



# Article Spatial-Temporal Differentiation of Soil Biochemical Parameters and Their Relationship with Nitrogen Resources during the Vegetation Period of Selected Crops

Agnieszka Wolna-Maruwka <sup>1,</sup>\*<sup>1</sup>, Aleksandra Grzyb <sup>1,</sup>\*<sup>1</sup>, Remigiusz Łukowiak <sup>2</sup><sup>1</sup>, Jakub Ceglarek <sup>3</sup>, Alicja Niewiadomska <sup>1</sup> and Dariusz Kayzer <sup>4</sup>

- <sup>1</sup> Department of Soil Science and Microbiology, Poznan University of Life Sciences, Szydłowska 50, 60-656 Poznan, Poland; alicja.niewiadomska@up.poznan.pl
- <sup>2</sup> Department of Agricultural Chemistry and Environmental Biogeochemistry, Poznan University of Life Sciences, Wojska Polskiego 38/42, 60-625 Poznan, Poland; remigiusz.lukowiak@up.poznan.pl
- <sup>3</sup> Environmental Remote Sensing and Soil Science Research Unit, Faculty of Geographical and Geological Sciences, Adam Mickiewicz University, Krygowskiego 10, 61-680 Poznan, Poland; jakub.ceglarek@amu.edu.pl
   <sup>4</sup> Department of Mathematical and Statistical Mathematical Mathematical Company University of Life Sciences
- <sup>4</sup> Department of Mathematical and Statistical Methods, Poznan University of Life Sciences, Wojska Polskiego 28, 60-637 Poznan, Poland; dariusz.kayzer@up.poznan.pl
- \* Correspondence: amaruwka@up.poznan.pl (A.W.-M.); aleksandra.grzyb@up.poznan.pl (A.G.)

Abstract: Understanding the spatial-temporal variability of soil enzymatic activity and its relationship with nitrogen (N) resources in the soil and crop yield is crucial in rational management practices of mineral fertilization. The scarcity of comprehensive studies on geostatic analyses of agricultural soils and plant yields, which would take into account both temporal and spatial variability, was the reason for undertaking this research. The aim of this study was to determine the spatial and temporal variability of the activity of soil enzymes, such as acid (PAC) and alkaline (PAL) phosphatases, urease (URE) and protease (PROT), the content of N-NH<sub>4</sub> (ammonium ions), N-NO<sub>3</sub> (nitrate ions), phosphorus (P), pH, moisture, as well as crop yield on a conventionally managed farmland of 40 ha. During the two-year experiment, soil samples were collected from 37 measurement points. Wheat was the first tested crop, followed by oilseed rape. It was shown that all the tested soil parameters showed temporal and spatial variability, and a significant number of them were significantly higher in July. The creation of raster maps showing the distribution of the tested parameters allowed for the observation of the considerable activity of PAC, PAL, URE, and PROT, as well as a high application of N-NO<sub>3</sub> in the southern part of the field during the growth of the plants. The statistical analysis revealed a negative interaction between the  $N-NH_4$  and  $N-NO_3$  and the urease in the soil under the cultivation of plants. The pH and the percentage of moisture in the soil also had higher values in the south of the field. This pointed to the existence of separate production zones in the south-central part of the field, characterized by a higher yield of wheat and rape. On the basis of the conducted research, it was unequivocally stated that the values of enzymatic and chemical parameters of the soil were reflected in the size of the yield obtained, which allows conclusions to be drawn with respect to the rational management of N in the production process, laying the foundations for precision agriculture.

Keywords: geostatistics; soil enzymes; nitrogen ions; yield; precision farming; spatial variability

# 1. Introduction

According to the assumptions of the Food and Agriculture Organization of the United Nations (FAO), by 2050, the world population will exceed 9 billion. In order to meet the food needs of a dynamically developing society, food production is expected to have increased by at least 70% by then. At the same time, taking into account the guidelines of the European Biodiversity Strategy (2020) [1], the challenge for modern agriculture is to maintain plant production at the current level while reducing the amount of mineral fertilizers used by 30% and reducing the loss of nutrients from the soil by 50%.



Citation: Wolna-Maruwka, A.; Grzyb, A.; Łukowiak, R.; Ceglarek, J.; Niewiadomska, A.; Kayzer, D. Spatial-Temporal Differentiation of Soil Biochemical Parameters and Their Relationship with Nitrogen Resources during the Vegetation Period of Selected Crops. *Agriculture* 2023, *13*, 2034. https://doi.org/ 10.3390/agriculture13102034

Academic Editors: Othmane Merah, Hailin Zhang, Purushothaman Chirakkuzhyil Abhilash, Magdi T. Abdelhamid and Bachar Zebib

Received: 5 September 2023 Revised: 14 October 2023 Accepted: 19 October 2023 Published: 22 October 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The ideal solution that meets the requirements of EU programs is sustainable management of plant production, consisting of the proper management of crop residues and limiting the use of mineral fertilizers thanks to precise dosing of appropriate doses of mineral fertilizers depending on the biochemical properties of the soil in a given part of the field [2,3].

The spatio-temporal variation of soil enzymatic parameters and their relationship with N resources in the soil depending on the type of plant cultivated is an important topic from the point of view of precision agriculture. Understanding how soil enzyme activity changes over space and time in an agricultural field and how it interacts with N resources can provide valuable information on nutrient cycling, ecosystem productivity, management of the soil environment, and, therefore, plant yields of economic importance.

Although in recent years, some studies have gradually implemented geostatistical tools on the spatial and temporal distribution of nutrients in agricultural soils [4,5] and crop plants [6,7], as well as analyzed the microbiological and enzymatic variability of soils [8–11], there is still a lack of studies that would take into account a comprehensive analysis of the above interactions.

The arable field in the horizontal arrangement is not uniform, not only in terms of grain size and humus content (factors determining the soil's capacity for cations) but also in pH and water conditions. Agricultural land use is a dynamic process characterized by constant changes in both vegetation cover and management practices. Agricultural practices and plant residues left on the field lead to a diversification of the soil's nutrient content [12,13]. The spatial variability of the cultivated field is superimposed by another developmental variability, defined in this study as time, resulting from the development of the crop and its changing demand for nitrogen and elements balancing this component over time.

Nitrogen is a key factor in plant production, and differences between plant species in the timing of N uptake can be an important feature in regulating microbial community composition and ecosystem productivity [14]. In modern classical agriculture, fertilizers, mainly minerals, are the main source of N. However, N is also released into the soil from plant residues and organic fertilizers with the participation of soil microorganisms. Unfortunately, the use of fertilizers for crops, considered on a global scale, is low and ranges between 30 and 50%. This condition means that most of the component is dispersed in the environment, posing a threat to aquatic and terrestrial ecosystems [15,16].

In the period from the start of spring vegetation until flowering, plants intensively absorb N from soil resources, supplemented by the decomposition of post-harvest residues and the use of mineral fertilizers. However, this does not happen evenly. The main reason for differences in the supply of plants with nutrients in the field is the variability of basic soil properties, which in turn results in spatial differentiation of the supply of plants with water and nutrients during the growing season [17,18]. According to the principles of precision agriculture, the variability of Nmin content in the soil is the basis for determining variable N doses in fertilizers. Effective correction of the mineral fertilizer dose, in accordance with the assumptions of sustainable agriculture, requires data on the potential of the soil to release N from soil resources [19,20].

Both mineral fertilizers and root secretions during the growing season, as well as post-harvest residues with a different C:N ratio, determine the directions of changes in the composition and size of the population of soil microorganisms, as well as its enzymatic activity [21].

However, the temporal and spatial variability of soil nutrients and microbial succession and activity during the return of soil nutrients after application is still poorly understood [11]. The assessment of soil enzymatic activity is considered one of the most sensitive indicators of the availability of nutrients for crops, as well as an index of the level of activity of microorganisms involved in these processes, depending on natural or artificial physicochemical conditions in the soil environment [22,23].

According to the Carbon Acidity and Mineral Protection (CAMP) theory, the rate of growth, multiplication, and metabolic activity of the microbial population in the soil depends on factors that control the availability of Nmin [24]. Averill and Waring [25] and Dai et al. [26] state that the size, growth, and structure diversity of soil microbes are positively correlated with the content of N, organic carbon, pH, and available forms of alkaline cations (calcium, magnesium, potassium) or phosphorus. According to Koch et al. [27], factors determining the temporal variability of the composition and metabolic activity of microorganisms in the soil also include seasonal changes in temperature, humidity, and the type of cultivated plant.

According to Ghazali et al. [28] and Slessarev et al. [29], soil reaction and moisture are two of the main factors determining the proper development and activity of soil microorganisms. In the soil, there is a relationship between the above parameters, which in turn translates into the availability of nutrients for plants and microorganisms.

The reaction regulates the soil's ability to store and release nutrients and thus significantly contributes to controlling soil productivity. However, soil pH is not an independent regulator of soil fertility because even small changes in the water balance cause a sudden transition from alkaline to acidic soil, which results in a change in the availability of nutrients.

Acosta-Martínez and Waldrip [30] noted that the study of spatial and temporal activity of enzymes requires advanced visualization technology, including the creation of raster maps of a given agricultural field, for rational N management. Geostatistics provides a set of statistical tools to describe and model spatial patterns, make predictions at unsampled locations, and assess the uncertainty of these predictions Al-Omran et al. [31]. Making maps of the spatial variability of soil resulting from its chemical composition, physical properties, and activity of microorganisms enables a detailed analysis of the production space in the technology of precision agriculture and is the basis for carrying out variable agrotechnical treatments.

Ignoring the spatial variability of soil properties and its impact on plant growth may result in unwise cultivation practices, such as excessive fertilization and liming of the soil, long-term retention of nutrients in forms inaccessible to plants, and even lower yields [32]. In order to rationally manage N in the production process, it is necessary to determine not only the current level of mineral N content but also organic forms that are substrates of the ammonification process and, subsequently, nitrification. The analysis of the spatial differentiation of soil physicochemical properties provides the basis for precision farming, which is currently promoted and implemented in the most economically developed countries.

The aim of this research was to determine the variability of selected soil parameters and plant yield in the spatio-temporal system of the cultivated field, as well as to determine the type of mutual relationship between soil biochemical activity, selected physicochemical parameters, including soil N resources, and plant yield weight.

At the same time, it was assumed that the spatio-temporal distribution of PAC, PAL, URE, and PROT activity is variable and depends on the physical and chemical parameters of the soil and is related to the quantitative characteristics of the cultivated plants (yield weight). Considering the significant spatio-temporal variability of the listed soil properties and plant yield, the direction of this variability and the type of interaction between the variables studied were identified and defined in the conducted research. The created maps defining the distribution of the above-mentioned features will form the basis for the precise application of appropriate doses of mineral fertilizers.

# 2. Materials and Methods

# 2.1. Research Object

The field experiment was carried out in 2019 and 2020 on a 40-hectare agricultural field located in Kobylniki, Kościan County, Poland (52°04′20.4″ N 16°32′21.3″ E), on soil classified as lessive soil, from slightly loamy sands to medium loam. The soil texture was

determined using the Pruszczyński method using a hydrometer for sand, silt, and clay fractions [33]. In the field, 37 points were established in the raster system at strictly defined georeferenced points (Figure 1).



**Figure 1.** Arrangement of georeferenced measurement points on the 40-hectare field at Kobylniki, Poland. The places where soil samples were collected are marked with numbers (30–66).

The experiment was carried out on the sequence of two test plants: winter wheat (*Triticum aestivum* L.) cultivar Gustaw and winter oilseed rape (*Brassica napus* L.) cultivar DK Extract at a sowing rate of 350 seeds m<sup>-2</sup> and 50 seeds m<sup>-2</sup>, respectively. Agrotechnical and cultivation procedures were carried out in accordance with the principles of good agricultural and experimental practice for the two crop species. For wheat, organic fertilization was used—35 t·ha<sup>-1</sup> manure (under the forecrop) and a 20 m<sup>3</sup>·ha<sup>-1</sup> slurry application—followed by mineral fertilization with N (1st—61 kg·ha<sup>-1</sup>; 2nd—94 kg·ha<sup>-1</sup>; 3rd—40 kg·ha<sup>-1</sup>). Pre-sowing fertilizers with P (69 kg·ha<sup>-1</sup>), K (120 kg·ha<sup>-1</sup>), magnesium (Mg) (18 kg·ha<sup>-1</sup>), and sulfur (S) (37.5 kg·ha<sup>-1</sup>) were used in the cultivation of oilseed rape. After sowing, N (1st—34 kg·ha<sup>-1</sup>; 2nd—63 kg·ha<sup>-1</sup>; 3rd—115 kg·ha<sup>-1</sup>), Mg (32.5 kg·ha<sup>-1</sup>), and S (65 kg·ha<sup>-1</sup>) were applied.

# 2.2. Climate

The local climate, classified as intermediate between Atlantic and continental, is seasonally variable. One of the characteristics of the region's climate is the frequent, though irregular, occurrence of periods without precipitation, which have a negative impact on the development of plants. Precipitation in the period from January to July amounted to 231 mm in 2019, including 22.8 mm in July, and 309 mm in 2020, including 65 mm in July. Air temperatures in both years were higher compared to the corresponding long-term averages, with the average temperature from June to August equal to 19 °C and 1 °C in the winter.

# 2.3. Soil Sampling

For biochemical analyses, soil samples were taken from the topsoil (0–0.3 m) with a soil auger (Eijkelkamp Agrisearch Equipment, Giesbeek, the Netherlands). Around each measurement point, an area of 1 m in diameter was created, from which three sub-

plots were randomly selected. Soil samples were collected from each sub-plot, and then a cumulative sample was prepared and placed in a sterile plastic bag and a portable cooler (4 °C). In both years of this study, samples were collected on four dates: before the start of crop growth, during the flowering of the crop, during harvest, and before the next growing season (saturation of the soil sorption complex (with cations)) (Table 1).

Table 1. Sampling dates in 2019–2020.

Year	2019				
Term	Ι	II	III	IV	
Winter wheat	13.02 before the start of crop growth	3.0203.06he start of growthflowering of the crop		22.10 saturation of the soil sorption complex	
Year	2020				
Term	V	VI	VII	VIII	
Winter oilseed rape	13.02 before the start of crop growth	21.04 flowering of the crop	07.07 harvest	22.10 saturation of the soil sorption complex	

# 2.4. Enzymatic Activity

Biochemical analyses were performed using the spectrophotometric method (Rayleigh UV1800, Beijing, China). Soil enzyme activity studies were based on measurements of alkaline (EC 3.1.3.1) and acid (EC 3.1.3.2) phosphatases, protease (EC 3.4), and urease (EC 3.5.1.5) activity.

Activity of PAC and PAL was assessed with the use of sodium p-nitrophenyl phosphate as a substrate. After one hour of incubation at 37 °C, filtrate was measured at 400 nm wavelength. The obtained value was expressed as  $\mu$ mol PNP·g<sup>-1</sup> dm·h<sup>-1</sup> [34]. The activity of protease was based on sodium caseinate as a substrate and measured after 1 h incubation at 50 °C with 578 nm wavelength [35]. Enzyme activity was expressed in  $\mu$ mol tyrosine·g<sup>-1</sup> dm·h<sup>-1</sup>. Activity of urease was assessed with the use of urea as a substrate; after 18 h of incubation at 37 °C, filtrate was measured at 410 nm wavelength, and the obtained value was expressed as  $\mu$ g N-NH<sub>4</sub>·g<sup>-1</sup> dm·18 h<sup>-1</sup> [36].

### 2.5. Nitrogen

The content of N-NH<sub>4</sub> and N-NO<sub>3</sub> in the soil was determined in samples of sieved fresh soil. Twenty-gram soil samples were shaken for 1 h with 100 mL of 0.01 M potassium sulfate (K<sub>2</sub>SO<sub>4</sub>) solution (soil/solution ratio 1:5; m/v). N-NO<sub>3</sub> concentrations were determined by the colorimetric method using flow injection analyses (FIAstar5000, FOSS, Hoganas, Sweden). The N-NO<sub>3</sub> concentration analysis method consists of two basic steps: reduction of nitrate to nitrite using a cadmium column and then colorimetric determination of nitrite based on the Griess–Ilosvay reaction with N-(1-naphthyl) ethylenediamine dichloride as a diazotizing agent. The measurement was carried out at a wavelength of 540 nm. Total soil N<sub>min</sub> was calculated as the sum of N-NH<sub>4</sub> and N-NO<sub>3</sub> and expressed in kg ha<sup>-1</sup> [37].

# 2.6. Phosphorus

The amount of phosphorus was determined in samples of dried and sieved soil at the beginning and end of the experiment. 100 mL of Mehlich 3 extraction solution (0.2M CH<sub>3</sub>COOH, 0.25M NH<sub>4</sub>NO<sub>3</sub>, 0.015M NH<sub>4</sub>F, 0.013M HNO<sub>3</sub>, 0.001M EDTA) was added to five grams of soil (soil/solution ratio 1:10; m/v) and shaken for 5 min at 200 rpm on an Eberbach shaker (MI, USA) [38]. The mixture was filtered using filter paper. The filtrate was analyzed colorimetrically for P (colorimetric P) at 880 nm using a Jasco V-630 spectrophotometer (Pfungstadt, Germany).

#### 6 of 27

## 2.7. Yield

Harvesting of wheat and rape was carried out in one stage at the beginning of July. The average yield was estimated for each point from an area with a diameter of 1 m. The yield was expressed as kg·ha<sup>-1</sup>. The harvest index (*HI*), known as the agricultural yield index, is an indicator expressing the share of useful yield in the total biomass. Its value was calculated using the following equation and expressed in % [39].

$$HI = rac{seed \ yield}{seed \ and \ straw \ yield}$$

# 2.8. Statistics

Statistical analyses were performed using the Statistica 13.3 software (StatSoft Inc., Cracow, Poland). Separately, for each year of analysis, two-way ANOVA was applied for the sampling date and place because the results between the years were not comparable. Tukey's test at a significance level of p = 0.05 was used. The Pearson correlation coefficient was used to quantify the strength of the relationships between the microbial biomass and DHA activity. To illustrate the relationship between soil and plant parameters, principal component analysis (PCA) and the Pearson correlation coefficient were used. Spatial variability of selected properties was estimated by the fitting of experimental semi-variograms, calculated according to the following formula:

$$\hat{\gamma}(h) = rac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(X_i) - Z(X_i + h)]^2$$

where *h* is the lag distance, N(h) is the number of pairs for distance *h* and  $X_i$ , and  $X_i + h$  relates to the value of the variable at locations separated by the distance *h*.

Spatial variability mapping for each property, characterized by a fitted semi-variogram, was carried out utilizing the kriging interpolation method. This process was executed using the R programming language, specifically employing the R library geoR. Initially, this library was used to load spatial data, and subsequent visual plotting was employed to assess the presence of any discernible trends. If deemed necessary, we applied either a first or second-order trend removal. The function "plot.variogram" was utilized to identify the most suitable variogram for each property, which was subsequently employed in the "krige" function, where either ordinary or universal kriging was selected. The outcome, i.e., the prediction grids, were exported in .tiff format using the raster library and then imported into QGIS software, where the final maps were created. Additionally, heatmaps showing normalized values of properties for each sample point were created. When applied to a tabular format, heatmaps are useful for cross-examining multivariate data, showing variance across multiple variables, revealing any patterns, displaying whether any variables are similar to each other, and detecting if any correlations exist between them. Heatmaps allow a comparison of the distribution of values in sample locations at a glance, easily spotting points with relatively high or low values of measured properties.

#### 3. Results

# 3.1. Spatial–Temporal Variability of Soil Biochemical Activity

Our research, presented in the form of Table 2, showed that most of the analyzed biochemical parameters differed statistically significantly depending on the date and place of soil sampling.

Parameter	Term	Variant	Interaction	
	Wheat			
Acid phosphatase (PAC)	720.97 **	37.85 **	6.34 **	
Alkaline phosphatase (PAL)	47.13 **	29.09 **	6.38 **	
Urease (URE)	117.91 **	79.91 **	15.90 **	
Protease (PROT)	15,415.22 **	8.24 **	9.62 **	
N-NH <sub>4</sub>	232.46 **	103.46 **	59.95 **	
N-NO <sub>3</sub>	5960.52 **	190.00 **	86.83 **	
	Rapeseed			
Acid phosphatase (PAC)	2320.83 **	31.41 **	19.20 **	
Alkaline phosphatase (PAL)	624.56 **	35.54 **	16.52 **	
Urease (URE)	37.80 ***	34.97 ***	13.54 ***	
Protease (PROT)	418.24 ***	14.66 ***	8.37 ***	
N-NH <sub>4</sub>	42.609 ***	24.77 ***	17.39 ***	
N-NO <sub>3</sub>	3363.67 **	20.24 **	15.79 **	

**Table 2.** *F*-test statistics and significance levels of two-way analysis of variance for the enzymatic activity associated with variants and terms research fixed factors (\*\*\* p = 0.001; \*\* p = 0.01).

Analyzing the activity level of acid phosphatase (PAC), urease (URE), and protease (PROT) in the tested soil variants, it was shown that in the first year of this study, it was higher than in 2020. Alkaline phosphatases (PAL) showed higher activity in the soil under cultivation of winter rape (second year of research) (Figure 2). Considering the time changes in the activity of both types of phosphatases, it was found that they showed the highest values during rapeseed harvest (VII term) and the lowest in the III research term (wheat harvest), which was most likely the result of different plant demand for phosphorus (Figure 2). The observations also allowed us to conclude that the post-harvest residues of the tested plants introduced into the soil during their mineralization had a different effect on the activity level of the tested enzymes, as they significantly stimulated it, which was observed on the fourth date of the analysis, or inhibited it, which was shown in the case of rape residues (term VIII). Nevertheless, the average value of the discussed parameters was noticeably higher in the soil variants cultivated with rapeseed (Figure 2). Also, the level of urease activity analyzed throughout the experiment was significantly related to the date of soil sampling and the type of cultivated plant (Figure 2). A decrease in its activity was observed between the start of spring vegetation and the flowering of wheat and rapeseed, while an increase was observed between the flowering and harvesting of plants. Cultivation of both tested plants, in particular rape, contributed to a decrease in the activity of the URE. Nevertheless, in the soil objects under the cultivation of wheat, a higher value of the discussed parameter was found than in the case of rape.

Similar observations were made with respect to the influence of the type of plant on the level of protease activity, also noting a higher value of this parameter in the soil variants where wheat was grown. In the course of the research, the average value of PROT activity in the soil decreased in the flowering phase of wheat (period II) and then increased sharply during plant harvest (period III), reaching a maximum value of  $0.109 \,\mu$ mol tyrosine·g<sup>-1</sup>·d.m.·h<sup>-1</sup>. However, a significant decrease in the activity of the enzymes in question, caused by the cultivation of rapeseed, was found in subsequent dates of this study (Figure 2).

The above considerations clearly show that both the plant species, its development phase, and the associated different composition of root secretions influenced the level of soil enzymatic variability. In the case of all tested enzymes, a decrease in their activity was noted in the flowering phase, which confirms the above thesis. Depending on the development phase, some root secretions may act as signaling molecules that induce or inhibit the production of specific soil enzymes. 0.15

0.10

0.05

ab

 $\mu$ mol PNP·g<sup>-1</sup> d.m. of soil·h<sup>-1</sup>

PAC

<u>ab</u>

a

bc

bc

þ





**Figure 2.** Mean acid (PAC) and alkaline (PAL) phosphatases, urease (URE), and protease (PROT) activity values for terms I–VIII. Mean values followed by the same letter do not differ significantly at p = 0.05. Terms: I—before sowing of wheat crop; II—flowering of wheat crop; III—harvest of wheat crop; IV—soil complex saturation; V—before sowing of oilseed rape crop; VII—flowering of oilseed rape crop; VII—harvest of oilseed rape crop; VIII—soil complex saturation.

Comparing the spatial distribution of enzyme activity analyzed in the soil before the start of vegetation of both plants and during their harvest, it was shown that it was variable and depended on the type of tested enzyme. For example, PAC, similarly to PAL, reached the highest level of activity in the first term of the analysis, among others, at points 36, 40, and 54; URE reached the highest level of activity at points 30, 34, and 52. The cultivation of crops contributed to the modification of soil conditions; therefore, the activity of soil enzymes in the wheat harvesting phase (term III) took other values. PAC obtained the highest values at 30, 31, 32, 40, and 41; PAL obtained the highest values at 30, 48, 49, 50, and 57; URE obtained the highest values at 34, 35, 37, 38, 45, and 46 (Figures 3–6).



**Figure 3.** Spatial changes in acid phosphatase (PAC) activity in terms I (before sowing of the wheat crop), III (harvest of the wheat crop), V (before sowing of the oilseed rape crop), and VII (harvest of the oilseed rape crop). The places where soil samples were collected are marked with numbers (30–66).

The activity of the above-mentioned enzymes was different in the soil variants grown under rape. Before the start of vegetation (term V), the highest activity of PAC was recorded at points 41, 42, 43, and 59; PAL at points 32, 33, and 39; URE at 39, 44, 57, 58, and 66; and PROT in variant 40 and 66. As in the case of wheat, cultivation of rapeseed plants changed the spatial distribution of the level of soil enzyme activity, indicating the highest activity of PAC at points 34, 40, 47, and 55; PAL at points 47, 55, and 65; URE at 35, 48, 49, 55 and 65; and the highest PROT activity was observed practically in the entire western part of the field (Figures 3–6).

Considering the average value of the activity level of all soil enzymes under wheat cultivation, it was shown that it was at the lowest level at points 31, 57, 61, 62, and 63, located in the eastern and western parts of the field, respectively. On the other hand, in the case of rape, it was at the lowest level at points 31, 41, 42, 61, 62, 65, and 66. The highest values of the discussed parameters, depending on the type of cultivated plant, were recorded in soil samples taken from points 32, 33, 38, 46, and 48 (Figure 7).





Analyzing the spatial distribution of the activity of the tested soil enzymes under the cultivation of wheat and rape, it was shown that it varied and depended on the phase of plant growth and physicochemical factors of the soil. The principal component analysis (PCA) revealed the presence of various relationships, not only between the activity of the enzymes in the tested soil variants and soil chemical parameters but also the yield of plants (Figure 8). In wheat cultivation, the level of PAC, PAL, and URE activity correlated positively with pH and soil moisture. Moreover, a positive relationship was found between the value of all analyzed soil enzymatic parameters and grain yield. This type of interaction, with the exception of PAL, was not observed in the case of rapeseed. In the soil variants cultivated by this plant, the soil reaction correlated positively with the value of all enzymes. Statistical analysis showed a negative correlation of both phosphatases with the content of available phosphorus in the soil under wheat cultivation (Figure 8). It was also shown that the activity of URE correlated negatively with the content of ammonium ions in the soil under the cultivation of the tested plants (Figure 8).



**Figure 5.** Spatial changes in urease (URE) activity in terms I (before sowing of the wheat crop), III (harvest of the wheat crop), V (before sowing of the oilseed rape crop), and VII (harvest of the oilseed rape crop). The places where soil samples were collected are marked with numbers (30–66).

# 3.2. Spatial-Temporal Variability of Soil Physicochemical Parameters

During the research, the pH in the analyzed soil variants showed very high variability, ranging from 3.5 to 6.5. The changes in the value of this parameter were significantly affected by the season because, in winter, these values ranged from 3.5 to 5.0, and in the summer period, these values ranged from 5.0 to 6.5 (Figure 9). Moreover, the percentage of soil moisture during the experiment was characterized by high seasonal variability, with the highest values in the winter periods in both years of research (average above 13.5%). The lowest moisture of the analyzed soil variants was observed in the first year of this study, in the summer, when it was, on average, about 4% (Figure 9).

The wheat growth phase had an impact on soil pH; the average value at the tested measurement points increased between the I and III terms by 0.5 to 1 unit. The average percentage of soil moisture decreased from 13.5% in the first term to 4.4% in the third term. Similar observations were made in the case of rapeseed cultivation, showing an increase in the average pH value by 1 to 2 units at the analyzed measurement points of the field between the V and VII terms of analyses and a decrease in the average water content in the soil from 13.7% in the V to 9.0% in the rapeseed harvesting phase.



**Figure 6.** Spatial changes in protease (PROT) activity in terms I (before sowing of the wheat crop), III (harvest of the wheat crop), V (before sowing of the oilseed rape crop) and VII (harvest of the oilseed rape crop). The places where soil samples were collected are marked with numbers (30–66).

The average concentration of mineral N in the tested soil objects, determined on the basis of the content of N-NH<sub>4</sub> and N-NO<sub>3</sub> ions, was significantly higher in the first year of this study than in the second. The highest content of ammonium ions during the experiment was observed in the wheat harvesting phase, where it was  $38.47 \text{ kg}\cdot\text{ha}^{-1}$ , while the lowest value, equal to  $8.88 \text{ kg}\cdot\text{ha}^{-1}$ , was recorded in the VI term (Figure 10). In addition, a significantly lower average concentration of ammonium ions was found in the analyzed soil variants compared to the content of N-NO<sub>3</sub>. Similar observations were made with respect to the content of N-NO<sub>3</sub> ions in the soil. Also, in this case, their highest concentration was recorded in the III term of this study (69.17 kg·ha<sup>-1</sup>) and the lowest in the VI term (5.66 kg·ha<sup>-1</sup>) (Figure 10).

In the winter period, in the analyzed soil variants, a higher content of N-NH<sub>4</sub> ions was observed (terms I and V), which could be conducive to the nitrification process and lead to soil acidification. Considering the influence of the growth phase of the tested plants on the content of ammonium and nitrate ions in 37 soil variants, a recurring trend was observed, with a high concentration of the analyzed ions in both years of this study, in July (plant harvest—dates III and VII) and a noticeable decrease in their content in the autumn months (date IV and VIII). Only the content of phosphorus (P) was very stable in the analyzed soil variants in both years of this study and averaged 108.16 mg kg<sup>-1</sup> in the first and 109.2 mg kg<sup>-1</sup> in the second year of the experiment (Table 3).



**Figure 7.** Heatmap of the variables relative to the sampling site for winter wheat and oilseed rape. Acid (PAC) and alkaline (PAL) phosphatases, urease (URE), and protease (PROT).

Wheat



**Figure 8.** Dependences among the analyzed biological and chemical parameters during (**A**) winter wheat and (**B**) winter oilseed rape cultivation. Acid (PAC) and alkaline (PAL) phosphatases, urease (URE), and protease (PROT).



**Figure 9.** Mean soil pH and soil moisture values relative to terms I–VIII. Mean values followed by the same letter do not differ significantly at p = 0.05. Terms: I—before sowing of wheat crop; II—flowering of wheat crop; III—harvest of wheat crop; IV—soil complex saturation; V—before sowing of oilseed rape crop; VII—flowering of oilseed rape crop; VII—harvest of oilseed rape crop; VIII—soil complex saturation.



**Figure 10.** Mean values of N-NH<sub>4</sub> concentration relative to terms I–VIII. Mean values followed by the same letter do not differ significantly at p = 0.05. Terms: I—before sowing of wheat crop; II—flowering of wheat crop; III—harvest of wheat crop; IV—soil complex saturation; V—before sowing of oilseed rape crop; VII—flowering of oilseed rape crop; VII—harvest of oilseed rape crop; VIII—soil complex saturation.

By analyzing the spatial distribution of physicochemical parameters in soil variants before the start of plant vegetation and during their harvest, it was shown that it was variable and depended on the type of cultivated plant. During the cultivation of wheat, soil moisture had the highest values at points 48, 55, and 56 and the highest pH at points 33, 38, 39, 46, 54–57, and 65. In the second year of this study, during rapeseed vegetation, the highest moisture was recorded at points 48, 55, 56, 65, and 66, and the highest pH was at 32, 33.38, 39, and 55 (Figure 7).

In the first term of the analyses, the highest content of ammonium and nitrate ions was recorded, among others, in variants 52–54. Wheat cultivation caused modification of soil conditions; therefore, the concentration of ammonium ions in the phase of its harvest (III term) had the highest values at points 58, 61, 62, 65, and 66, and nitrate had the highest values at points 53, 54, 56, 58, 65, and 66 (Figures 11 and 12).

However, the concentration of N ions in the soil variants under rape cultivation was different. Before the start of plant vegetation (term V), the highest concentration of N-NH<sub>4</sub> ions was recorded at points 30, 33, 39, and 41, and the highest concentration of nitrate ions was recorded at points 45, 53, and 58. Cultivation of rapeseed plants also changed the spatial distribution of the ion concentration level, indicating the highest content of N-NH<sub>4</sub> at points 31, 50, and 53 and N-NO<sub>3</sub> at points 31, 49, 50, 53, and 54 (Figures 11 and 12).

Considering the average value of the concentration of ammonium and nitrate ions during the cultivation of the tested plants, it was shown that it was at the highest level at points 31, 52, 53, 54, 56, 58, 61, and 66, located in the north-eastern part of the field (Figure 7). For two years of research, the pH and humidity correlated with many of the tested parameters. Positive correlations were observed with the enzymatic activity of PAL, PROT, URE, moisture, wheat yield, and harvest index (Figure 8).

Sampling	2019	2020	Sampling	2019	2020	
Point	Term I	Term VIII	Point	Term I	Term VIII	
30	$166.82 \ ^{a} \pm 1.07$	$143.47~^{\rm ab}\pm 1.26$	49	$89.06 \text{ b} \pm 1.32$	$109.43~^{\rm ab}\pm 1.13$	
31	173.50 $^{\rm a} \pm 1.32$	158.70 $^{\rm a} \pm 1.02$	50	76.57 $^{ m b} \pm 1.17$	$102.67~^{ m ab}\pm 1.27$	
32	114.67 $^{\mathrm{ab}}\pm1.11$	$81.65 \text{ b} \pm 0.66$	51	56.71 $^{ m b} \pm 1.28$	72.38 $^{ m b} \pm 1.29$	
33	$85.51 \text{ b} \pm 0.79$	$88.38 \text{ b} \pm 1.08$	52	$113.44~^{ m ab}\pm 1.19$	146.65 $^{\mathrm{ab}}\pm1.19$	
34	138.87 $^{\mathrm{ab}}\pm1.15$	77.25 $^{ m b}\pm 0.85$	53	76.34 $^{ m b} \pm 0.96$	164.59 a $\pm$ 0.99	
35	178.64 a $\pm$ 0.84	$66.23^{\text{ b}} \pm 1.05$	54	$81.70 \ ^{ m b} \pm 1.39$	150.56 a $\pm$ 1.08	
36	$68.29^{b} \pm 1.20$	$86.75^{\rm \ b} \pm 0.76$	55	90.42 $^{ m b} \pm 0.99$	76.52 $^{ m b} \pm 1.08$	
37	$50.62^{ m bc} \pm 0.64$	$63.45^{\text{ b}} \pm 1.21$	56	110.58 $^{\rm ab}\pm 0.91$	88.26 $^{ m b} \pm 1.26$	
38	66.50 $^{ m b} \pm 0.59$	$104.48~^{ m ab}\pm 0.95$	57	92.34 $^{ m b}$ $\pm$ 1.37	175.36 $^{\mathrm{a}}\pm0.68$	
39	$117.65~^{ m ab}\pm 0.90$	$115.61 \ ^{ab} \pm 0.89$	58	64.31 $^{ m b} \pm 0.72$	107.44 $^{\mathrm{ab}}\pm0.71$	
40	$100.87 \ ^{ m b} \pm 1.12$	$127.66^{\ ab} \pm 1.18$	59	$135.96 \ ^{ m ab} \pm 0.46$	69.39 $^{ m b} \pm 1.12$	
41	$113.80~^{\rm ab}\pm 1.12$	$146.34~^{ m ab}\pm 0.84$	60	134.37 <sup>ab</sup> ±1.26	37.53 $^{\rm c} \pm 1.25$	
42	$145.46~^{ m ab}\pm 1.63$	$108.61 \ ^{ab} \pm 1.29$	61	$122.60 \ ^{ m ab} \pm 1.15$	142.60 $^{\rm ab} \pm$ 2.22	
43	$61.36 \text{ b} \pm 0.89$	$64.52 ^{\mathrm{b}} \pm 1.35$	62	153.75 $^{\mathrm{a}}\pm1.62$	134.65 $^{\mathrm{ab}}\pm0.98$	
44	90.30 $^{ m b} \pm 0.82$	92.65 $^{ m b} \pm 1.04$	63	145.77 $^{\mathrm{ab}}\pm1.10$	125.72 $^{\mathrm{ab}}\pm1.25$	
45	75.44 $^{ m b}\pm 0.82$	$128.56~^{ m ab}\pm 0.70$	64	191.45 a $\pm$ 1.30	187.48 a $\pm$ 0.95	
46	$67.36^{\text{ b}} \pm 0.99$	$64.27^{\text{ b}} \pm 0.84$	65	169.19 a $\pm$ 1.08	190.54 $^{\mathrm{a}}\pm1.30$	
47	71.72 $^{ m b} \pm 1.13$	$36.63 \text{ c} \pm 1.27$	66	170.61 $^{\rm a}\pm1.16$	160.65 a $\pm$ 1.44	
48	39.44 $^{\rm c}\pm0.95$	$45.50\ ^{\mathrm{c}}\pm1.02$				

**Table 3.** Mean values and standard deviation of phosphorus concentration relative to terms I and VIII.

<sup>a-c</sup>—Mean values in the column followed by the same letter do not differ significantly at p = 0.05.

Based on the obtained results, it was also shown that in the soil under wheat cultivation, the concentration of N-NH<sub>4</sub> ions correlated positively with the concentration of N-NO<sub>3</sub> ions and the yield of plants, while in the second year of this study, the content of N-NH<sub>4</sub> ions showed this kind of interaction with the level of acid phosphatase activity and crop yield. In the soil for wheat cultivation, a negative correlation was also found between the content of phosphorus and the activity of both phosphatases, pH, and moisture, as well as plant yield and harvest index. However, in the second year of this study, the phosphorus content correlated negatively with PAL activity and rapeseed yield and positively with soil reaction (Figure 8).

#### 3.3. Spatial Variability of Yield

The analysis of the obtained test results showed that the average yield weight in the tested soil variants was much higher in the first year than in the second, amounting to 6.26 t/ha for wheat and 4.45 t/ha for rape, respectively (Figure 13).

Spatial analysis of wheat yield value showed its highest value at points 39, 48, 51, and 53 and its lowest value at points 31 and 63–66. In the case of rape, the highest yield weight values were observed at points 40, 44, 46, and 52. The lowest yield values were recorded in the northern part of the field at points 57, 63, and 64 (Figure 14).

The harvest index (HI) for wheat ranged from 44.29 to 48.58% and had the highest value at points 34, 39, 44, and 53 and the lowest value at points 31, 44, and 64–66. For rapeseed, HI values ranged from 28.07 to 34.81%, with the highest value at points 31, 47, 65, and 66 and the lowest value at 51, 53, and 61 (Table 4).

The statistical analysis carried out showed a significant effect of the type of soil variant on the yield weight of the tested plants, while the principal component analysis (PCA) revealed the existence of various relationships between the chemical parameters of the soil, the activity of soil enzymes and the yield of both wheat and rapeseed (Figure 8). In the first year of this study, wheat yield and HI correlated with many factors, including PAC activity, PAL activity, URE activity, pH, % soil moisture, and concentration of N-NH4 ions. In the second year, rapeseed yield correlated only with PAL activity and N-NH4 ion



concentration. However, its harvest index positively correlated with URE, pH, and soil moisture.

**Figure 11.** Spatial changes in N-NH<sub>4</sub> in terms I (before sowing of the wheat crop), III (harvest of the wheat crop), V (before sowing of the oilseed rape crop) and VII (harvest of the oilseed rape crop). The places where soil samples were collected are marked with numbers (30–66).

Table 4. Harvest index (HI) for winter wheat and winter rapeseed.

Sampling _ Point	Harvest Index (%)		Sampling	Harvest Index (%)		Sampling	Harvest Index (%)	
	Wheat	Rapeseed	Point	Wheat	Rapeseed	Point	Wheat	Rapeseed
30	46.47 <sup>b</sup>	33.33 <sup>a</sup>	43	48.51 <sup>a</sup>	30.81 <sup>a</sup>	55	47.84 <sup>ab</sup>	33.78 <sup>a</sup>
31	43.80 <sup>d</sup>	34.81 <sup>a</sup>	44	44.29 <sup>c</sup>	33.48 <sup>a</sup>	56	46.99 <sup>ab</sup>	29.55 <sup>b</sup>
32	47.56 <sup>ab</sup>	31.63 <sup>a</sup>	45	45.88 <sup>bc</sup>	31.03 <sup>a</sup>	57	45.57 <sup>bc</sup>	32.00 <sup>a</sup>
33	47.93 <sup>ab</sup>	31.31 <sup>a</sup>	46	47.70 <sup>ab</sup>	33.02 <sup>a</sup>	58	47.06 <sup>ab</sup>	29.30 <sup>b</sup>
34	48.38 <sup>a</sup>	32.21 <sup>a</sup>	47	46.95 <sup>b</sup>	34.41 <sup>a</sup>	59	47.45 <sup>ab</sup>	32.73 <sup>a</sup>
35	46.30 <sup>b</sup>	32.12 <sup>a</sup>	48	47.04 <sup>a</sup>	33.14 <sup>a</sup>	60	46.81 <sup>b</sup>	30.12 <sup>ab</sup>
36	46.64 <sup>b</sup>	33.14 <sup>a</sup>	49	45.75 <sup>bc</sup>	31.68 <sup>a</sup>	61	45.60 <sup>bc</sup>	28.16 <sup>b</sup>
37	46.72 <sup>b</sup>	32.83 <sup>a</sup>	50	47.30 <sup>ab</sup>	30.95 <sup>a</sup>	62	46.84 <sup>b</sup>	30.77 <sup>a</sup>
38	47.55 <sup>ab</sup>	30.00 <sup>ab</sup>	51	47.97 <sup>ab</sup>	28.07 <sup>b</sup>	63	46.77 <sup>b</sup>	32.35 <sup>a</sup>
39	48.08 <sup>a</sup>	30.93 <sup>a</sup>	52	47.89 <sup>ab</sup>	32.58 <sup>a</sup>	64	45.21 <sup>bc</sup>	31.82 <sup>a</sup>
40	45.88 <sup>bc</sup>	32.24 <sup>a</sup>	53	48.58 <sup>a</sup>	28.22 <sup>b</sup>	65	45.15 <sup>bc</sup>	34.04 <sup>a</sup>
41	48.14 <sup>a</sup>	32.58 <sup>a</sup>	54	46.72 <sup>b</sup>	30.09 <sup>ab</sup>	66	45.08 <sup>bc</sup>	34.04 <sup>a</sup>
42	46.43 <sup>b</sup>	32.82 <sup>a</sup>						

<sup>a–d</sup>—Mean values in the column followed by the same letter do not differ significantly at p = 0.05.



**Figure 12.** Spatial changes in N-NO<sub>3</sub> in terms I (before sowing of the wheat crop), III (harvest of the wheat crop), V (before sowing of the oilseed rape crop) and VII (harvest of the oilseed rape crop). The places where soil samples were collected are marked with numbers (30–66).



**Figure 13.** Mean yield  $(t \cdot ha^{-1})$  in the wheat grain and oilseed rape seeds. Mean values followed by the same letter do not differ significantly at p = 0.05.



**Figure 14.** Spatial changes in yield  $(t \cdot ha^{-1})$  in the wheat grain and oilseed rape seeds. The places where soil samples were collected are marked with numbers (30–66).

# 4. Discussion

The average value of alkaline phosphatase activity was higher in the soil under rape cultivation, while the other enzyme activity values were higher, similar to the soil reaction and the content of ammonium and nitrate ions, under wheat cultivation. According to Jangid et al. [40], Pausch and Kuzyakov [41], and Zhao et al. [42], plants affect the physical and chemical properties of the soil, e.g., pH, redox gradient, or soil structure through their root secretions, and thus indirectly modify the number and activity of the soil microbiome. The chemical composition of root secretions depends on the type of plant, but they are rich in organic acids such as citrate, fumarate, malate, oxalate, and acetate, carbohydrates such as glucose, fructose, xylose, maltose, sucrose, galactose, and ribose, as well as amino acids and inorganic compounds such as  $CO_2$ , inorganic ions, protons, and anions related to the metabolic activity of roots [43–45]. Ouahmane et al. [46] have stated that organic acids are among the main factors affecting the succession of the soil microbiome and the level of its activity. However, Chaparro et al. [47] note that the production of root secretions with a given chemical composition is a process aimed at stimulating the activity of specific groups of microorganisms that have specific functions in the biochemical cycles of N and phosphorus transformations in the rhizosphere, which is also the plant's response to the demand for these macronutrients.

A possible explanation for the differences in the level of activity of the enzymes tested in our own research, depending on the type of plant, may also be found in the results of Galloway et al. [43], which indicate that wheat root secretions may contain large amounts of polysaccharide complexes that are an easily available source of C for microorganisms [48]. According to Blagodatskaya and Kuzyakov [49] and Hernández and Hobbie [50], saccharides can stimulate microorganisms, promoting the release of various types of enzymes, thereby intensifying the mineralization of soil organic matter.

Dotaniya et al. [51], Grzyb et al. [2], Hupe et al. [52], and Piotrowska-Długosz et al. [53] have affirmed that the temporal variation in the activity of soil enzymes is related to the development phases of plants. The research of the above-mentioned authors shows that in the period from the emergence of plants to their flowering, carbon, and N are deposited in the rhizosphere, which stimulates the value of the parameters, while after the plant flowering period, the amount of organic N substances in relation to C decreases in the rhizosphere, which in turn leads to a decrease in the activity of soil enzymes. However, the above observations are inconsistent with the results of our own research, in which a higher level of activity of the tested enzymes, regardless of the type of plant, was noted after the flowering phase of wheat or rapeseed. A similar trend was observed by Siczek et al. [54], analyzing the effect of wheat and faba bean root secretions on the level of urease, protease, and acid phosphatase activity. The authors noted an increase in the values of the

20 of 27

above-mentioned parameters after the flowering phase of plants, which can be accounted for by the qualitative and quantitative change in the chemical profile of root secretions during plant maturation and the change in the size of the roots of the tested plants, which thereby improve the water and air conditions of the soil.

According to Richardson and Simpson [55] and Margalef et al. [56], an increase in phosphatase activity between the flowering and harvesting of crop plants may be part of the plant response to phosphorus deficiency because, in addition to microorganisms, plant roots play an important role in the production of these enzymes. Moreover, Heflik et al. [57], Turner et al. [58], and Pang et al. [59] found that the deficit of this macroelement in the soil stimulated the secretion of acid phosphatases by plants.

The principal component analysis (PCA) conducted as part of our research also revealed a negative relationship between the phosphorus content in the soil under the cultivation of the tested plants and the activity level of both phosphatases, in particular PAL.

Soil enzymes are also subject to time variation, conditioned by changes in ambient temperature related to the seasons. Studies on their temporal variability have shown contradictory trends, showing activity peaks in different seasons, as well as their positive and negative responses to climate influences (temperature, humidity) [60,61]. Piotrowska-Długosz and Wilczewski [62] proved that the activity of enzymes analyzed in arable soil in Polish conditions was significantly higher in April than in August in both years of research.

From the analysis of the spatial distribution of the activity of all tested soil enzymes under the cultivation of wheat and rape, it was found that they had the highest values at points 32, 33, 46, and 48, with particularly high values in variant 38. The lowest enzyme activity values were recorded at points 31, 61, 62, and 63. Acosta-Martinez et al. [63], Grzyb et al. [2], Sinsabaugh et al. [23], and Stursová and Baldrian [60] report that the activity of specific soil enzymes may vary depending on the composition of plant residues and the relative availability of nutrients, along with other factors such as soil type. According to Philippot et al. [64], Rousk et al. [65], and Turner [66], soil pH, soil texture, and land use are some of the most important determinants of biomass and soil microbial activity. pH value affects their conformation, adsorption on solid surfaces, ionization, and solubility of substrates and cofactors. In the study of Xu et al. [67] and Zheng et al. [68], protease activity significantly decreased with increasing soil pH, while urease activity increased with increasing soil pH. This is confirmed by our own research, in which in the first year, at points with high pH, PROT was lower (55-57, 65); however, in the second year, no such strong relationship was observed. It was additionally noted that the activity of URE was higher at points with higher pH in both years of this study (33, 39, 54–57). Furthermore, both phosphatases reacted to soil pH. Higher pH favored higher PAC activity and lower PAL activity.

Soil moisture also affected the activity of soil enzymes. Sinsabaugh et al. [23] found that during dry periods, soils contain less microbial biomass and show reduced enzymatic activity. This is visible in our own research, where the low activity of all tested enzymes occurred at points with low soil moisture (31, 40, 41, 61–63).

The principal component analysis (PCA) confirmed the existence of close relationships between the value of soil pH and soil moisture and the level of PAL, PAC, and URE activity under wheat cultivation. In the case of rapeseed cultivation, a positive correlation with the pH value was observed only in the case of PAL, PROT, and URE.

Based on the obtained results, it was found that the average concentration of Nmin in the tested soil objects was also much higher in the first year of this study than in the second, which suggests a higher demand for this element in rapeseed than in wheat. Research by Brennan and Bolland [69] shows that these plant species differ in their reaction to the availability of N in the soil. According to the above-mentioned authors, the higher doses of N recommended for rapeseed result from the higher critical demand for this element during the formation of its biomass. Also, Avice and Etienne [70] and Bouchet et al. [71]

report that winter rape is characterized by high N uptake, especially in the autumn and winter, and thus a high demand for N fertilizers.

The analysis of the spatial distribution of N ions under the cultivation of both tested plants revealed a significantly lower concentration of ammonium ions in the analyzed soil variants compared to N-NO<sub>3</sub> ions. Studies by Kabala et al. [72] also indicated a significantly lower concentration of N-NH<sub>4</sub> ions than N-NO<sub>3</sub> in soil solutions under sorghum cultivation, which the authors explain is due to their lower mobility in soil solutions.

According to Vasu et al. [18], the uptake of nutrients by plants from the soil during their growth and development leads to spatial variability in their distribution. This phenomenon depends on the type of plant and its growth rate. This is confirmed by the results of our study, where in the first year of research, the highest concentration of both N ions was observed at point 58. In the second year, the highest concentration of N-NH<sub>4</sub> ions was noted at point 50 and N-NO<sub>3</sub> at 52 and 53. Shafreen et al. [73] state that the distribution of nitrogen compounds in soils depends on their geological features, climatic conditions, as well as organic matter content and microbial activity.

Differences in the content of the analyzed N ions in the tested soil variants also resulted from the time variability of the experiment. Both in the first and second years of our own research, the highest concentration of ammonium and nitrate ions was observed in the summer period (periods III and VII). Fluctuations in nitrate concentrations in the soil solution during the growing season of winter wheat, winter rye, winter barley, and sugar beet have also been described by other researchers [74]. According to Georgallas et al. [75], Perego et al. [76], and Sierra et al. [77], high concentrations of nitrates analyzed in arable soils in the summer may result from the use of mineral nitrogen fertilization in previous weeks, as well as from high air temperatures which are conducive to rapid mineralization of crop residues or organic fertilization used in previous years. Research results by Kabala et al. [72] confirm that both ammonium and nitrate ions reached maximum concentrations in the soil under sorghum cultivation in June and July and minimum concentrations in September and October. On the other hand, research by Below [78] shows that the content of N-NO<sub>3</sub> and N-NH<sub>4</sub> ions in the soil is also affected by the developmental stage of plants, which is associated with different intensities of nitrate ion uptake from the soil. The authors suggest that plants absorb N-NH<sub>4</sub> ions faster than N-NO<sub>3</sub> during early vegetative growth, while in later stages, N-NO<sub>3</sub> ions are absorbed faster, which is explained by the lack of fully functional N-NO<sub>3</sub> ion uptake and assimilation systems in young plants.

From the research of Turner et al. [58], it is evident that PROT and URE correlate positively with the amount of organic N in the soil and negatively with the content of mineral N. However, the level of their activity is largely regulated by the type of soil and its moisture [2]. The statistical analysis showed a negative interaction between the content of ammonium ions and the activity of urease in the soil under the cultivation of wheat and rapeseed. In addition, no positive relationship was observed between the content of N-NH<sub>4</sub> and N-NO<sub>3</sub> ions and the level of protease activity, either in the first year or during rapeseed cultivation [78,79]. In the first year of this study, a negative relationship was also noted between the content of nitrate ions and the concentration of soil phosphorus. This type of relationship was confirmed by Shen et al. [80], according to whom soil P deficiency during the cultivation of lupine plants stimulated the release of protons and citrate secretion by the roots in conjunction with their inhibition of nitrate uptake.

On the basis of the obtained results of our own research, a negative correlation was also shown between the content of ammonium and nitrate ions and soil moisture under wheat cultivation and a positive correlation with nitrate ions under rape cultivation. Alharbi [81] made different observations in his research, showing a positive relationship between soil moisture and the ammonification process. According to the above, with high soil moisture, the air content within it decreases, the ammonification process intensifies, and the soil pH increases. On the other hand, with low soil moisture, the percentage of air in the soil increases, so the nitrification process will dominate, leading to a decrease in soil pH. The yield of crops in the field also showed obvious spatial variation due to the inherent spatial variability of soil biochemical and physical parameters. In our research, the yield of wheat and rape was higher in the south-central part of the field, which indicates the existence of separate production zones. Litke et al. [82], analyzing the average yield of wheat grain over a three-year study, found that it ranged from 4.7 to 9.5 t·ha<sup>-1</sup>. Assefa et al. [83], Harker et al. [84], and Assefa et al. [85], on the other hand, report that the average rapeseed yield weight obtained in a given year of research was, on average, from 2.5 to 5 t·ha<sup>-1</sup>. According to Rondanini et al. [86] and Beres et al. [87], rapeseed yields have not improved significantly over the last four decades and are still lower than cereal yields. Representative values of the harvest index for wheat varieties generally range from 30 to 60% and rape from 25% to 40% [15,39].

Undoubtedly, the most important and basic macronutrient determining the yield of plants is N. The response of plants to N nutrition in terms of yield weight may vary by location. Spatial analysis of the distribution of the content of the tested nitrate ions and the yield of wheat and rapeseed confirmed this relationship. In the research facilities where the yield of both plants was high, the average concentration of ammonium and nitrate ions was low. This relationship can be seen at points 39, 48, and 51. This suggests that plants take up a lot of N in order to produce a large amount of yield. In the measurement points where a low yield was noted (variants 31, 58, 65, 66), even though soil N was present, it was not actively taken up by the plants. According to Delin [88], different crop N utilization may be due to spatial differences in N losses, fungal diseases, competition from weeds, or a limited supply of other nutrients. Weymann et al. [89] have pointed out that plant yield is a result of complex interactions between plant genotype, soil, pest, and weather conditions and decisions made during the plant growth and development phase. In the research by Basso et al. [90], Zhang et al. [91], and Zhao et al. [92], soil texture and nutrients showed moderate spatial variability, which affected water and N dynamics during plant growth and ultimately resulted in spatial yield variability. A sandy texture can cause excessive water infiltration and leaching of NO3-N, which reduces N uptake and, consequently, yield. Also, Mueller et al. [93] found that between 60 and 80% of the global variation in the yield of major crops is due to factors related to soil resources and climate. Results of the field experiments of Nowosad et al. [94] and Ray et al. [95] point to the influence of weather conditions, especially temperature and precipitation, on plant development, seed yield, and seed composition.

According to Bartomeus et al. [96] and Xuan et al. [97], in addition to nutrients, the yield of crops is influenced by the pH value of the soil and its moisture [98], and Haberle and Svoboda [99] showed that water availability is one of the strongest factors determining the uptake and efficiency of N use by the plant, which affects the yield. The results of our research showed that the highest yield of plants was obtained at points 39, 55, and 56, characterized by high soil moisture and pH above 6. According to Kumaraswamy and Shetty [100], drought-related stress is one of the main factors contributing to impaired functioning plant metabolism and can lead to a loss of about 30–70% of the productivity of field crops during their growth. Moreover, low soil pH significantly affects plant growth, reducing its yield by up to 69% [101]. Hurtado et al. [102] note that spatial variability of soil acidity conditions can occur even in areas with seemingly uniform cultivation and precise correction of soil acidity, and effective use of agricultural inputs and improvement of natural soil processes are important factors in increasing yields.

Factors affecting the yield will also directly affect the harvest index (HI). Thus, all of the above information is in line with a number of studies that show that the HI is influenced by plant genetic variation and environmental variation within a specific climatic region, as well as abiotic stresses, sowing dates, plant density, and row spacing. [14,103–105].

#### 5. Conclusions

It was shown that the spatial structure of most of the tested variables differed statistically significantly depending on the time and place of soil sampling and the type of plant. Frequently changing soil conditions resulting from the cultivation of the tested plants favored changes in the activity of the tested enzymes and in the physicochemical composition of the soil, which translated into the yield of both plants.

The highest temporal stability was recorded in the case of pH values and alkaline phosphatase activity in the soil under wheat cultivation. However, no similar trend was observed in the variability of the tested soil parameters during the two-year experiment. Nevertheless, in the harvest phase of the tested plants, most of the analyzed enzymatic and physicochemical parameters of the soil reached the highest values.

However, the occurrence of characteristic areas in the field was observed in which the analyzed parameters stood out with only high or only low values.

In the case of wheat, high activity of the tested enzymes was found in the southern part of the field. The obtained parameters are reflected in the spatial distribution of wheat yield, with its highest values in the south-central part of the field, which may indicate high soil productivity in the above-mentioned place. This is confirmed by the second year of research, where a higher rapeseed yield was obtained in the south-central part of the field. Also, the percentage of soil moisture and the high activity of most of the enzymes tested in this area confirm that the N study site has several zones with the same level of productivity. Based on the above information, it can be concluded that geostatistical techniques can help quantify and map spatial and temporal patterns of soil enzymatic parameters and soil resources that translate into crop yield.

Obtaining this information is necessary for the correct diagnosis of soil fertility and, thus, for the development of techniques for the effective and precise application of mineral fertilizers, especially nitrogen.

Author Contributions: Conceptualization, A.W.-M. and A.G.; methodology, A.W.-M.; A.G., R.Ł. and J.C.; software, A.W.-M., D.K. and J.C.; validation, A.W.-M. and R.Ł.; formal analysis, A.G. and R.Ł.; investigation, A.G. and R.Ł.; resources, A.W.-M. and R.Ł.; data curation, A.G.; writing—original draft preparation, A.W.-M. and A.G.; writing—review and editing, A.W.-M. and A.N.; visualization, J.C. and D.K.; supervision, A.W.-M.; project administration, A.N. and D.K.; funding acquisition, A.W.-M. All authors have read and agreed to the published version of the manuscript.

**Funding:** Publication was financed within the framework of the Polish Ministry of Science and Higher Education's program "Regional Excellence Initiative" in the years 2019–2023 (No. 005/RID/2018/19)", financing amount 12 000 000.00 PLN.

Institutional Review Board Statement: Study did not require ethical approval.

Data Availability Statement: Not available.

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

#### References

- 1. European Commission. *Committee and the Committee of the Regions Eu Biodiversity Strategy for 2030 Bringing Nature Back into Our Lives;* European Commission: Brussels, Belgium, 2020.
- Grzyb, A.; Wolna-Maruwka, A.; Niewiadomska, A. Environmental Factors Affecting the Mineralization of Crop Residues. *Agronomy* 2020, 10, 1951. [CrossRef]
- 3. Grzebisz, W.; Łukowiak, R. Nitrogen Gap Amelioration Is a Core for Sustainable Intensification of Agriculture—A Concept. *Agronomy* **2021**, *11*, 419. [CrossRef]
- Tian, L.; Zhao, L.; Wu, X.; Fang, H.; Zhao, Y.; Hu, G.; Yue, G.; Sheng, Y.; Wu, J.; Chen, J.; et al. Soil Moisture and Texture Primarily Control the Soil Nutrient Stoichiometry across the Tibetan Grassland. *Sci. Total Environ.* 2018, 622–623, 192–202. [CrossRef]
- Wang, F.; Xue, K.; Fu, W. Effects of Soil Nitrogen and Phosphorus Contents on Ecological Stoichiometry of Wheat Leaf. Chin. J. Eco-Agric. 2019, 27, 60–71. [CrossRef]
- 6. Zhang, H.; Ru, H.; Jiao, F.; Xue, C.; Guo, M. C, N, P, K Stoichiometric Characteristic of Leaves, Root and Soil in Different Abandoned Years in Loess Plateau. *Huan Jing Ke Xue* 2016, *37*, 1128–1138. [PubMed]
- Rivas-Ubach, A.; Sardans, J.; Pérez-Trujillo, M.; Estiarte, M.; Peñuelas, J. Strong Relationship between Elemental Stoichiometry and Metabolome in Plants. *Proc. Natl. Acad. Sci. USA* 2012, 109, 4181–4186. [CrossRef]
- Chen, Y.; Chen, L.; Peng, Y.; Ding, J.; Li, F.; Yang, G.; Kou, D.; Liu, L.; Fang, K.; Zhang, B.; et al. Linking Microbial C:N:P Stoichiometry to Microbial Community and Abiotic Factors along a 3500-km Grassland Transect on the Tibetan Plateau. *Glob. Ecol. Biogeogr.* 2016, 25, 1416–1427. [CrossRef]

- 9. Piotrowska-Długosz, A.; Długosz, J. Spatio-Temporal Variability of Soil Beta-Glucosidase Activity at the Arable Field Scale. *Pol. J. Soil Sci.* 2017, *50*, 107. [CrossRef]
- Długosz, J.; Piotrowska-Długosz, A. Spatial Variability of Soil Nitrogen Forms and the Activity of N-Cycle Enzymes. *Plant Soil Environ.* 2016, 62, 502–507. [CrossRef]
- Wang, Y.; Liu, L.; Tian, Y.; Wu, X.; Yang, J.; Luo, Y.; Li, H.; Awasthi, M.K.; Zhao, Z. Temporal and Spatial Variation of Soil Microorganisms and Nutrient under White Clover Cover. *Soil Tillage Res.* 2020, 202, 104666. [CrossRef]
- 12. Martínez-Casasnovas, J.A.; Martín-Montero, A.; Auxiliadora Casterad, M. Mapping Multi-Year Cropping Patterns in Small Irrigation Districts from Time-Series Analysis of Landsat TM Images. *Eur. J. Agron.* **2005**, *23*, 159–169. [CrossRef]
- 13. Watson, S.J.; Luck, G.W.; Spooner, P.G.; Watson, D.M. Land-Use Change: Incorporating the Frequency, Sequence, Time Span, and Magnitude of Changes into Ecological Research. *Front. Ecol. Environ.* **2014**, *12*, 241–249. [CrossRef]
- 14. Larsen, K.S.; Michelsen, A.; Jonasson, S.; Beier, C.; Grogan, P. Nitrogen Uptake During Fall, Winter and Spring Differs Among Plant Functional Groups in a Subarctic Heath Ecosystem. *Ecosystems* **2012**, *15*, 927–939. [CrossRef]
- Cassman, K.G.; Dobermann, A.; Walters, D.T. Agroecosystems, Nitrogen-Use Efficiency, and Nitrogen Management. AMBIO J. Hum. Environ. 2002, 31, 132–140. [CrossRef] [PubMed]
- 16. Erisman, J.W.; Bleeker, A.; Galloway, J.; Sutton, M.S. Reduced Nitrogen in Ecology and the Environment. *Environ. Pollut.* 2007, 150, 140–149. [CrossRef] [PubMed]
- 17. Łukowiak, R.; Grzebisz, W.; Ceglarek, J.; Podolski, A.; Kaźmierowski, C.; Piekarczyk, J. Spatial Variability of Yield and Nitrogen Indicators—A Crop Rotation Approach. *Agronomy* **2020**, *10*, 1959. [CrossRef]
- Vasu, D.; Singh, S.K.; Sahu, N.; Tiwary, P.; Chandran, P.; Duraisami, V.P.; Ramamurthy, V.; Lalitha, M.; Kalaiselvi, B. Assessment of Spatial Variability of Soil Properties Using Geospatial Techniques for Farm Level Nutrient Management. *Soil Tillage Res.* 2017, 169, 25–34. [CrossRef]
- 19. St. Luce, M.; Whalen, J.K.; Ziadi, N.; Zebarth, B.J. Nitrogen Dynamics and Indices to Predict Soil Nitrogen Supply in Humid Temperate Soils. *Adv. Agron.* **2011**, *112*, 55–102.
- 20. Tian, L.; Dell, E.; Shi, W. Chemical Composition of Dissolved Organic Matter in Agroecosystems: Correlations with Soil Enzyme Activity and Carbon and Nitrogen Mineralization. *Appl. Soil Ecol.* **2010**, *46*, 426–435. [CrossRef]
- Chavarría, D.N.; Verdenelli, R.A.; Serri, D.L.; Restovich, S.B.; Andriulo, A.E.; Meriles, J.M.; Vargas-Gil, S. Effect of Cover Crops on Microbial Community Structure and Related Enzyme Activities and Macronutrient Availability. *Eur. J. Soil Biol.* 2016, 76, 74–82. [CrossRef]
- 22. Delgado-Baquerizo, M. Obscure Soil Microbes and Where to Find Them. ISME J. 2019, 13, 2120–2124. [CrossRef]
- 23. Sinsabaugh, R.L.; Lauber, C.L.; Weintraub, M.N.; Ahmed, B.; Allison, S.D.; Crenshaw, C.; Contosta, A.R.; Cusack, D.; Frey, S.; Gallo, M.E.; et al. Stoichiometry of Soil Enzyme Activity at Global Scale. *Ecol. Lett.* **2008**, *11*, 1252–1264. [CrossRef] [PubMed]
- 24. Cusack, D.F.; Silver, W.L.; Torn, M.S.; Burton, S.D.; Firestone, M.K. Changes in Microbial Community Characteristics and Soil Organic Matter with Nitrogen Additions in Two Tropical Forests. *Ecology* **2011**, *92*, 621–632. [CrossRef] [PubMed]
- 25. Averill, C.; Waring, B. Nitrogen Limitation of Decomposition and Decay: How Can It Occur? *Glob. Chang. Biol.* 2018, 24, 1417–1427. [CrossRef] [PubMed]
- Dai, Z.; Su, W.; Chen, H.; Barberán, A.; Zhao, H.; Yu, M.; Yu, L.; Brookes, P.C.; Schadt, C.W.; Chang, S.X.; et al. Long-term Nitrogen Fertilization Decreases Bacterial Diversity and Favors the Growth of Actinobacteria and Proteobacteria in Agro-ecosystems across the Globe. *Glob. Chang. Biol.* 2018, 24, 3452–3461. [CrossRef]
- Koch, O.; Tscherko, D.; Kandeler, E. Temperature Sensitivity of Microbial Respiration, Nitrogen Mineralization, and Potential Soil Enzyme Activities in Organic Alpine Soils. *Glob. Biogeochem. Cycles* 2007, 21. [CrossRef]
- 28. Ghazali, M.F.; Wikantika, K.; Harto, A.B.; Kondoh, A. Generating Soil Salinity, Soil Moisture, Soil PH from Satellite Imagery and Its Analysis. *Inf. Process. Agric.* 2020, 7, 294–306. [CrossRef]
- Slessarev, E.W.; Lin, Y.; Bingham, N.L.; Johnson, J.E.; Dai, Y.; Schimel, J.P.; Chadwick, O.A. Water Balance Creates a Threshold in Soil PH at the Global Scale. *Nature* 2016, 540, 567–569. [CrossRef]
- Acosta-Martínez, V.; Waldrip, H.M. Soil Enzyme Activities as Affected by Manure Types, Application Rates, and Management Practices. In *Applied Manure and Nutrient Chemistry for Sustainable Agriculture and Environment*; Springer: Dordrecht, The Netherlands, 2014; pp. 99–122.
- Al-Omran, A.M.; Al-Wabel, M.I.; El-Maghraby, S.E.; Nadeem, M.E.; Al-Sharani, S. Spatial Variability for Some Properties of the Wastewater Irrigated Soils. J. Saudi Soc. Agric. Sci. 2013, 12, 167–175. [CrossRef]
- Saiz-Rubio, V.; Rovira-Más, F. From Smart Farming towards Agriculture 5.0: A Review on Crop Data Management. Agronomy 2020, 10, 207. [CrossRef]
- 33. Mocek, A.; Drzymała, S.; Maszner, P. *Geneza Analiza i Klasyfikacja Gleb*; Wydawnictwo Akademii Rolniczej im. Augusta Cieszkowskiego: Poznań, Polska, 2006.
- 34. Alef, K.; Nannipieri, P. (Eds.) Methods in Applied Soil Microbiology and Biochemistry; Academic Press: London, UK, 1995; ISBN 0125138407.
- 35. Ladd, J.N.; Butler, J.H.A. Short-Term Assays of Soil Proteolytic Enzyme Activities Using Proteins and Dipeptide Derivatives as Substrates. *Soil. Biol. Biochem.* **1972**, *4*, 19–30. [CrossRef]
- Zantua, M.I.; Bremner, J.M. Comparison of Methods of Assaying Urease Activity in Soils. Soil. Biol. Biochem. 1975, 7, 291–295. [CrossRef]

- Lityński, T. Analiza Chemiczno-Rolnicza: Przewodnik Metodyczny Do analizy Gleby i Nawozów; Gorlach, E., Jurkowska, H., Eds.; Państ. Wydaw. Naukowe: Warszawa, Poland, 1976.
- 38. Mehlich, A. Mehlich 3 Soil Test Extractant: A Modification of Mehlich 2 Extractant. *Commun. Soil Sci. Plant Anal.* **1984**, *15*, 1409–1416. [CrossRef]
- Dai, J.; Bean, B.; Brown, B.; Bruening, W.; Edwards, J.; Flowers, M.; Karow, R.; Lee, C.; Morgan, G.; Ottman, M.; et al. Harvest Index and Straw Yield of Five Classes of Wheat. *Biomass Bioenergy* 2016, *85*, 223–227. [CrossRef]
- Jangid, K.; Williams, M.A.; Franzluebbers, A.J.; Schmidt, T.M.; Coleman, D.C.; Whitman, W.B. Land-Use History Has a Stronger Impact on Soil Microbial Community Composition than Aboveground Vegetation and Soil Properties. *Soil Biol. Biochem.* 2011, 43, 2184–2193. [CrossRef]
- Pausch, J.; Kuzyakov, Y. Photoassimilate Allocation and Dynamics of Hotspots in Roots Visualized by <sup>14</sup>C Phosphor Imaging. J. Plant Nutr. Soil Sci. 2011, 174, 12–19. [CrossRef]
- 42. Zhao, Y.; Liu, H.; Wang, R.; Wu, C. Interactions between Dicyandiamide and Periphytic Biofilms in Paddy Soils and Subsequent Effects on Nitrogen Cycling. *Sci. Total Environ.* **2020**, *718*, 137417. [CrossRef]
- Galloway, A.F.; Akhtar, J.; Marcus, S.E.; Fletcher, N.; Field, K.; Knox, P. Cereal Root Exudates Contain Highly Structurally Complex Polysaccharides with Soil-binding Properties. *Plant J.* 2020, 103, 1666–1678. [CrossRef]
- 44. Hinsinger, P.; Plassard, C.; Jaillard, B. Rhizosphere: A New Frontier for Soil Biogeochemistry. J. Geochem. Explor. 2006, 88, 210–213. [CrossRef]
- 45. Lugtenberg, B.J.J.; Bloemberg, G.V. Life in the Rhizosphere. In Pseudomonas; Springer: Boston, MA, USA, 2004; pp. 403-430.
- Ouahmane, L.; Thioulouse, J.; Hafidi, M.; Prin, Y.; Ducousso, M.; Galiana, A.; Plenchette, C.; Kisa, M.; Duponnois, R. Soil Functional Diversity and P Solubilization from Rock Phosphate after Inoculation with Native or Allochtonous Arbuscular Mycorrhizal Fungi. *Ecol. Manag.* 2007, 241, 200–208. [CrossRef]
- 47. Chaparro, J.M.; Badri, D.V.; Vivanco, J.M. Rhizosphere Microbiome Assemblage Is Affected by Plant Development. *ISME J.* 2014, *8*, 790–803. [CrossRef]
- Zhang, X.; Dippold, M.A.; Kuzyakov, Y.; Razavi, B.S. Spatial Pattern of Enzyme Activities Depends on Root Exudate Composition. Soil Biol. Biochem. 2019, 133, 83–93. [CrossRef]
- 49. Blagodatskaya, E.; Kuzyakov, Y. Active Microorganisms in Soil: Critical Review of Estimation Criteria and Approaches. *Soil Biol. Biochem.* **2013**, *67*, 192–211. [CrossRef]
- 50. Hernández, D.L.; Hobbie, S.E. The Effects of Substrate Composition, Quantity, and Diversity on Microbial Activity. *Plant Soil* **2010**, 335, 397–411. [CrossRef]
- 51. Dotaniya, M.L.; Kushwah, S.K.; Rajendiran, S.; Coumar, M.V.; Kundu, S.; Subba Rao, A. Rhizosphere Effect of Kharif Crops on Phosphatases and Dehydrogenase Activities in a Typic Haplustert. *Natl. Acad. Sci. Lett.* **2014**, *37*, 103–106. [CrossRef]
- Hupe, A.; Schulz, H.; Bruns, C.; Haase, T.; Heß, J.; Joergensen, R.G.; Wichern, F. Even Flow? Changes of Carbon and Nitrogen Release from Pea Roots over Time. *Plant Soil* 2018, 431, 143–157. [CrossRef]
- 53. Piotrowska-Długosz, A.; Siwik-Ziomek, A.; Długosz, J.; Gozdowski, D. Spatio-Temporal Variability of Soil Sulfur Content and Arylsulfatase Activity at a Conventionally Managed Arable Field. *Geoderma* **2017**, *295*, 107–118. [CrossRef]
- 54. Siczek, A.; Frąc, M.; Kalembasa, S.; Kalembasa, D. Soil Microbial Activity of Faba Bean (Vicia faba L.) and Wheat (Triticum aestivum L.) Rhizosphere during Growing Season. *Appl. Soil Ecol.* **2018**, *130*, 34–39. [CrossRef]
- Richardson, A.E.; Simpson, R.J. Soil Microorganisms Mediating Phosphorus Availability Update on Microbial Phosphorus. *Plant Physiol.* 2011, 156, 989–996. [CrossRef]
- Margalef, O.; Sardans, J.; Fernández-Martínez, M.; Molowny-Horas, R.; Janssens, I.A.; Ciais, P.; Goll, D.; Richter, A.; Obersteiner, M.; Asensio, D.; et al. Global Patterns of Phosphatase Activity in Natural Soils. *Sci. Rep.* 2017, 7, 1337. [CrossRef]
- 57. Heflik, M.; Kandziora, M.; Nadgórska-Socha, A.; Ciepal, R. Acid Phosphatase Activity in Plants Grown in Heavy Metals Contaminated Sites. *Environ. Prot. Nat. Resour.* 2007, 32, 151–154.
- Turner, S.; Schippers, A.; Meyer-Stüve, S.; Guggenberger, G.; Gentsch, N.; Dohrmann, R.; Condron, L.M.; Eger, A.; Almond, P.C.; Peltzer, D.A.; et al. Mineralogical Impact on Long-Term Patterns of Soil Nitrogen and Phosphorus Enzyme Activities. *Soil Biol. Biochem.* 2014, 68, 31–43. [CrossRef]
- 59. Pang, X.; Ning, W.; Qing, L.; Bao, W. The Relation among Soil Microorganism, Enzyme Activity and Soil Nutrients under Subalpine Coniferous Forest in Western Sichuan. *Acta Ecol. Sin.* **2009**, *29*, 286–292. [CrossRef]
- Štursová, M.; Baldrian, P. Effects of Soil Properties and Management on the Activity of Soil Organic Matter Transforming Enzymes and the Quantification of Soil-Bound and Free Activity. *Plant Soil* 2011, 338, 99–110. [CrossRef]
- Wallenstein, M.D.; Mcmaoth, S.K.; Schmiel, J.P. Seasonal Variation in Enzyme Activities and Temperature Sensitivities in Arctic Tundra Soils. *Glob. Chang. Biol.* 2009, 15, 1631–1639. [CrossRef]
- 62. Piotrowska-Długosz, A.; Wilczewski, E. Soil Phosphatase Activity and Phosphorus Content as Influenced by Catch Crops Cultivated as Green Manure. *Pol. J. Environ. Stud.* **2014**, 23, 157–165.
- Acosta-Martínez, V.; Acosta-Mercado, D.; Sotomayor-Ramírez, D.; Cruz-Rodríguez, L. Microbial Communities and Enzymatic Activities under Different Management in Semiarid Soils. *Appl. Soil Ecol.* 2008, 38, 249–260. [CrossRef]
- Philippot, L.; Bru, D.; Saby, N.P.A.; Čuhel, J.; Arrouays, D.; Šimek, M.; Hallin, S. Spatial Patterns of Bacterial Taxa in Nature Reflect Ecological Traits of Deep Branches of the 16S RRNA Bacterial Tree. *Environ. Microbiol.* 2009, 11, 3096–3104. [CrossRef]

- 65. Rousk, J.; Bååth, E.; Brookes, P.C.; Lauber, C.L.; Lozupone, C.; Caporaso, J.G.; Knight, R.; Fierer, N. Soil Bacterial and Fungal Communities across a PH Gradient in an Arable Soil. *ISME J.* **2010**, *4*, 1340–1351. [CrossRef] [PubMed]
- 66. Turner, B.L. Variation in PH Optima of Hydrolytic Enzyme Activities in Tropical Rain Forest Soils. *Appl. Environ. Microbiol.* 2010, 76, 6485–6493. [CrossRef]
- Xu, Z.; Zhang, T.; Wang, S.; Wang, Z. Soil PH and C/N Ratio Determines Spatial Variations in Soil Microbial Communities and Enzymatic Activities of the Agricultural Ecosystems in Northeast China: Jilin Province Case. *Appl. Soil. Ecol.* 2020, 155, 103629. [CrossRef]
- Zheng, H.; Liu, Y.; Zhang, J.; Chen, Y.; Yang, L.; Li, H.; Wang, L. Factors Influencing Soil Enzyme Activity in China's Forest Ecosystems. *Plant Ecol.* 2018, 219, 31–44. [CrossRef]
- 69. Brennan, R.F.; Bolland, M.D.A. Comparing the Nitrogen and Potassium Requirements of Canola and Wheat for Yield and Grain Quality. J. Plant Nutr. 2009, 32, 2008–2026. [CrossRef]
- Avice, J.-C.; Etienne, P. Leaf Senescence and Nitrogen Remobilization Efficiency in Oilseed Rape (*Brassica napus* L.). J. Exp. Bot. 2014, 65, 3813–3824. [CrossRef] [PubMed]
- Bouchet, A.-S.; Laperche, A.; Bissuel-Belaygue, C.; Snowdon, R.; Nesi, N.; Stahl, A. Nitrogen Use Efficiency in Rapeseed. A Review. Agron. Sustain. Dev. 2016, 36, 38. [CrossRef]
- Kabala, C.; Karczewska, A.; Gałka, B.; Cuske, M.; Sowiński, J. Seasonal Dynamics of Nitrate and Ammonium Ion Concentrations in Soil Solutions Collected Using MacroRhizon Suction Cups. *Environ. Monit. Assess.* 2017, 189, 304. [CrossRef]
- Shafreen, M.; Vishwakarma, K.; Shrivastava, N.; Kumar, N. Physiology and Distribution of Nitrogen in Soils. In *Soil Nitrogen Ecology*; Springer: Berlin/Heidelberg, Germany, 2021; pp. 3–31.
- Kroes, J.; Roelsma, J. Simulation of Water and Nitrogen Flows on Field Scale; Application of the SWAP–ANIMO Model for the Müncheberg Data Set. In *Modelling Water and Nutrient Dynamics in Soil–Crop Systems*; Springer: Dordrecht, The Netherlands, 2007; pp. 111–128.
- Georgallas, A.; Dessureault-Rompré, J.; Zebarth, B.J.; Burton, D.L.; Drury, C.F.; Grant, C.A. Modification of the Biophysical Water Function to Predict the Change in Soil Mineral Nitrogen Concentration Resulting from Concurrent Mineralization and Denitrification. *Can. J. Soil Sci.* 2012, 92, 695–710. [CrossRef]
- 76. Perego, A.; Basile, A.; Bonfante, A.; De Mascellis, R.; Terribile, F.; Brenna, S.; Acutis, M. Nitrate Leaching under Maize Cropping Systems in Po Valley (Italy). *Agric. Ecosyst. Environ.* **2012**, 147, 57–65. [CrossRef]
- Sierra, C.A.; Trumbore, S.E.; Davidson, E.A.; Vicca, S.; Janssens, I. Sensitivity of Decomposition Rates of Soil Organic Matter with Respect to Simultaneous Changes in Temperature and Moisture. J. Adv. Model. Earth Syst. 2015, 7, 335–356. [CrossRef]
- Below, F.E. Nitrogen Metabolism and Crop Productivity. In *Handbook of Plant and Crop Physiology*; CRC Press: Boca Raton, FL, USA, 2001; pp. 385–406.
- 79. Jat, H.S.; Datta, A.; Choudhary, M.; Sharma, P.C.; Dixit, B.; Jat, M.L. Soil Enzymes Activity: Effect of Climate Smart Agriculture on Rhizosphere and Bulk Soil under Cereal Based Systems of North-West India. *Eur. J. Soil Biol.* **2021**, *103*, 103292. [CrossRef]
- Shen, J.; Yuan, L.; Zhang, J.; Li, H.; Bai, Z.; Chen, X.; Zhang, W.; Zhang, F. Phosphorus Dynamics: From Soil to Plant. *Plant Physiol.* 2011, 156, 997–1005. [CrossRef] [PubMed]
- Alharbi, A. Effect Of Mulch On Soil Properties Under Organic Farming Conditions In Center Of Saudi Arabia. Mech. Agric. Conserv. Resour. 2017, 63, 161–167.
- Litke, L.; Gaile, Z.; Ruža, A. Effect of Nitrogen Fertilization on Winter Wheat Yield and Yield Quality. Agron. Res. 2018, 16, 500–509. [CrossRef]
- 83. Assefa, Y.; Roozeboom, K.; Stamm, M. Winter Canola Yield and Survival as a Function of Environment, Genetics, and Management. *Crop Sci.* 2014, *54*, 2303–2313. [CrossRef]
- Harker, K.N.; O'Donovan, J.T.; Turkington, T.K.; Blackshaw, R.E.; Lupwayi, N.Z.; Smith, E.G.; Klein-Gebbinck, H.; Dosdall, L.M.; Hall, L.M.; Willenborg, C.J.; et al. High-Yield No-till Canola Production on the Canadian Prairies. *Can. J. Plant Sci.* 2012, 92, 221–233. [CrossRef]
- 85. Assefa, Y.; Prasad, P.V.V.; Foster, C.; Wright, Y.; Young, S.; Bradley, P.; Stamm, M.; Ciampitti, I.A. Major Management Factors Determining Spring and Winter Canola Yield in North America. *Crop Sci.* **2018**, *58*, 1–16. [CrossRef]
- Rondanini, D.P.; Gomez, N.V.; Agosti, M.B.; Miralles, D.J. Global Trends of Rapeseed Grain Yield Stability and Rapeseed-to-Wheat Yield Ratio in the Last Four Decades. *Eur. J. Agron.* 2012, 37, 56–65. [CrossRef]
- 87. Béreš, J.; Bečka, D.; Tomášek, J.; Vašák, J. Effect of Autumn Nitrogen Fertilization on Winter Oilseed Rape Growth and Yield Parameters. *Plant Soil. Environ.* **2019**, *65*, 435–441. [CrossRef]
- 88. Delin, S. Within-Field Variations in Grain Protein Content?Relationships to Yield and Soil Nitrogen and Consistency in Maps Between Years. *Precis. Agric.* 2004, *5*, 565–577. [CrossRef]
- 89. Weymann, W.; Böttcher, U.; Sieling, K.; Kage, H. Effects of Weather Conditions during Different Growth Phases on Yield Formation of Winter Oilseed Rape. *Field Crops Res.* 2015, 173, 41–48. [CrossRef]
- 90. Basso, B.; Cammarano, D.; Grace, P.R.; Cafiero, G.; Sartori, L.; Pisante, M.; Landi, G.; De Franchi, S.; Basso, F. Criteria for Selecting Optimal Nitrogen Fertilizer Rates for Precision Agriculture. *Ital. J. Agron.* **2009**, *4*, 147. [CrossRef]
- 91. Zhang, S.; Huffman, T.; Zhang, X.; Liu, W.; Liu, Z. Spatial Distribution of Soil Nutrient at Depth in Black Soil of Northeast China: A Case Study of Soil Available Phosphorus and Total Phosphorus. *J. Soils Sediments* **2014**, *14*, 1775–1789. [CrossRef]

- 92. Zhao, W.; Zhang, J.; Müller, C.; Cai, Z. Effects of PH and Mineralisation on Nitrification in a Subtropical Acid Forest Soil. *Soil Res.* 2018, *56*, 275. [CrossRef]
- 93. Mueller, K.E.; Tilman, D.; Fornara, D.A.; Hobbie, S.E. Root Depth Distribution and the Diversity–Productivity Relationship in a Long-Term Grassland Experiment. *Ecology* **2013**, *94*, 787–793. [CrossRef]
- Nowosad, K.; Liersch, A.; Popławska, W.; Bocianowski, J. Genotype by Environment Interaction for Seed Yield in Rapeseed (Brassica napus L.) Using Additive Main Effects and Multiplicative Interaction Model. *Euphytica* 2016, 208, 187–194. [CrossRef]
- 95. Ray, D.K.; Gerber, J.S.; MacDonald, G.K.; West, P.C. Climate Variation Explains a Third of Global Crop Yield Variability. *Nat. Commun.* **2015**, *6*, 5989. [CrossRef]
- 96. Bartomeus, I.; Gagic, V.; Bommarco, R. Pollinators, Pests and Soil Properties Interactively Shape Oilseed Rape Yield. *Basic Appl. Ecol.* **2015**, *16*, 737–745. [CrossRef]
- 97. Xuan, W.; Beeckman, T.; Xu, G. Plant Nitrogen Nutrition: Sensing and Signaling. Curr. Opin. Plant Biol. 2017, 39, 57-65. [CrossRef]
- Semenov, M.A.; Jamieson, P.D.; Martre, P. Deconvoluting Nitrogen Use Efficiency in Wheat: A Simulation Study. Eur. J. Agron. 2007, 26, 283–294. [CrossRef]
- 99. Haberle, J.; Svoboda, P.; Raimanová, I. The Effect of Post-Anthesis Water Supply on Grain Nitrogen Concentration and Grain Nitrogen Šeld of Winter Wheat. *Plant Soil Environ.* 2008, 54, 304–312. [CrossRef]
- Kumaraswamy, S.; Shetty, P.K. Critical Abiotic Factors Affecting Implementation of Technologicalinnovations in Rice and Wheat Production: A Review. Agric. Rev. 2016, 37, 268–278. [CrossRef]
- 101. Ngoune Liliane, T.; Shelton Charles, M. Factors Affecting Yield of Crops. In *Agronomy—Climate Change and Food Security*; IntechOpen: London, UK, 2020.
- Hurtado, S.M.C.; Silva, C.A.; de Resende, Á.V.; Von Pinho, R.G.; Inácio, E.D.S.B.; Higashikawa, F.S. Spatial Variability of Soil Acidity Attributes and the Spatialization of Liming Requirement for Corn. *Ciênc. Agrotecnol.* 2009, 33, 1351–1359. [CrossRef]
- 103. Engel, R.E.; Long, D.S.; Carlson, G.R. Predicting Straw Yield of Hard Red Spring Wheat. Agron. J. 2003, 95, 1454-1460. [CrossRef]
- Chen, J.; Engbersen, N.; Stefan, L.; Schmid, B.; Sun, H.; Schöb, C. Diversity Increases Yield but Reduces Harvest Index in Crop Mixtures. Nat. Plants 2021, 7, 893–898. [CrossRef]
- 105. Kuai, J.; Sun, Y.; Zuo, Q.; Huang, H.; Liao, Q.; Wu, C.; Lu, J.; Wu, J.; Zhou, G. The Yield of Mechanically Harvested Rapeseed (*Brassica napus* L.) Can Be Increased by Optimum Plant Density and Row Spacing. *Sci. Rep.* **2015**, *5*, 18835. [CrossRef]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.