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Original Research

Spatial Variability of Total and Mineral Nitrogen Content and Activities of the N-Cycle Enzymes in a Luvisol Topsoil

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Abstract

The aim of this study was to evaluate and compare the spatial variability of total nitrogen (TN), mineral nitrogen content (N-NO_3 and N-NH_4) and activities of the enzymes involved in the soil N cycle (urease – UR, nitrate reductase – NR, arginine deaminase activity – ADA) in a Luvisol surface horizon. Fifty soil samples were collected in a square sampling grid (10 m x 10 m) system. The results were evaluated using classic statistical and geostatistical methods. Most of the studied properties were distributed normally with the exception of NR activity and nitrate nitrogen (N-NO_3) content, which were distributed log-normally. Variation of coefficients (CV%) for total and mineral nitrogen forms was low, for UR and ADA activities moderate, and for NR activity high. The contribution of nugget variance in total variability (sill) was noted for UR and NR activities, and for TN content. The ranges of spatial influence calculated for the values of the studied properties ranged from 10-40 m. Kriged maps showed that soil UR and ADA activities and N-NO_3 content were irregularly distributed in the soil surface horizon, while more regular spatial distribution was noted for NR activity and for TN and ammonium nitrate (N-NH_4) content.

Keywords: total nitrogen, mineral nitrogen, N-cycle enzymes, spatial variability, geostatistics

Introduction

Nitrogen in the soil exists mainly in organic forms. The main part of organic N occurs in soil humus as the protein fraction and as the products of their hydrolysis, amino acids bounded with polyphenols, sugars, and compounds of these products with soil minerals [1, 2]. Mineral forms of N, such as ammonium (NH_4^+) and nitrate (NO_3^-), usually account for a small portion of total N, but they are considered to be the preferred source of N for microorganisms and plants [3, 4]. The transformation of organic N to mineral forms and reverse can be carried out mainly during biological processes. Important processes in the nitrogen cycle include mineralization, nitrification, denitrification and fixation [1, 3]. Many of the processes are carried out by microorganisms by means of specific enzymes, either to produce energy or to accumulate nitrogen in the form needed for their growth. In the process of denitrification, dissimilatory nitrate reductase catalyses the first step by reducing NO_3^- to NO_2^- [3]. This process is performed in anaerobic conditions, and microorganisms use the nitrate as an electron acceptor in the place of oxygen during respiration [5]. Another enzyme involved in the N-cycle is urease, which catalyses the hydrolysis of urea-type substrates to NH_3 and CO_2. Urease activity is mainly of a microbial origin and its activity is mostly extracellular, and is associated with soil organic matter and clay minerals [6]. Because urea is continuously released into the soil environment as a product of the degra-

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dation of arginine, uric acid, and purines and pyrimidines of mammalian origin, as well as the importance of urea as a fertilizer, urease activity is one of the earliest and most often assayed enzymes [3]. Recently, the ability of a soil to ammonify arginine has been used as an index of microbial biomass activity since the ammonia released from arginine is due to the activity of microbial cells, and not to extracellular enzymes [4]. The activities of the N-cycle enzymes provide evidence of the intensity of the transformation of the soil nitrogen compounds and can be considered as an index of N-availability for plants [5].

The spatial variability of soil properties is considered to have a significant effect on nutrient cycling processes [7, 8], biomass turnover rate and transport processes in soil, e.g. organic pollutants [9]. Assessing the spatial variability of soil properties will help to develop better nutrient management strategies [10, 11], which is important from an economic point of view for site-specific farming as well as for environmental protection purposes. Since N-mineral forms are the main factors of soil pollution and water eutrophication [3], spatial distribution of these forms, especially on a field or regional scale, is of special significance.

The spatial distribution of soil properties was evaluated using both classical statistics [12, 13] and geostatistical techniques [14-18]. Geostatistics provides a set of statistical tools such as the autocorrelogram and semivariogram that help to characterize the spatial variability of every property separately as well as their spatial interactions [19, 20]. Soil spatial structure was investigated at different scales (cm, m, km) and with various objectives [11, 15, 18, 21, 22]. Most studies on spatial variability were focused on physical and chemical properties [14, 16, 19, 23-29], but an increasing number of studies are concentrating on the heterogeneity of microbiological and biochemical soil properties [13, 15, 17, 18, 21, 22, 30]. The aim of this study was to determine the spatial variability of total and mineral nitrogen concentrations and the activities of enzymes involved in N transformations in surface horizons of Luvisol using statistical and geostatistical tools.

Material and Methods

Study Site Characteristics and Soil Sampling Procedure

The study was carried out in a grid-pattern 90 m x 40 m plot in an 80-ha agricultural field located in the village of Orlinek near Mrocza (Cuiavia-Pomerania region; 53º15'31"N, 17º32'43"E; northwestern Poland). The area selected for research is partially covered with *Luvisols* [31]. The soil is a loamy sandy soil (clay 6%, sand 79%, silt 15%) with TOC and TN content ranging 5.8-9.0 $g \cdot kg^{-1}$ and 0.65-1.12 $g \cdot kg^{-1}$, respectively. Soil reactions varied from acid to neutral (pH_{KCl} of 5.04-7.01). Winter wheat (*Triticum aestivum* L.) was cultivated as the forecrop after winter rapeseed (*Brassica napus* L.). 50 soil samples were collected directly after the harvest (August 2007) at regular intervals (10 m) from the 0-20 cm top layer across the field (5 rows and 10 columns). Each sample consisted of 10 individual sub-samples taken randomly from a circular area with a radius of 2 m from the node point. Field-moist samples were sieved (<2 mm) and stored at 4ºC in a plastic box for not less than 2 days in order to stabilize microbial activity and then analyzed for enzymatic activities over two weeks. Samples for the determination of $N\text{-}NO_3$ and $N\text{-}NH_4$ content were stored in cooled boxes immediately after collection and kept frozen at -18ºC. Soil samples were analyzed for physical and chemical properties after air-drying at room temperature and sieving (<2 mm).

Soil Analyses

Physical and chemical properties were assessed in triplicate according to standard methods. A particle-size was carried out using the Cassagrande method modified by Proszyński; sand fraction content was determined by sieving; pH in 1 mol KCl·dm^3 was measured using a potentiometer in soil:solution suspensions (1:2.5); total organic carbon (TOC) and total nitrogen (TN) contents were measured using a Vario Max CN dry combustion analyser. $N\text{-}NO_3$ and $N\text{-}NH_4$ were extracted from field-moist soil with KCl and K_2SO_4, respectively, and nitrate nitrogen content was determined spectrophotometrically after establishing the color compound using phenoldisulphonic acid in an anhydrous medium [32], and the ammonium nitrogen concentration was assayed using the indophenol blue method [33].

Arginine deaminase activity (ADA) was measured using the Kandeler [34] method. Ammonium released by ADA was extracted with 2M KCl and determined colorimetrically by the indophenol blue reaction [35]. The blue color was formed over the reaction of NH_4^+ ions with phenol and hydrochlorite at an alkaline pH (Berthelot reaction). Soil urease activity was assayed as described by Kandeler and Gerber [36]. The concentration of ammonium ions extracted with KCl solution was assessed spectrophotometrically at 690 nm. The determination was based on the reaction of sodium salicylate with NH_4^+ in the presence of sodium dichloroisocyanurate, which forms a green-colored complex under alkaline pH conditions. Assimilatory nitrate reductase activity (NR) was determined according to Kandeler [34] using KNO_3 as the substrate. After a 24 h incubation of soil samples at 25ºC, the released nitrites were extracted with a 4M KCl solution and determined colorimetrically at 520 nm [37]. All enzymatic assays were performed in triplicate. The data were corrected for oven-dry (105ºC) moisture content. The same procedure was followed for the controls as for the enzyme assay, but the substrate was added to the soil after incubation and immediately prior to stopping the reaction. One unit of enzyme activity was defined as the number of mg of product released by 1 kg of dried soil per 1 h (for UR and ADA) and 24 h (for NR).

Statistical and Geostatistical Analysis

Classical statistics was used to study the central tendencies (mean and median) and the variability (standard devi-

Table 1. Statistics of soil properties (n=50).

Properties	Min	Max	Mean	Geometric mean	Median	SD	Skewness	Kurtosis	CV (%)
NR*	0.053	0.73	0.21	0.18	0.19	0.12	2.04	5.95	59.1
UR	1.28	3.97	2.29	2.22	2.26	0.56	0.46	0.25	42.4
ADA	0.57	2.24	1.12	1.08	1.08	0.36	1.09	1.26	31.6
TN	0.65	1.12	0.80	0.80	0.79	0.097	1.24	1.96	12.1
NO_3-N*	5.43	26.2	12.6	12.4	12.4	1.38	0.90	0.43	10.9
NH_4-N	4.48	8.46	6.76	6.68	6.94	1.06	-0.72	-0.50	15.6

*log-transformed data, NR – nitrate reductase activity (mgN-NO_2·kg^{-1}·$24h^{-1}$), UR – urease activity (mg N-NH_4·kg^{-1}·h^{-1}) ADA – arginine deaminase activity (mgN-NH_4·kg^{-1}·h^{-1}), TN – total nitrogen content (g·kg^{-1}), N-NO_3 – nitrate nitrogen content (mg·kg^{-1}), N-NH_4 – ammonium nitrogen content (mg·kg^{-1}), SD – standard deviation, CV (%) – coefficient of variation

ation, minimum and maximum, coefficient of variation) of the sample population. The data were tested for normality using the Shapiro-Wilk test (Statistica v. 9.0).

Soil spatial variability was evaluated by calculating an experimental variogram that quantifies the mean variability between neighbouring samples as a function of the spatial separation distance [19]. A semivariogram is a graphical indication of the degree of spatial autocorrelation measured for a particular random variable in a sample set. It displays the changes in semivariance between samples as the distance between them increases. Semivariance is defined as half the expected square differences between sample values separated by a given distance h or lag h [38]. The semivariance function $\gamma(h)$ at a given lag (h) is estimated using the following equation [39]:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i) - Z(x_i + h)]^2 \quad (1)$$

...where $\gamma(h)$ is a semivariance function, Z is a regionalized variable, $Z(x_i)$ is a measured sample at point x_i, and $Z(x_i+h)$ is a measured sample at point (x_i+h), $N(h)$ in the number of pairs separated by distance h or lag.

A semivariogram consists of three basic parameters that describe the spatial structure: nugget effect, sill, and range. The *nugget effect* (C_o), known as the random variance, represents variability not accounted for by the model either because of fine-scale variability (i.e. less than the sampling interval) or measurement error [39]. If the semivariogram curve passes through the origin, it fully describes the spatial dependency of the soil property (*sill*-C_o+C) (total variance) with spatial dependency accounting for all of the semivariance within the range. The range is defined as the distance at which the sill is achieved, and represents the average maximum distance over which two samples are related. This represents the distance within which spatial autocorrelation is strongest [25].

The spatial variability of the studied properties was categorized into classes based on the percentage of total variance (*sill*), present as random variance: $[C_o/(C_o+C)]\cdot 100$, proposed by Cambardella et al. [14]. When the ratio was less than 25%, the variable had a strong spatial dependence; if the ratio was between 25-75%, the variable had a moderate dependence; otherwise, the variable was considered randomly correlated (pure nugget effect). Semivariogram models were cross-validated and the punctual kriging procedure was used to obtain point estimates of soil parameters at unsampled locations [40]. Maps illustrating the spatial variance of the determined properties were drawn on the basis of the semivariograms. Geostatistical calculations were done using Isatis software (Geovariance Co.).

Results

Descriptive Statistics of the Properties Studied

The basic statistical parameters of the properties within the studied area are presented in Table 1. Almost all data were distributed normally according to the Shapiro-Wilk test (Statistica v. 9.0) and the calculation was based on row data. The exceptions were N-NO_3 content and NR activity, which did not show normal distribution and were log-transformed. Since the transformation improved the normality of their distribution, further analyses were performed with the corrected data.

Normal distribution of the UR and ADA activities, as well as TN and N-NH_4 row data, was confirmed by similar values of means and medians. Median values were also very close to the mean values for NR activity and nitrate-N content after log-transformation, and the SD was significantly lower than the mean (especially for N-NO_3 data), which is an important condition for normality (Table 1).

The shape of the distribution of the properties studied was described by skewness. Most of the variables were positively skewed, only N-NH_4 data showed a negative value of skewness demonstrating a left-sided asymmetry. The UR activity coefficients of skewness were close to 0, suggesting an almost symmetric distribution. Positive kurtosis indicated a relatively peaked distribution, whereas the negative one suggested a flat distribution compared with the normal distribution. Ammonium-N concentration, N-NO_3 content

Table 2. Parameters of variogram models.

Properties	Model*	Nugget (C_o)	Sill (C_o+C)	C_o/(C_o+C), %	Range (m)	SD^
NR	L, NE	0.0092	0.0107	86.0	-	W
UR	Sph, L, NE	0.045	0.227	19.8	10	S
ADA	Sph, L	-	0.089	-	13	-
TN	Sph, L, NE	0.005	0.0079	63.3	19	M
$N\text{-}NO_3$	Sph, L	-	16.4	-	14	-
$N\text{-}NH_4$	Sph, L	-	1.23	-	40	-

*Sph – spherical, L – linear, NE – nugget effect, E – exponential, ^ SD – spatial dependence, S – strong, M – moderate, W – weak, NR – nitrate reductase activity ($mgN\text{-}NO_2 \cdot kg^{-1} \cdot 24\ h^{-1}$), UR – urease activity ($mg\ N\text{-}NH_4 \cdot kg^{-1} \cdot h^{-1}$), ADA – arginine deaminase activity ($mgN\text{-}NH_4 \cdot kg^{-1} \cdot h^{-1}$), TN – total nitrogen content ($g \cdot kg^{-1}$), $N\text{-}NO_3$ – nitrate nitrogen content ($mg \cdot kg^{-1}$), $N\text{-}NH_4$ – ammonium nitrogen content ($mg \cdot kg^{-1}$)

after log-transformation and UR activity were the soil properties of kurtosis close to 0 (Table 1).

Coefficient of variation (CV) is a useful statistical tool for measuring the spatial variability of soil properties [41]. According to the classes based on CV [%] values proposed by Wilding [42] for assessing the soil properties variability variation of coefficients for total N and mineral forms was little, while in the case of UR and ADA, activity was moderate. Although the logarithmic transformation reduced the CV values of NR activity from 86% to 55.6%, it still showed a high magnitude of variability (Table 1).

Analysis of correlation revealed no significant correlation coefficients for most of the parameters investigated (data are not presented). Only TOC concentrations were significantly and positively correlated with TN content (r=0.639, $p<0.01$, n=50) and with the $N\text{-}NH_4$ content (r=0.351, $p<0.05$). No significant correlation was found between pH_{KCl} values and enzymatic activities, except for ADA activity (r=0.423, $p<0.05$, n=50), while pH_{KCl} was significantly but negatively correlated with $N\text{-}NH_4$ content (r=-0.468, $p<0.05$, n=50) and UR activity (r=-0.301, $p<0.05$, n=50). NR activity was significantly and positively correlated with $N\text{-}NO_3$ content (r=0.491, $p<0.05$, n=50) and UR activity with ADA activity (r=0.393, $p<0.05$, n=50).

Spatial Structure Analysis of Soil Properties

Linear or mixed (spherical/linear) models, with or without nugget effects, were fitted to the semivariograms calculated in order to characterize the spatial variability of the studied properties. Since row data of nitrate-N content and NR activity were not distributed normally, semivariance was tested using log-normal data (Table 2, Figs. 1a, e).

The NR, UR activities, and TN content showed a random variance (*nugget variance*) in the total variance (*sill*). With reference to this fact the spatial variability of those properties was categorized into classes based on the percentage of the total variance (*sill*) present as random variance [14] (Table 2). UR activity showed a nugget/sill ratio of 19.8%, indicating a strong spatial variability. Nugget semivariance for NR activity and TN content was large compared with total variance (86.0 and 63.3% of *sill*), suggesting a weak and moderate spatial structure, respectively. The results indicated that less than 20% of UR activity variability was due to random variability and that the structural variance accounted for more than 80%. Properties strongly spatially dependent could be controlled by intrinsic factors such parent material, topography, and/or soil types [8].

Ranges of influence calculated for the variables of the studied values were 10-40 m. Since the range is the maximum distance over which results are correlated [43], the sampling grid assumed for the studied properties (10 m) was suitable and therefore all variables (except for NR activity) appeared to be spatially autocorrelated (Table 2, Fig. 1).

Kriged maps of the spatial distribution of the properties being studied were prepared on the basis of semivariogram models (Figs. 2, 3). The soil UR and ADA activities and $N\text{-}NO_3$ concentration were irregularly distributed in the soil surface horizon, but to some degree they exhibited a similar variation in distribution structure (Figs. 2b, 2c, 3b). Higher enzyme activities and $N\text{-}NO_3$ concentrations were detected in the northwestern and southwestern parts of the field, 60-90 m in length for enzymes activities and 50-90 m in length for $N\text{-}NO_3$ content. A more regular spatial distribution was noted for NR activity and for TN and $N\text{-}NH_4$ contents (Figs. 2a, 3a, 3c). Nitrate reductase activity was clearly higher in the southwestern and northeastern corners of the field. The highest TN content was shown at 15-25 m of length and 0-20 m of width, while the lowest values were obtained in the centre of field length (30-60 m) and 0-30 m of field width. A band of relatively higher soil $N\text{-}NH_4$ content ran vertically from the north to the south of the field at 30-80 m of the field length.

Discussion

Nitrogen turnover in soil, including N mineralization and N uptake by soil microorganisms, the role of enzyme systems responsible for these processes, and their regulation have been investigated in a large number of studies [44]. A great many of the studies have dealt with the spatial

distribution of total and mineral N content [14, 16, 22, 24, 26, 28, 29, 45, 46]. However, less attention has been paid to the spatial distribution of the enzymatic activities of the N-cycle [12, 13, 15, 21, 22].

The studied properties varied significantly in spatial variability. Enzymatic activities were more variable than TN and mineral-N concentrations, which was confirmed by the coefficients of variation values (Table 1). This corresponded well with the earlier findings of Sebai et al. [47]. The coefficients of variation calculated for enzymatic activities in this study ranged from 24.5 to 55.6%, while CV for TN and mineral-N contents showed little variability (CV=<16%). In general, biological properties are considered more spatially variable than physical and chemical parameters, which is caused by the fact that biological variables are more sensitive to different natural and anthropogenic factors. The coefficient of variation of ADA activity in this study as well as in the study by Stark et al. [15]

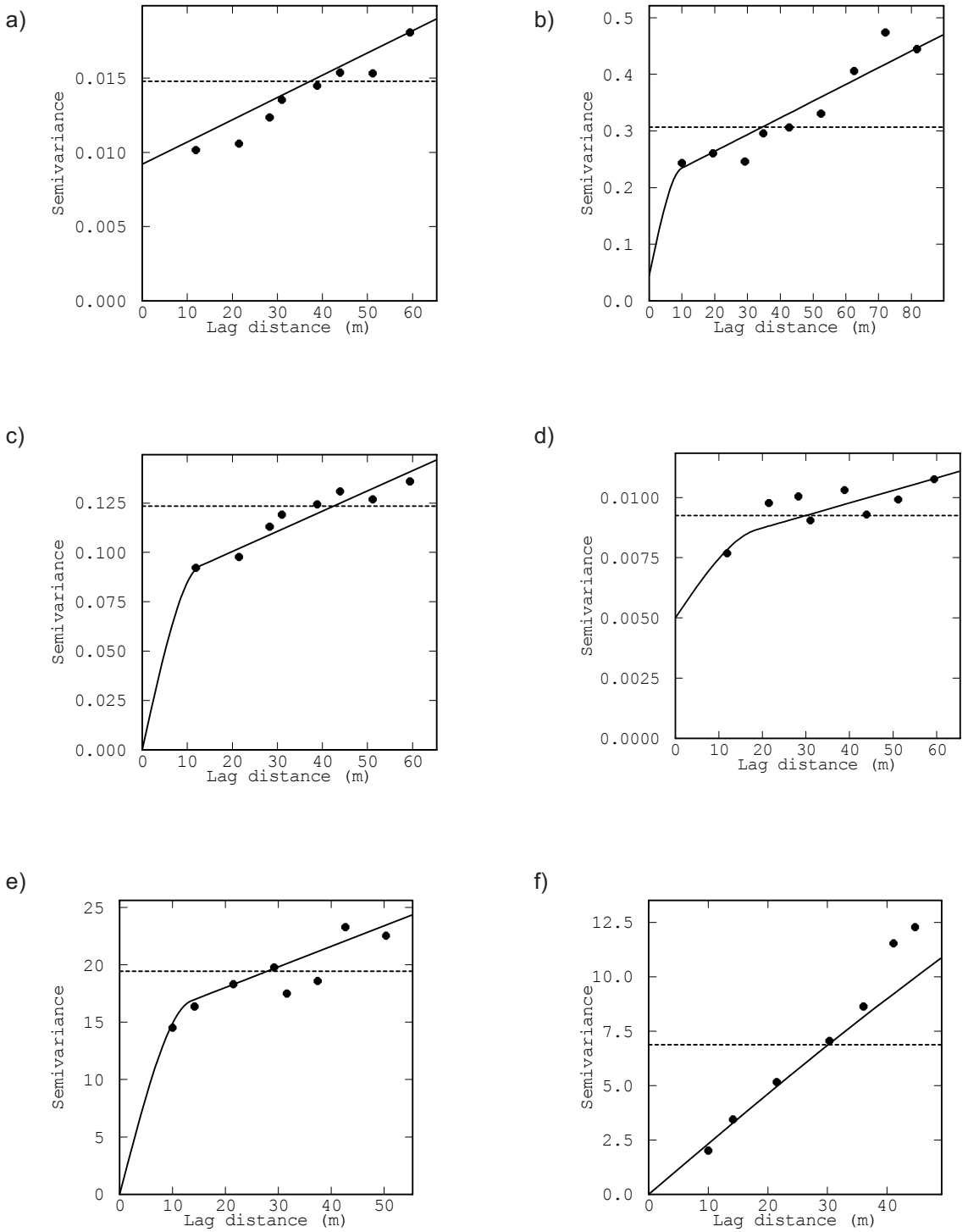

Fig. 1. Experimental semivariograms of a) nitrate reductase activity, b) urease activity, c) arginine deaminase activity, d) total nitrogen content, e) N-NO_3 content, f) N-NH_4 content.

was qualified to the moderate class of variability (32.1% and 22.5%, respectively), while Bonmati et al. [12] reported a higher CV value of UR activity than the one found in this study (59.7% and 24.5%, respectively). Some of chemical properties, however, especially those connected with water or solute transport, are among the most variable [25]. Soil N-NO_3 is considered to be one of the most changing chemical properties, both in time and in space [45], which was confirmed by a high standard deviation (SD) and coefficient of variations (CV%) [48]. According to Mulla and McBratney [25], Hergert et al. [49], and Wollenhaupt et al. [50], soil nitrate content reveals a moderate coefficient of variation (CV=28-58%), while in the study of Stein et al. [48] nitrate-N data exhibited a high magnitude of variability (CV up to 227%). In general, the spatial distribution of soil nitrates is known to be log-normal [51-53], while the spatial variability of total N is distributed normally [14, 27]. The latter findings were confirmed in this study. A high degree of positive skewness of nitrate-N before log-transformation (2.04) was in agreement with other studies [27, 54].

Enzymatic activity involved in total denitrification was highly skewed and was close to a lognormal distribution [55]. Similarly, in this study NR activity data were also not distributed normally and their log-transformation was necessary.

The spatial variability of the soil parameters under study was also confirmed by a geostatistical analysis, but they differed significantly in the pattern of variation, which was shown in particular by the semivariogram parameters (Table 2, Fig. 1).

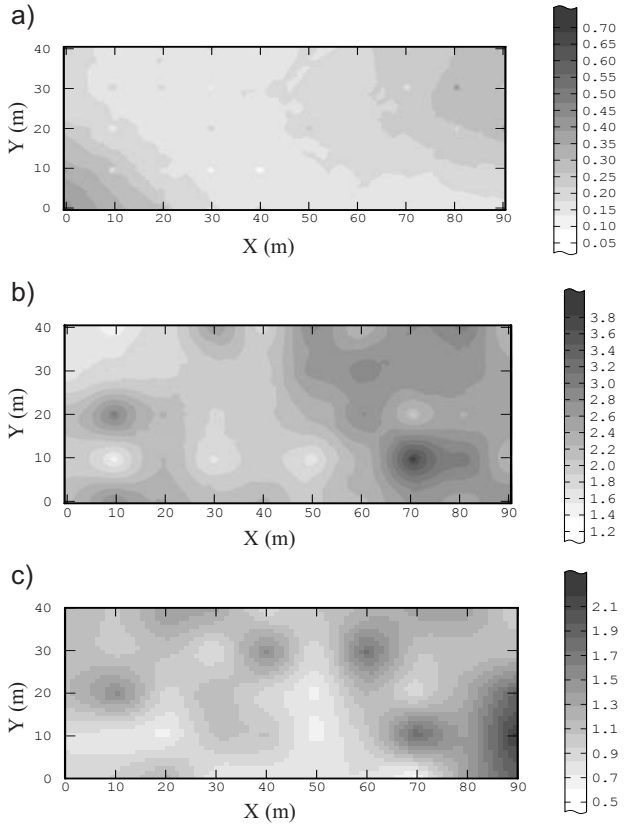

Fig. 2. Spatial distribution of a) nitrate reductase activity, b) urease activity, c), arginine deaminase activity.

The ratio of *nugget effect* (C_o) to *sill* (C_o+C) is an important index for investigating spatial structures and enables a comparison of the relative size of the nugget effect among soil properties [39, 49, 56]. The semivariograms produced in this study indicated a strong spatial dependence only for UR activity, which can be influenced by variability in natural factors, such as soil texture and mineralogy [14]. A higher contribution of nugget effect to total variance in UR activity (31.3%) was found by Aşkin and Kizilkaya [21]. NR activity in their study was characterized by a variogram with a nugget/total semivariance ratio >75%, which suggested the influence of external factors, such as the application of fertilizers and other agrotechnical measures, which may control the variability of this enzyme activity [14]. A medium class of spatial variability was noted for TN content. Some other studies have shown a lower contribution of nugget variance to total variance (*sill*) in TN variability. Thus, in the study of Lu et al. [46] the C_o/C_o+C ratio for TN content ranged from 7.7 to 21.1%, indicating a strong spatial dependence while a lower ratio of 1.2 % and 2.9 % was noted by Peigné et al. [17] and Yanai et al. [57], respectively.

According to Jung et al. [16], the main disadvantage of geostatistical interpolation of soil properties is the need for a large number of soil samples that must be collected and analyzed in order to have a valid representation of the unsampled area, which is time-consuming and triggers a higher cost in the research. Therefore, it is important to plan well and analyze an adequate number of soil samples. It turns out that the range, understood as the spacing between sample locations, is the most crucial for the decision regarding the semivariogram parameters [25]. If the sampling distance is bigger than the range, the data will no longer be spatially correlated, and as a result the geostatistics cannot be used [19]. In this study the ranges of spatial dependence among the studied properties varied from 10 m to 40 m, suggesting that the sampling scheme (10 m x 10 m) was adequate and the data were spatially correlated within the studied area. The same property can vary significantly within the range, which is caused mainly by the sampling distance; usually the longer the sampling distance the higher the range of influence. For example, the zone of influence for urease activity was 19.3 km in the case when the soil was sampled at 4.5 km intervals [21]; however, it reached 124.7 m when samples were collected at a distance of 15 m [22], while the relevant value was 10 m when samples were taken at a distance of 10 m (Table 2). Differential range values were noted for TN concentrations: 19.2-25 m [58], 33.8 m [47], 42.5 m [27], 50 m [17], and 208-650 m [46]. According to Cahn et al. [59], different ranges of spatial correlation for nutrients may be related to the mobility of the ions. In this study nitrates, which are more mobile than the N-NH_4 form, had a shorter range of spatial correlation (14 m) as compared with the range of the ammonium form (40 m). Other studies showed longer N-NO_3 content ranges: 37 m [27], 40-275 m [50], while in the case of the N-NH_4 content the ranges were 55.6 m and 60.4 m [29], which was mainly due to a different sampling scale.

In this study no significant correlation coefficients were found between total and mineral-N contents and the N-cycle enzymes, except for NR activity and N-NO_3 content. This fact can be partly explained by the suggestion put forward by McGill and Cole [60], who stated that the enzymes involved in N mineralization are less responsive to variation in N demand than the P-mineralizing enzymes are to P demand. According to those authors, nitrogen in organic matter is bound between C atoms in a varied configuration, and inorganic N can only be released through multi-step pathways involving a set of enzymes that selectively eliminate particular types of C-N bonds. Moreover, the early products of the decomposition of N organic compounds often have fates other than those of a complete mineralization. Both UR and ADA activities were significantly and positively correlated with TOC and negatively with TN, but they did not correlate significantly with ammonium-N and nitrate-N contents [61]. Nitrate reductase is an adaptive enzyme and is synthesized only in the presence of NO_3^- ions, while in a soil solution it is repressed by NH_4^+ ions [62, 63]. This is in an agreement with the results obtained in this study where a significant positive correlation coefficient was shown between the values of nitrate-N content and NR activity ($r=0.491$, $p<0.05$). However, no significant correlation was found between the N-cycle enzymes and TOC content, which has often been found in other studies [13, 22, 43]. Arginine deaminase activity was correlated significantly with the carbon content in soil, but was poorly related to soil pH and ammonia content [64].

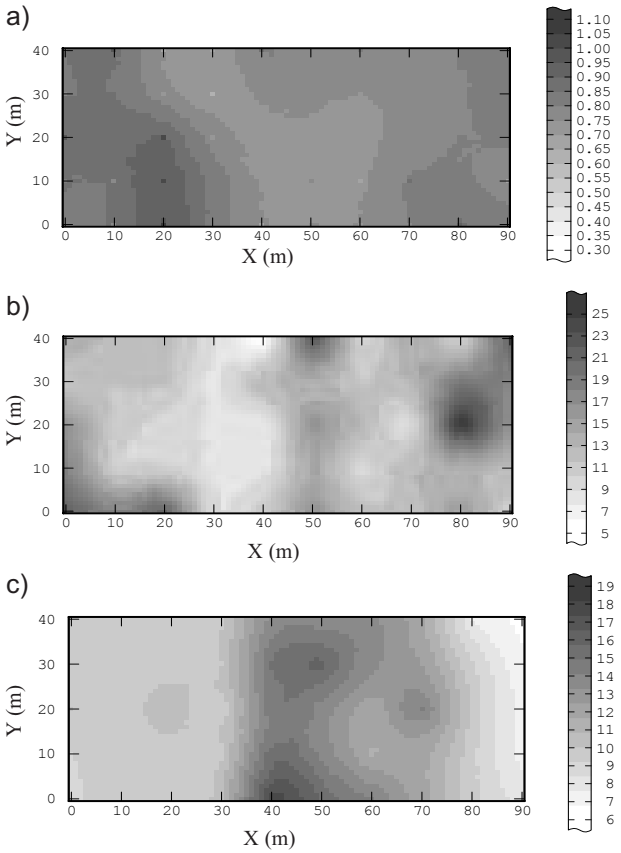

Fig. 3. Spatial distribution of a) total nitrogen content, b) N-NO_3 content, c) N-NH_4 content.

The study of soil spatial variability may be of help in gaining a better understanding of field soil processes and in the optimization of strategies for site-specific management, e.g. fertilization. Nutrient maps based on a geostatistical analysis are used regarding the phosphorus and potassium data since these nutrients show a comparatively stable spatial distribution pattern as the consequence of a high proportion of structural variance and a high range of values [27]. In the case of mobile ions such as nitrate, this approach has been less effective due to high variability and low spatial correlation [27]. Nevertheless, several studies have concentrated on the spatial variability of N-NO_3 concentrations because of its economic and ecological importance [23, 26, 27, 58, 65, 66]. The results obtained in this study for both N mineral forms showed that they were influenced only by the structural variance, which indicates a high spatial dependence and is inconsistent with other studies [14, 27]. However, the ammonium-N content showed a higher range value, indicating a stronger spatial correlation than N-NO_3 and seems to be a better property for maps produced for site-specific management purposes.

Conclusions

The results provide information on the spatial variability of total and mineral N content, as well as the enzymatic activities of the N-cycle in the arable field scale. The spatial variability of the studied properties differed considerably, which was clearly visible in the shape of the semivariograms and kriged maps (Table 2, Figs. 1-3). Generally, higher spatial variability, as shown by the CV% values, was noted for enzymatic activities rather than for total and mineral N content. Semivariograms of the spatial structure of the parameters studied showed a high contribution of *nugget variance* (C_o) to total variability (*sill*) only for NR activity and for total-N content, which indicates that they were strongly influenced by external factors like agricultural treatments (fertilization, agrotechnical measures, pesticides). However, mineral-N content and ADA activity were only affected by the structural variance (lack of the nugget effect) represented by variability in soil texture or mineralogy. This can help to understand and predict the contribution of internal factors (i.e. soil type, topography) in the total variability of soil properties, which can mask the influence of soil management practices (tillage, crop rotation).

Since the spatial structure of soil properties is complex and contrasting range values have been reported, future research should mainly be concerned with the size of the studied area and the sampling point intervals. Therefore, a proper sampling scheme and the separation distance between sampling points for any future data collection is of special importance and should be done prior to the regular experiment in order to reduce the time and the effort of sample collection and data gathering in future studies. The results showed that the current scale of sampling was suitable for a correct description of the soil variability of the studied properties within the investigated field.

Additional research of spatial structure of ammonium and nitrate-N forms taking into consideration different field size and sampling scale as well as seasonal variation should be considered before any conclusions regarding the applicability of the results for site-specific management of the studied site can be drawn.

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