61 **	−0.24	0.35 *	0.54 **	0.20	0.29	0.06
N–L59			1.00	0.13	0.07	0.09	0.67 ***	0.09	0.01	0.11	−0.11
N–L75				1000	0.75 ***	−0.48 **	0.43 **	0.95 ***	−0.10	0.06	0.35 *
N–L89					1.00	−0.47 **	0.42 *	0.74 ***	0.48 **	0.52 **	−0.20
SPAD31						1.00	−0.06	−0.52 **	−0.15	−0.24	−0.12
SPAD59							1.00	0.36 *	0.07	0.19	−0.08
SPAD75								1.00	−0.04	0.14	0.31
SEPTTR									1.00	0.85 ***	−0.88 ***
PUCCRT										1.00	−0.73 ***

***, **, * indicate significant differences between wheat traits at $p < 0.001$, $p < 0.01$, and $p < 0.05$, respectively; ns—non significant; Legend: GY—grain yield; TGW—thousand grain weight; N–L, SPAD—nitrogen content in leaves and SPAP indices of winter wheat at respective BBCH stages, 31, 59, 75, 89; SEPTTR—*Zymoseptoria tritici*; PUCCRT—*Puccinia recondita*; GREENT—green test.

Table A3. Correlation matrix of nitrogen economy indices in winter wheat and grain yield, n = 36.

Traits	TGW	PFP–N	Ygap	Ngap	Ngrain	Ntotal	NHI	NUA
GY	0.94 ***	0.00	0.29	0.41 *	0.98 ***	0.91 ***	−0.57 ***	0.43 *
TGW	1.00	0.94 ***	0.24	0.33 *	0.94 ***	0.87 ***	−0.53 **	0.42 *
PFP–N		1.00	0.29	0.41 *	0.98 ***	0.91 ***	−0.57 ***	0.43 *
Ygap			1.00	0.99 ***	0.25	−0.11	0.60 ***	0.70 ***
Ngap				1.00	0.35 *	0.01	0.48 **	−0.61 ***
Ngrain					1.00	0.92 ***	−0.56 ***	0.48 *
Ntotal						1.00	−0.84 ***	0.76 ***
NHI							1.00	−0.95 ***

***, **, * indicate significant differences between wheat traits at $p < 0.001$, $p < 0.01$, and $p < 0.05$, respectively; ns—non-significant; Legend: GY—grain yield; TGW—thousand grain weight; Ygap, Ngap—yield and nitrogen gaps; Ngrain, Ntotal—nitrogen accumulated in grain and its total accumulation; NHI—nitrogen harvest index; NUA—nitrogen unit accumulation.

Appendix B

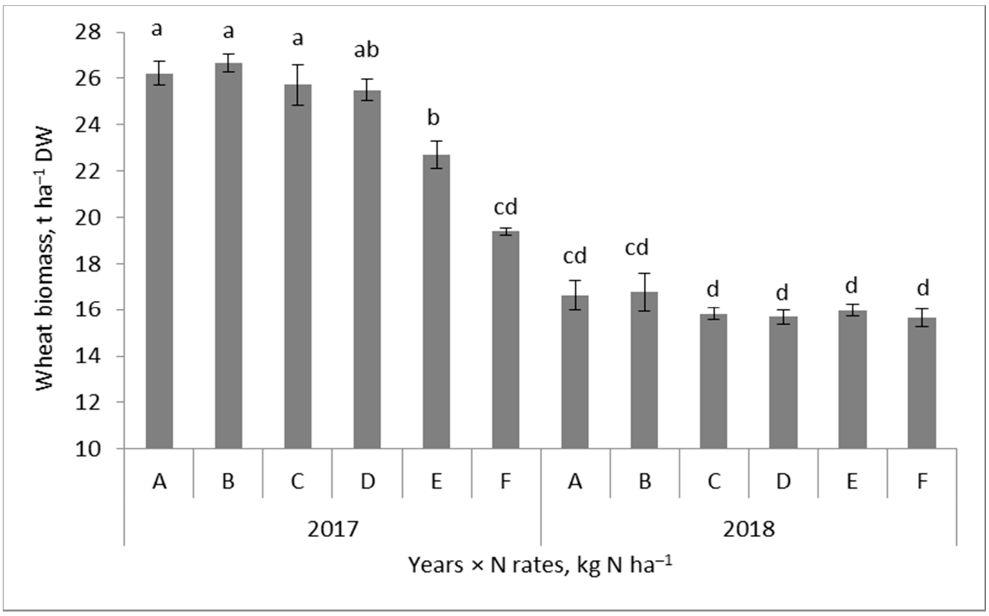

Figure A1. Effect of plant protection methods on the biomass of winter wheat at harvest. Similar letters indicate a lack of significant differences between experimental treatments using Tukey's test. The vertical bar in the column is the standard error of the mean.

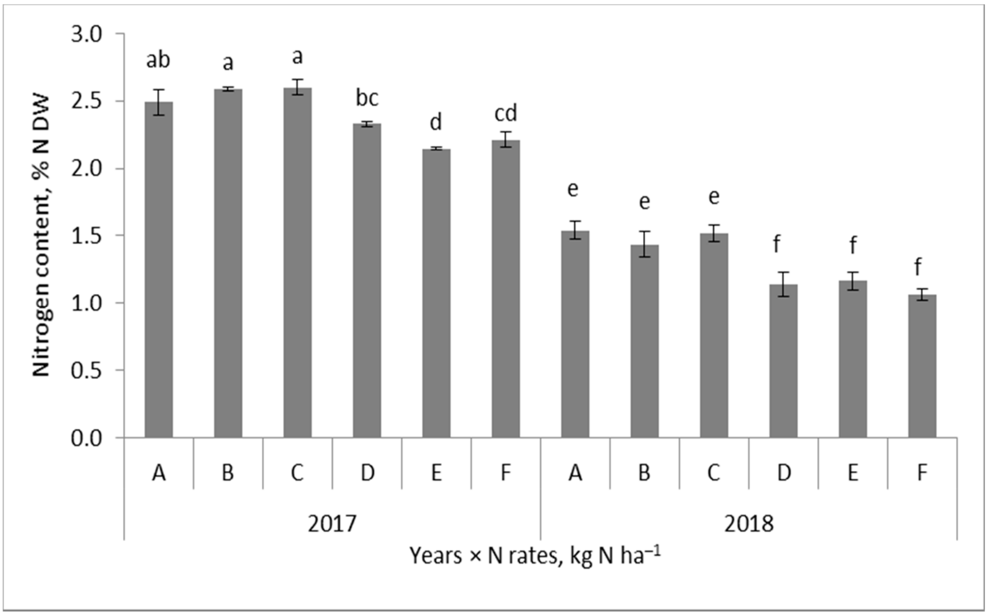

Figure A2. Effect of plant protection methods on the nitrogen content in leaves of winter wheat at BBCH 75. Similar letters indicate a lack of significant differences between experimental treatments using Tukey's test. The vertical bar in the column is the standard error of the mean.

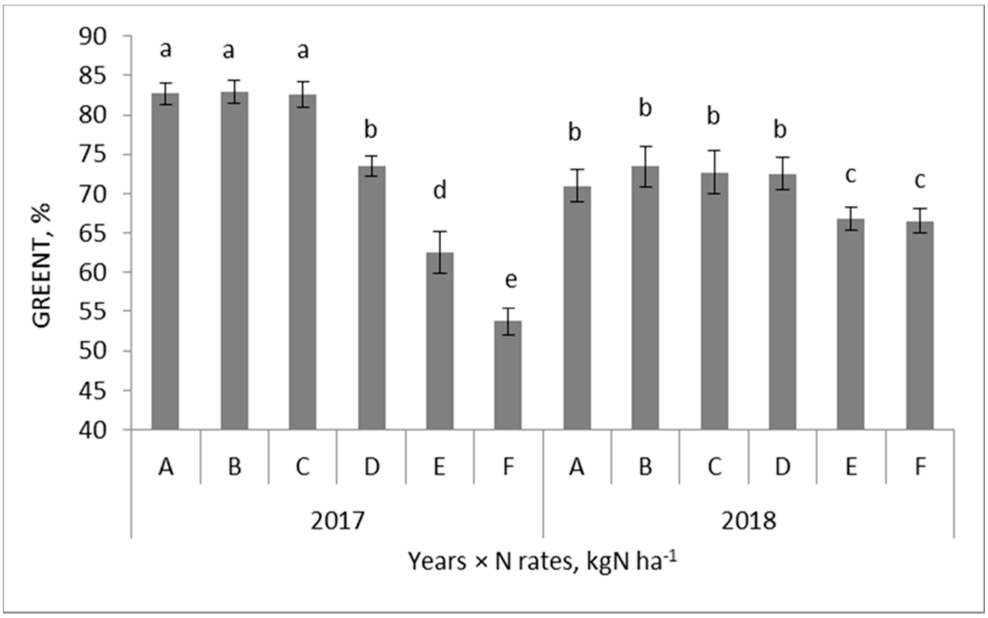

Figure A3. Effect of plant protection methods on the GREENT index of winter wheat at BBCH 75. Similar letters indicate a lack of significant differences between experimental treatments using Tukey's test. The vertical bar in the column is the standard error of the mean.

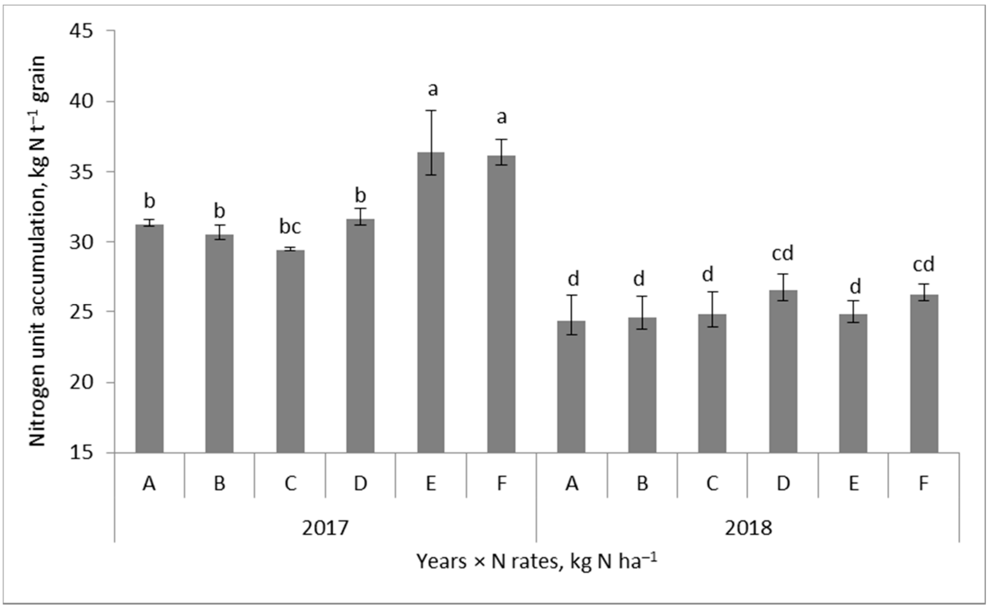

Figure A4. Effect of plant protection methods on the nitrogen unit accumulation index (NUA) of winter wheat at BBCH 75. Similar letters indicate a lack of significant differences using Tukey's test. The vertical bar in the column refers to the standard error of the mean.

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