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Significance of the spatial speciation of phosphorous in agricultural soils for the interpretation of variability

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Summary

The main objective of the present research work was to investigate the spatial dynamics of soil P pools in an agricultural field where P was fertilised in organic and inorganic form. P was analysed using four extraction methods with different extraction force. Extractants used were aqua regia (AR), $0.43M$ nitric acid (WH), $0.05M$ ammonium acetate $+ 0.02M$ Na_2EDTA (AAC) and $0.01M$ calcium chloride ($CaCl_2$). Organic P, soil texture, pH, Fe, $CaCO_3$ and total carbon concentrations were determined in air-dried soil samples employing standard methods. All investigated P fractions that were representative of functional P pools displayed a weak spatial autocorrelations. The spatial autocorrelation was quantitatively analysed using variography. The pools did not only differ with respect to their spatial ranges, but also in their distribution patterns and strength of autocorrelations. The overall weak structural component of the autocorrelation was attributed to the high P status of the field. The ranges of P fractions decreased in the order: $CaCl_2$-P > P_{org} > AAC-P > WH-P > AR-P. The main environmental factors that controlled the spatial distribution of individual P pools were: Ca-phosphate for the sparingly available (AR-P), absorption capacity of the soil for the reversibly available (AAC-P) and the distribution of manure for the organic P pool (P_{org}). Due to the high variance of the readily available P pool its distribution could not be modelled satisfactory. The results of this study clearly demonstrate that investigations of the biochemical cycling of P by means of soil tests should be evaluated in the context of site-specific soil characteristics.

Key words: Spatial speciation, phosphorus, variogram analysis, manure, fertilisation, organic P, Soil analysis

Zusammenfassung

Die Bedeutung räumlich abhängiger Phosphorbindungsformen in landwirtschaftlichen Böden für die Interpretation von Variabilität

Ziel dieser Arbeit war es die räumliche Dynamik verschiedener P-Bindungsformen in landwirtschaftlichen Böden, die sowohl organisch als auch mineralisch mit P gedüngt wurden, zu untersuchen. Die P Gehalte wurden mittels vier Extraktionsmethoden unterschiedlicher Extraktionskraft bestimmt. Bei den Extraktionslösungen handelte es sich um Königswasser (AR), $0.43M$ Salpetersäure (WH), $0.5M$ Amonium-Acetat EDTA (AAC) und $0.01M$ Calcium-Chlorid ($CaCl_2$). Des weiteren wurde der Gehalt an organisch gebundenem P, Textur, pH, Fe, Zn, $CaCO_3$ und C_{gesamt} bestimmt. Alle untersuchten P-Bindungsformen (P-Pools) zeigten eine schwache räumliche Autokorrelation, die mittels geostatistischer Methoden (Variographie) quantitativ bestimmt werden konnte. Die P Pools unterschieden sich nicht nur hinsichtlich ihrer räumlichen Verteilungsmuster, sondern auch in der Stärke ihrer Autokorrelation. Die generell schwache Autokorrelation der P-Pools wurde auf den hohen P Gehalt des Bodens zurückgeführt. Die Reichweiten nahmen in folgender Reihenfolge ab: $CaCl_2$-P > P_{org} > AAC-P > WH-P > AR-P. Die Hauptfaktoren der räumlichen Verteilung waren: Ca-Phosphate für das langsam verfügbare P (AR-P), die spezifische P Absorptionskapazität des Bodens für das reversibel verfügbare P (AAC-P) und die Applikation von organischem P-Dünger für den organischen P Pool (P_{org}). Auf Grund der hohen Variabilität des leicht verfügbaren P konnte die räumliche Verteilung dieses P Pools nicht zufrieden stellend modelliert werden. Die Ergebnisse dieser Arbeit zeigen, dass eine räumliche Evaluierung der Bindungsformen ein hilfreiches Instrument sein kann, um die Mobilität eines Nährstoffes in der Umwelt zu erfassen. Deshalb sollte bei der Auswahl von Analysemethoden im Rahmen grossflächiger Landschaftsanalysen der Bezug dieser Verfahren zu räumlichen Umweltfaktoren berücksichtigt werden.

Schlüsselworte: organisches P, Phosphor, Variogram-Analyse, räumliche Variabilität, Bodenuntersuchung, Düngung, Gülle

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1 Introduction

The concept of balanced fertilisation aims at a harmonisation of agronomic and ecological demands (Vermeulen et al.,1998). From the viewpoint of plant nutrition and soil science, the acceptable level of a P surplus in soils which are sufficiently supplied with available P is near to zero. This deviation from a balanced fertilisation is a consequence of a management practice whereby most agricultural fields are managed in conformity with a risk-averse "null hypothesis" that given uncertainty in space and time, uniform within-field treatment is an optimal strategy (McBratney and Whelan, 1999). The shortcomings of conventional fertiliser practices led to the development of site-specific nutrient management (SSNM), which aims at transferring the site-specific nutrient demand into variable fertiliser rates which match the spatial variability of soil and crop parameters (Haneklaus and Schnug, 2002) SSNM usually operates with digital agro-resource maps (DARMs) which are processed in geographical information systems (GIS) (Schroeder et al., 1997). High sampling density is needed to determine the entire variation and to obtain a "true" chemical image of the field, but in most cases this procedure is not economically feasible or sustainable for farmers (Lowenberg-Deboer and Boehlje, 1996). In order to develop economically sound sampling strategies as well as utilising ancillary data sources, it is essential to understand the spatial and temporal behaviour of nutrients within the soil.

It has long been recognised that the biological availability of a nutrient depends not simply on its concentration, but also on its chemical form in the soil system (Ure and Davidson, 1995). Thus, for a balanced fertilisation it is necessary to quantify not only the instantly plant-available P fraction, but also P which can be released from soil resources during crop growth (Van Noordwijk et al., 1990). Rather than focusing on standard P tests, which are thought to represent the plant available, or reversibly bound P pool, the speciation of fertiliser P within agricultural fields will provide supposedly more detailed information about the interaction of plant nutrients with other soil factors and management practices. As there is a considerable disagreement about relating soil P test methods to specific P pools the present study adopted the system of Guo and Yost (1998) who proposed to partition the total soil P reserve into three discreet functional pools: readily available, reversibly available, and sparingly available. The readily available P pool represents P in solution that is readily accessible by plant roots. The reversibly available P denotes the soil P reserve that can be converted into soluble (readily available) P, by either edaphon or weathering during crop growth. In contrast the sparingly available P is not available within one or more crop cycles, but a small fraction of this pool may become available during long-term soil transformation processes.

The main objective of this work was therefore to investigate the spatial dynamics of functional soil P pools in agro-ecosystems. Special emphasis was placed on the employment of variography as a tool to evaluate the spatial speciation of P which is defined as the chemical reactivity of soil P with site-specific environmental factors and the subsequent formation of geochemical species that display different spatial dependencies (Gassner et al., 2002).

2 Materials and Methods

Warberg (E 10°54', N 52°10') is located on the fringe of the fertile lowlands of the Magdeburger Boerde, Germany. The Boerde is characterised by glacial aeolinan loess deposits. The farm in Warberg is situated in a gently rolling landscape whereby fields are separated through drainage channels. The soil is a dark Luvisol (typic Hapludalf), with an average depth of about 1 m, followed by a carbonate rich C horizon. The field under investigation (Grosser Born) is about 16 ha in size, with a slope ranging from 1-4 %. Mineral, water soluble P fertiliser was applied every three years based on the official fertiliser recommendation for this region (LK Hannover, 1993). Additionally, swine manure, with an average concentration of 7 % P was irregularly applied; application rates were in line with the German ordinance of fertilisation (DüngeV, 1996). At the time of the study the last mineral fertiliser application was applied three years prior to sampling, while manure was applied recently.

In 2000, 161 geocoded topsoil (0-20 cm) samples were taken in a 30 m grid whereby 6 sample cores were collected per sampling point within a radius of < 1 m. Sample cores were mixed, air-dried and passed through a 2 mm sieve prior to analysis. Soil pH values were measured potentiometrically in $0,01$ M $CaCl_2$ suspension (1:10 w/v). Total carbon was determined by dry combustion employing a Leco equipment. $CaCO_3$ was analysed volumetrically using a Scheibler calcimeter (König, 1923). The clay content was determined indirectly according to Schnug and Haneklaus (1996). Fe was determined by atomic absorption spectrometry following aqua regia extraction (AbfKlaerV, 1992). Soil phosphorous was measured colourimetrically according to John (1968) and Schüller (1969) in four different extracts: 0.01 $CaCl_2$ ($CaCl_2$; 15), $0.5M$ CH_3COONH_4 + $0.5M$ CH_3COOH + $0.02M$ Na_2EDTA (AAC (Sillanpää, 1982)), $0.43M$ HNO_3 (WH (Westerhoff (1954/1955)), aqua regia (AR (AbfKlaerV, 1992)). Organic P (P_{org}) was determined by the acid ignition method using $0.1M$ H_2SO_4 (Saunders and Williams, 1955) followed by ICP-OES analysis. Additional, eight randomly selected samples were analysed for P according to the German standard P test (CAL; Schüller, 1969).

Under the intrinsic hypothesis, the semi-variance $\gamma(h)$ between two observation points separated by a distance

(lag) h is a function of distance and direction of separation, whereby the mean semi-variance for each lag h can be calculated according to:

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

The semi-variance at each lag h plotted against the total lag distance is known as the semi-variogram and is commonly modelled using a number of universal functions. In general, these models begin from an intercept at lag $h = 0$ of zero (or close to zero) and rise to a plateau semi-variance (sill) at some distance a, the range of spatial autocorrelation. The predominant model used in this study was a spherical model with a nugget effect:

$$\gamma(h) = \begin{cases} C_0 + C_1\left[\frac{3}{2}\frac{h}{a} - \frac{1}{2}\left(\frac{h}{a}\right)^3\right] & , \quad 0 < h \le a \\ C_0 + C_1 & , \quad h > a \\ 0 & , \quad h = 0 \end{cases}$$

whereby, C_0 is the intercept or nugget semi-variance, $C_0 + C_1$ is the sill (C) and a is the range (Gassner and Schnug, 2003).

Statistical analysis was conducted using SPPS Version 10. For geostatistical analysis Variowin Version 2.2 (Pannatier, 1996) was used. Although some variables showed a skewed distribution, rank normalisation did not change the experimental semi-variograms so that the original data was processed. Semi-variograms were standardised by dividing each semi-variogram value by the overall sample variance. If significant trends ($p < 0.05$) were detected semi-variograms were calculated on detrended residuals. Detrending was carried out by fitting a linear regression to the data in the trend direction.

3 Results and Discussion

A summary of the chemical characteristics of the soil in Warberg is given in Table 1. According to the results from the standard German P test (Schüller, 1969) and the official fertiliser recommendation (LK Hannover, 1993), the P status of the field was distinctly above the optimum range. This was also reflected in the low $C:P_{org}$ ratio of 75. The active mineralisation of P_{org} is triggered by the excretion of phosphatase by living plant roots under P limiting conditions (McGill and Cole, 1981; Clarholm 1993). In soils with a high concentration of plant available P, the release of phosphatase is repressed; thus during oxidation of organic matter, P_{org} tends to accumulate relative to carbon (C) resulting in a low $C:P_{org}$ ratio, generally < 100 (Smeck, 1985; Clarholm, 1993). Thus it was assumed that despite the application of manure P_{org} played only a minor role for the P nutrition of crops, because of an overfertilisation with mineral P. The variability of soil attributes is generally lower for static than in dynamic soil properties (Wilding and Drees, 1990; Goderya, 1998). Cahn et al., (1994) even suggested that increasing variability may relate to increasing nutrient mobility. A comparison of the individual P fractions with respect to their relative standard deviation (RSD %) showed that the highest overall variation was found for $CaCl_2$-P, the method with the lowest extraction force, and the lowest for AR-P, the method with the highest extraction force.

4 Chemical speciation of P in soils

The speciation of soil P into pools of different plant availability can either occur as molecular speciation which is a function of thermodynamic and kinetic properties of the chemical reactions between P and soil particles or by differentiated distributions among soil components such as organic matter or hydrous oxides.

In the first scenario, the spatial speciation is assumed to be low as P is retained with different energy in individual soil compounds, which tend to be in an equilibrium

Table 1:
Descriptive statistics of soil analysis data from grid soil sampling on field Grosser Born in Warberg (E 10°54', N 52°10')

		Minimum	Maximum	Mean	RSD %
$CaCl_2$-P	mg kg^{-1}	0.015	2.03	0.56	83
AAC-P	mg kg^{-1}	43.2	212	108	35
WH-P	mg kg^{-1}	81.5	749	184	47
AR-P	mg kg^{-1}	231	1150	477	26
P_{org}	mg kg^{-1}	61.00	346	143	26
pH		5.93	7.64	6.93	5
C_{tot}	%	0.81	2.76	1.07	24
$CACO_3$	%	<0.01	5.45	0.52	156
clay	%	10.4	31.6	18.3	24
Fe	mg kg^{-1}	1.09	2.20	1.52	15

among themselves and the soil solution. Their solubility is supposed to be just a function of the particular extractant used (Simonis, 1996). In the second scenario, the spatial speciation is assumed to be more pronounced as the distribution of different soil components with a particular bonding energy for P will result in a spatial differentiation of P species. First indication for the occurrence of spatial speciation is therefore the bivariate relation of P extracted by different extractants. If the P concentrations of two extractants show a high degree of covariance, it is suggested that the corresponding pools are in equilibrium with each other.
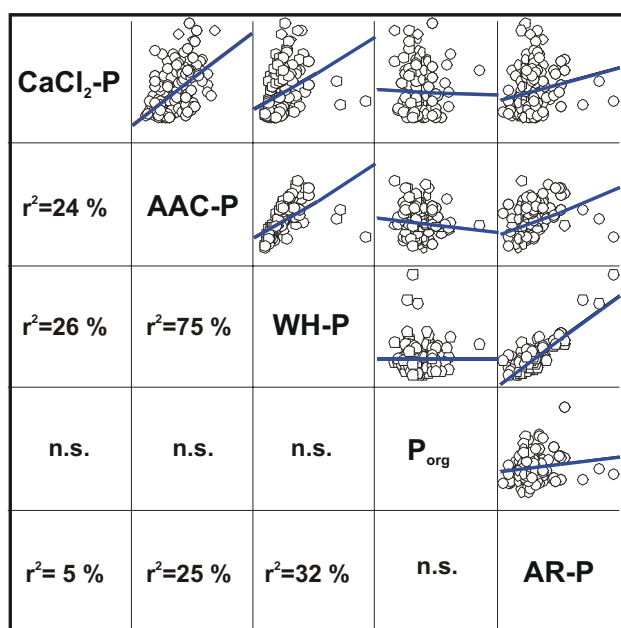

Fig. 1:
Scatterplots and linear regressions for P-species at Warberg, Grosser Born (n. s = not significant; all others p < 0.001)
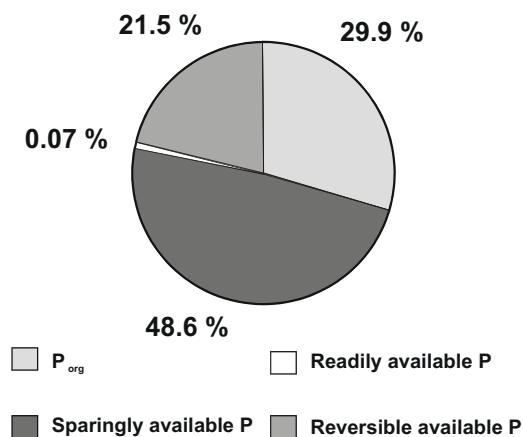

Fig. 2:
Percentage of functional P pools of the total soil P concentration in a Luvisol soil at Warberg, Grosser Born

All inorganic P fractions were found to be highly significantly (p < 0.001) correlated (Fig. 1). However, only between AAC-P and WH-P a correlation coefficient of r > 0.7 (r^2 > 50 %) was found, indicating that only these two P fractions were in equilibrium with each other. P_{org} was found not to be correlated with any of the inorganic P fractions.

The total soil P reserve of the soil can be estimated to consist to 30 % of organic and to 70 % of inorganic P. The inorganic P could further be distinguished into 0.1 % readily, 22 % reversibly and 50 % sparingly available P.

As a significant correlation between the individual P fractions was determined, principal component analysis (PCA) was carried out to investigate the interactions between different P species and their reaction with main soil chemical properties. The advantage of PCA over other multivariate analysis methods is that it circumvents the problem of multicollinarity (Bowermann and O`Connell, 1990; Mallarino et al., 1997).

The idea behind PCA is to group variables so that the correlation of two variables from different groups is small, while the correlation for two variables of the same group is high. Each group can be represented by a new variable that is created from the variables in the group, the so-called latent variable. The interpretation of the latent variable, which is the underlying factor that causes the variables of one group to co-vary, is the most crucial part of the PCA (Schnug, 1996).

Three principal components (PC) explained 69 % of the total variance within the data set, whereby the PC1 accounted for 36 %, PC2 for 19 % and PC3 of 14 % of the total variability (Table 2). High loadings (> 0.49) on PC1 were found for all mineral P species and soil pH. Because of the collective co-variance of this group of variables the latent variable is interpreted as mineral P fertilisation. PC2 was highly loaded (> 0.49) by clay, Fe and $CaCl_2$-P, whereby $CaCl_2$-P displayed a negative loading. The latent variable of this group is supposedly the P adsorption capacity. P_{org}, C_{tot} and $CaCO_3$ were collectively

Table 2:
Results of the rotated component matrix for soil parameters at Warberg, Grosser Born.

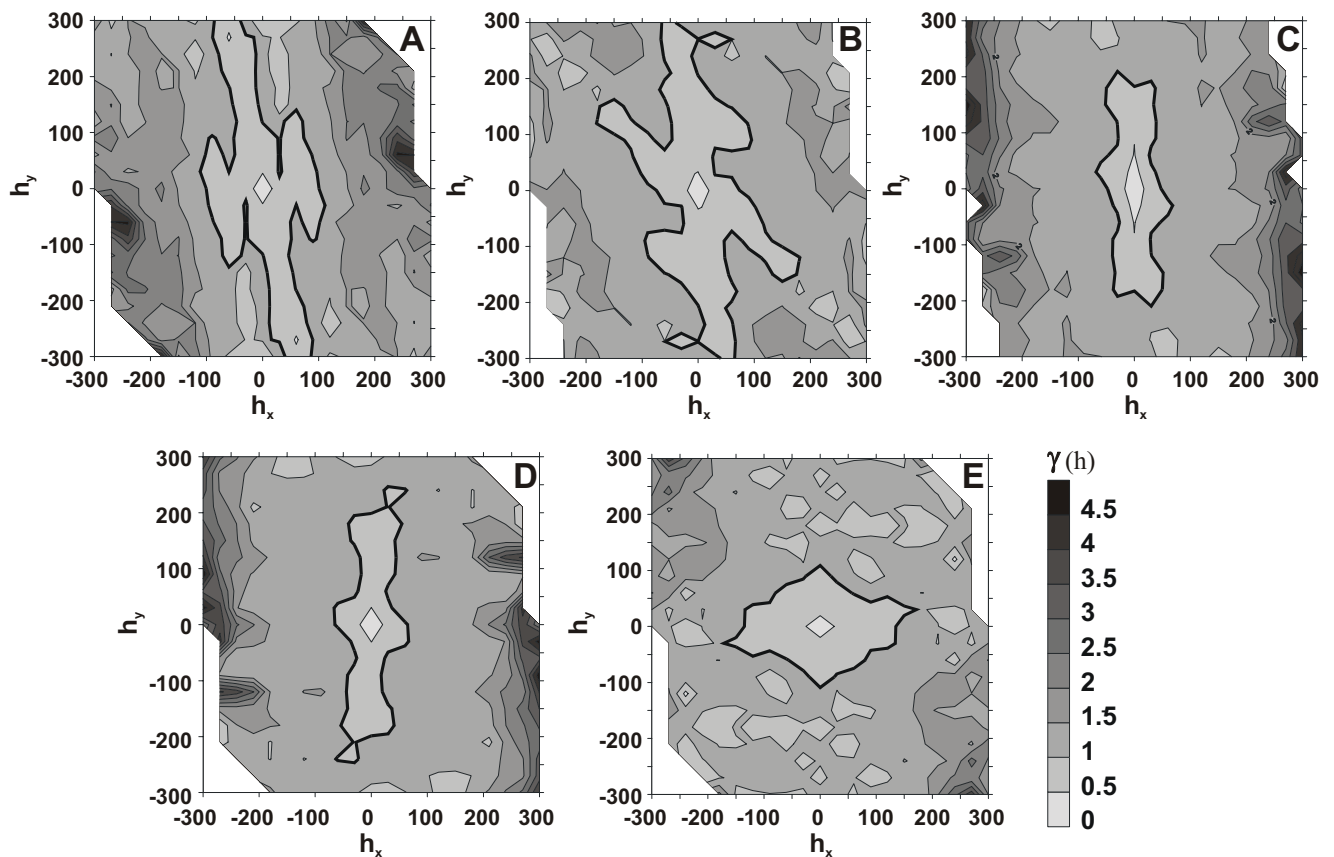|	PC 1	PC 2	PC 3
AAC-P	0.86	-0.03	-0.13
WH-P	0.82	0.18	0.38
AR-P	0.68	0.23	0.49
PH	0.62	0.41	0.14
$CaCl_2$-P	0.62	-0.62	-0.13
C_{tot}	0.36	0.08	0.80
clay	0.18	0.86	0.23
Fe	0.14	0.81	-0.13
$CACO_3$	0.11	0.14	0.54
P_{org}	-0.19	-0.13	0.69
Variance	36.10	18.59	14.24

Fig. 3:
Variogram maps for CaCl$_2$-P (A), AAC-P (B), WH-P (C), AR-P (D), P$_{org}$ (E) at Warberg, Grosser Born

explained by PC3. It is to note that AR-P also displayed a strong correlation with this group so that the latent variable of this group is thought to be the application of swine manure. The results of the PCA indicate that based on the chemical speciation the partitioning of the soil P reserves into functional P pools can be expected to result in different spatial distribution of these pools.

5 Variography

The variogram map is a two-dimensional plot of the experimental semi-variogram values in the system of coordinates (h$_x$, h$_y$). The centre of the map corresponds to the origin of the semi-variogram $\gamma(0) = 0$. Semivariogram values are low near the origin (0,0) and increase with the distance from the origin. When the variation is isotropic, the increase is fairly similar in every direction; hence the map shows concentric contour lines. Contrarily, geometric anisotropy appears in form of elliptical contour lines which major axis indicate the direction of maximum continuity (Gassner and Schnug, 2003). Geometrical anisotropy was found for AAC-P, AR-P and WH-P (Fig. 3)

AAC-P displayed a significant trend along the major slope line of the field, but after detrending the distribution was isotropic. For WH-P and AR-P the major and minor axes were the north-south (90 °) and east-west direction (0 °) of the field. The strong anisotropy was caused by three extreme values which where located within the headland on the western border of the field. Excluding these three data points, the distribution of both AR-P and WH-P was found to be omnidirectional. The spatial autocorrelation of CaCl$_2$-P and P$_{org}$ was found to be isotropic.

With the exception of the spatial distribution of CaCl$_2$-P, where a Gaussian model gave the best fit, a spherical model could be fitted to the experimental semi-variograms of all other P species (Table 3). The spatial distribution of the P species did not only differ with respect to their distribution pattern, but also in their spatial ranges and strength of the autocorrelation. The ranges of P fractions decreased in the order: CaCl$_2$-P > P$_{org}$ > AAC-P > WH-P > AR-P. For a under-fertilized loamy sand Gassner et al. (2002) reported a reversed pattern. This could indicate that over-fertilization has a strong impact on the spatial speciation of P. This is further confirmed by the large small-scale variation (nugget effect), which indicates that the interaction between applied P fertilizer and primary soil properties has not resulted yet in a strong spatial distribution pattern of P.

For the mineral P pools the range of the spatial autocorrelation of AR-P coincided with that of soil pH. It is well

Table 3:

Parameters for standardised semi-variogram models for P species and soil parameters at Warberg, Grosser Born

Parameter	Direction	Nugget (C_0)	C_1	Sill (C)	Sill/Nugget	Range a (m)
AR-P	Omni	0.55	0.48	1.03	53.3	85
WH-P	Omni	0.40	0.60	1.00	40.0	100
AAC-P	Omni	0.50	0.50	1.00	50.0	110
$CaCl_2$-P	Omni	0.70	0.34	1.04	67.3	160
P_{org}	Omni	0.55	0.46	1.01	54.5	135
clay	Omni	0.50	0.51	1.01	49.5	106
pH	Omni	0.33	0.62	0.95	34.7	73
$CaCO_3$	no spatial autocorrelation					
C_{tot}	no spatial autocorrelation					

known that in calcareous soils the precipitation of fertiliser P is controlled by Ca-minerals (Werner, 1969). This indicates that the factor governing the distribution of the sparingly available P pool is the distribution of Ca-phosphates.

As the Luvisol in Warberg can be described as severely over-fertilised, the reversibly available P pool represents P that has not been taken up by the crop during the growth season and also has not been converted to the sparingly available P pool. As the partitioning between the reversibly and the sparingly available P pool depends on the adsorption capacity of the soil it is suggested that the latter is the main factor governing the distribution of the reversibly available P pool. This assumption was confirmed as the spatial continuity of the reversibly available P pool (WH-P, AAC-P) was within the same range as the spatial distribution of the clay content. With a nugget variance of 0.7 the distribution of the readily available P pool ($CaCl_2$-P) can be described as almost random and could not be explained from the data set.

The low C:P_{org} indicates that active organic P mineralisation did not occur. Thus the spatial distribution of P_{org} is suggested to reflect distribution inaccuracies of the last manure amendment.

The loess derived soils of the Boerde landscape are some of the most homogeneous soils in Germany. Despite the low overall variance, expressed as the RSD for most of the P species (Table 1), the sill/nugget ratio which indicates the strength of the spatial autocorrelation was for all P species at least 40 %. Thus, on average 50 % of the observed variance occurred as small-scale variance within a distance that was smaller than the sampling interval of 30 m.

6 Conclusions

The geostatistical analysis revealed that different environmental factors resulted in the spatial speciation of P. It was possible not only to separate organic, readily, reversibly, and sparingly available P pools, but also based on the analysis of their spatial continuity to extract different environmental factors that resulted in the formation of these pools. Factors that could be allocated to control the distribution of individual P pools were: Ca-phosphate for the sparingly available, adsorption capacity of the soil for the reversibly available P pool and the distribution of manure for the organic P pool. Due to the high variance of the readily available P pool its distribution could not be modelled in a satisfying way. The random distribution of this pool is thought to reflect the strong influence of environmental factors (mineralisation, manure amendment, plant uptake) on this P fraction. The high small-scale variability of all P pools may be attributed to the high P status of the field. This high random component indicates that the interaction between applied P fertilizer and primary soil properties has not resulted yet in a strong spatial distribution pattern of P. Further exploitations of the concept of spatial speciation will take these factors into account. From the results of this study it is evident that geostatistical methods provide relevant information about the spatial variation of different P pools. Consequently, investigations of the biochemical cycling of P by means of soil tests should be evaluated in the context of site-specific soil characteristics. It is, therefore, concluded that an evaluation of the spatial speciation of a nutrient forms an essential part of an integrated soil management.

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