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SORPTION CAPACITY OF SANDY SOIL UNDER LONG-TERM FERTILISATION

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In this paper, the results of an investigation of the effects of particle-size distribution, soil organic matter content and its parameters on soil sorption capacity are presented and their mutual relationships in sandy soils under long-term fertilisation experiments are determined. Soil samples were taken at the experimental station of Warsaw University of Life Sciences located in Skierniewice, (Poland) in spring 2017. The study included 94- and 41-year-old experiments with mineral fertilisation (no fertilisation, NPK, CaNPK) and 25-year-old experiment with mineral fertilisation + farmyard manure (FYM) in 4-year cycle: FYM, FYM+NPK and FYM+CaNPK. The results show that in the 94-year-old experiment in NPK and CaNPK treatments, hydrolytic acidity (Ha) decreased in comparison with the control by 30% and 88%, respectively, while in 25- and 41-year-old experiments only the application of NPK significantly increased Ha values. The sum of basic cations increased by a factor of 10 at the most in the CaNPK treatment in the 94-year-old experiment. The same effect was also observed in the 25-year-old experiment. On the one hand, the sorption complex gradually became fully saturated as a result of fertilisation in the 94-year-old experiment. On the other hand, in the 25- and 41-year-old experiments, base saturation was substantially reduced. A higher humus stability was an important agent for improving soil sorption capacity in 41- and 94-year old experiments.

Key words: base saturation, cation exchange capacity, hydrolytic acidity, long-term fertilisation, sandy soil

Soil is a heterogeneous body consisting of inorganic and organic solid particles, air, water and living organisms. All aforementioned phases or components affect each other. Reactions of the solids affect air and water quality, air and water are key-factors of mineral substrate weathering, microorganisms catalyze numerous reactions and control biogeochemical cycling of elements and various substances, influencing soil quality and productivity. Humankind is dependent on soils – and to a certain extent good soils are dependent upon man and the use he makes of them (Foth 1990).

Soil sorption capacity is considered as one of the most significant factors affecting soil fertility. The term soil sorption capacity expresses its potential to sequester – or sorb – ions or molecules of different substances from the soil solution. This very important soil feature is associated with the soil colloidal complex that includes mineral and organic components. Thanks to this soil property, plant root system is supported by a supply of biogenic elements from the soil; meaning that farmers do not need to add these elements on a daily basis (Foth 1990; Lorandi 2012; Šimanský & Polláková 2014; Šimanský *et al.* 2018). Soil organic matter, especially the decomposed and humified variety, together with soil clay content significantly influence soil sorption capacity (Foth 1990, Manjaiah *et al.* 2019). In addition,

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the cation exchange capacity (CEC) is one of the most important parameters of soil sorption capacity and rages in sandy, loamy, clay and organic soils between 20 − 100, 200 − 300, 400 − 500 and more than 1,500 mmol (p^+)/kg of soil, respectively (Hanes 1999).

In arable soils, the soil sorption capacity can be altered by different soil management practices (Lorandi 2012; Šimanský & Polláková 2014). Fertilisers are an important factor of crop production, offer intensifying modern agriculture. In addition to the positive effects on crop yields, they also affect soil properties (Banerjee *et al.* 2019). Fertilisation improves crop supporting properties of sandy soils in particular, due to their coarse texture, high permeability and low water and nutrient storage capacity. In addition to the increase in yields, the use of fertilisers in the soil can increase the biomass of plants and roots, eventually resulting in SOM increase (Tian *et al.* 2015). Murawska *et al.* (2017) have shown that after 36 years of fertilising the sandy soil by NPK without or with farmyard manure, the content of SOM increased, and at the same time the quality of humus improved in this soil. Higher content of SOM and humus quality are considered to be major factors influencing soil sorption complex.

In this work, the effects of long-term fertilisation on changes in soil sorption capacity are focused. The objectives of this study are (i) to quantify the effects of long-term fertilisation on the soil sorption parameters of sandy soils and (ii) to identify feedbacks between soil sorption parameters and soil organic matter and particle-size distribution in long-term experiments with fertilisers and manure application. The following hypotheses were tested: (H1) application of mineral fertilisers and farmyard manure improves soil sorption capacity, mainly by increasing the SOM content, and (H2) the length of fertilisation significantly affects the relationship between soil sorption parameters, and SOM or soil clay content.

MATERIAL AND METHODS

The experimental field plot was located in Skierniewice (experimental station of Warsaw University of Life Sciences – SGGW; 51°57'54.3"N 20°09'31.8"E). The annual average temperature and precipitation are 8°C and 530 mm respectively, measured at a meteorological station in Skierniewice. The soil was classified as Arenic Planosol (IUSS Working Group WBR 2015). The soil were characterized by loamy sand or sandy loam texture in A-horizons and contained 76.0 − 88.2% of sand, 7.1 − 16.7% silt and 4.0 − 7.7% clay. The soils were relatively poor in organic carbon and their pH varied from strongly acidic to slightly acidic, depending on experiment option.

Prior to the experiment, the soil at the experimental site were cultivated using conventional agriculture techniques adequate of actual period. The oldest experiment was established in 1923 (94-year-old experiment), the second experiment in 1975 (41-year-old experiment) and the third in 1992 (25-year-old experiment). The experimental design is shown in Figure 1. In all experiments, each treatment had three replications. The investigated fertilisation treatments and planted crops are presented in Table 1. The study was carried out on 27 plots of 36 m^2 (4 m × 9 m) each. The spacing between the neighbouring replications was 2 m. In all long-term experiments, nitrogen was applied as ammonium sulphate (30 kg/ha of N every year from 1921 to 1976 and 90 kg/ha of N from 1976), phosphorus as superphosphate (every year at rate of 30 kg/ha of P_2O_5 from 1921 to 1976 and 26 kg/ha of P_2O_5 from 1976) and potassium as potassium chloride (30 kg/ha of K_2O every year from 1921 to 1976 and 91 kg/ha of K_2O from 1975). Calcium was introduced as 1.6 t/ha of CaO every 4 years. In 25-year-old experiment the used doses of farmyard manure at the plots were 25 t/ha every 4 years beginning from 1992.

The soils were sampled at a depth of 0 − 20 cm in autumn 2017. Three randomly distributed soil sub-samples per each plot were collected and mixed into one average sample. Soil samples were then air-dried, crushed and sieved (2 mm) for analyses. Standard procedures of soil analyses were used to determine soil characteristics. Particle-size distribution was analysed by the pipette method described by Hrivňaková *et al.* (2011). Soil pH was measured potentiometrically in distilled water (at ratio 1:2.5, soil: distilled water). Soil organic carbon content (SOC) was estimated by the Tyurin wet oxidation method (Dziadowiec & Gonet 1999). Fractional composition of humus was analysed using the Tyurin method as modified by Ponomareva and Plotnikova (Dziadowiec & Gonet 1999). Optical characteristics of humus quality were assessed as absorbance of humic substances and humic acids measured at wavelength of 465 and 650 nm using a Jenway Model 6400 spectrophotometer. Labile carbon content (C_L) was determined according to Łoginow *et al.* (1987). Soil sorption parameters such as: hydrolytic acidity (Ha) and sum of basic cations (SBC) were determined by the Kappen method (Hrivňáková *et al.* 2011) and based on values of Ha and SBC cation exchange capacity (CEC), and base saturation (Bs) were calculated according to Equations 1 – 2.

T a b l e 1

Experiment design

Experiment name	FYM	Mineral fertilisation	Crop rotation
94-year-old experiment with mineral fertilisation	No	No	Cereals from 1923
	No	NPK	
	No	CaNPK	
41-year-old experiment with mineral fertilisation	No	No	Cereals from 1923 to 1975, blueberry from 1976, no tillage from 1976
	No	NPK	
	No	CaNPK	
25-year-old experiment with mineral fertilisation + FYM in 4-year cycle	Yes	No	Cereals from 1923, farmyard manure from 1992
	Yes	NPK	
	Yes	CaNPK	

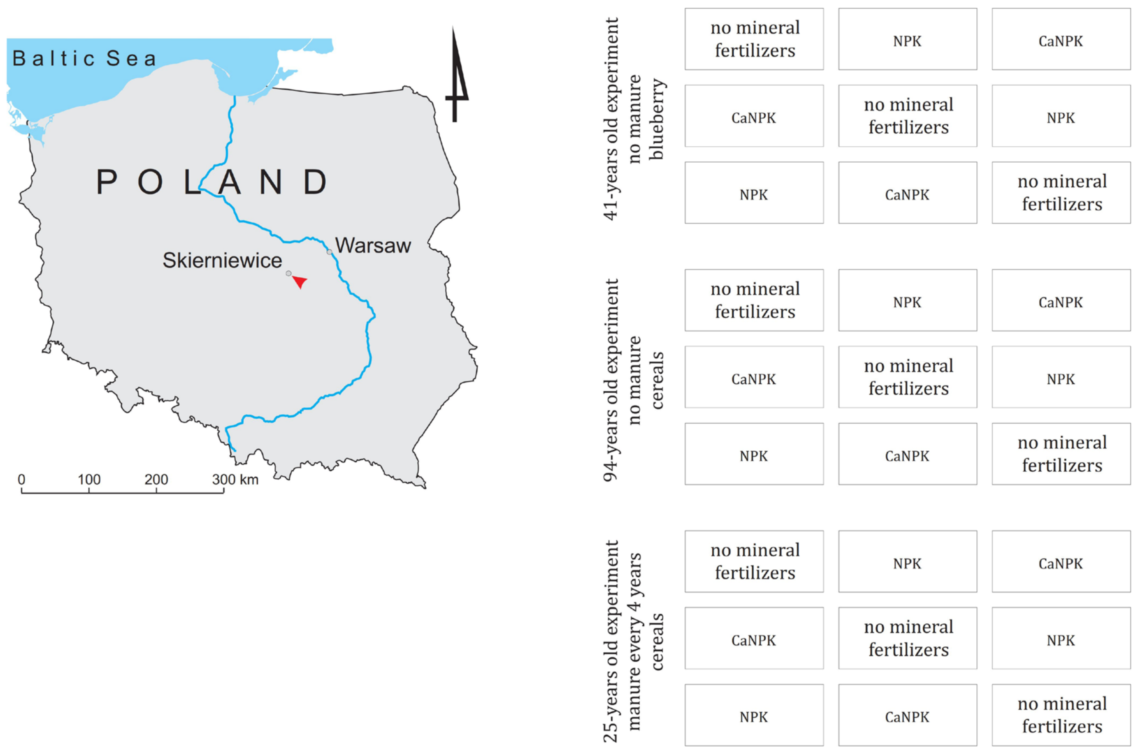

Figure 1. Study site location and schematic layout of the experimental field

$$CEC = Ha + SBC \quad (1)$$
$$Bs = SBC/CEC \times 100 \quad (2)$$

All data was analysed using the Statgraphics Centurion XV.I programme (Statpoint Technologies, Inc., USA). The data was analysed using one-way ANOVA and the means were compared with *LSD* test at $P < 0.05$. The link between the sorption parameters and SOM and particle-size distribution were assessed using a correlation matrix.

RESULTS AND DISCUSSION

Each experiment has been analysed separately and all experiments were based on the same soil type (Arenic Planosol) with comparable textures (clay content ranged from 4.40% to 5.77% in fertilisation experiments). We also compared soil parameters describing experiments of different duration. Fertilisation can affect soil properties in different ways as shown in our results (Figure 2). We found significant influence on soil pH in all long-term experiments, but the strength of the effect was modified by the duration of the experiment. Compared with the control plot, the NPK ($P > 0.05$) and CaNPK ($P < 0.05$) treatments increased soil pH by 25% and 86%, respectively in 94-year-old experiment, whereas in 41- and 25-year-old experiments the NPK treatment had only shown a significant decrease in the soil pH, which decreased by 24% and 16%, respectively. The pH was associated with SOC. Between SOC and soil pH exist negative linear relationship – the higher SOC content is the reason for a lower soil pH (Jagadamma *et al.* 2008). As Nardi *et al.* (2004) presented, soil acidification can be related to the SOM mineralisation process, which produces nutrients (in particular NH_3), whose oxidation may contribute to H^+ production (Tan 1998). This reaction may also be affected by mineral fertilisers, especially NH^+_4 sources (Havlin *et al.* 1999), an effect apparent also in our study (N applied as ammonium sulphate). In addition, application of CaO every 4 years significantly reduced soil acidification in all long-term experiments. Positive effect of liming on soil pH have been described previously by many authors (e.g. Merha *et al.* 2019). Soil pH negatively correlated with values of hydrolytic acidity (Ha) in all treatments and all long-term experiments. Higher values of soil pH resulted in

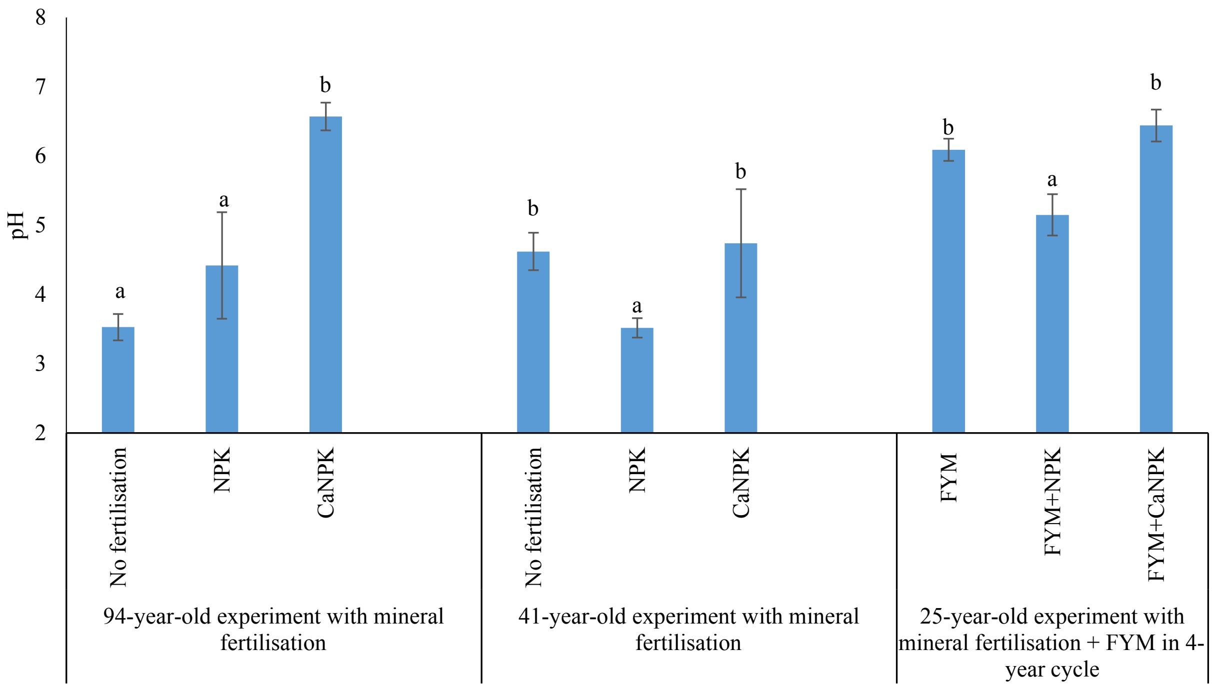

Figure 2. Effect of fertilisation on soil pH in long-term experiments

Different letters (a, b) between columns indicate that treatment means are significantly different at $P < 0.05$ according to *LSD* test.

lower Ha (in 94-year-old: $r = -0.986$, $P < 0.001$; in 41-year-old: $r = -0.887$, $P < 0.01$; in 25-year-old: $r = -0.896$, $P < 0.01$). Values of Ha were affected by long-term experiments. In 94-year-old experiment added NPK (NPK) and Ca in NPK treatment (CaNPK) decreased Ha by 30% and 88%, respectively compared with control treatment, while in 25- and 41-year-old experiment only application of NPK significantly increased Ha values. If all experiments were compared, the lowest values of Ha in control treatments were observed in 25-year-old experiment. Probably applied FYM every 4-year in this experiment is responsible for better values of Ha in comparison to other both experiments. Applied FYM to the soil can affect buffering capacity of soil (Hanes 1999).

In sandy soils, even a small increase in fine-grain fraction or SOM can significantly affect sorption capacity. Our results show that ninety-four years of continuous inputs of mineral fertilisers (NPK) increased the SOC content, while the application of CaNPK caused the SOC content to increase from 4.07 to 5.99 g/kg. The same effect was observed in the shorter experiments – in 41- and 25-years-old (Figure 3). More detailed results with respect to SOM parameters and humus quality in these experiments are presented in Šimanský *et al.* (2019). Up to 10 times, sum of basic cations (SBC) increased in CaNPK treatment at 94-year-old experiment. The same effect was observed in 25-year-old experiment, but on the other hand in 41-year-old experiment any significant effect on SBC values due to fertilisation was determined. This means that the SBC values were affected in all except the long-term fertilisation also by a combination of mineral and organic fertilisation. CEC increased significantly in the 94- and 25-year experiments due to the addition of Ca to NPK treatment, while in the 41-year experiment it has been significantly increased only in NPK. In this case it is associated with the extreme increase Ha (in this treatment). The results of Reeves (1997) also showed that the CEC increased after fertilisation with organic fertilisers and NPK fertiliser. The sorption complex gradually fully saturated as a result of fertilisation in the 94-year-old experiment, on the other hand, in 25- and 41-year-old experiments the base saturation substantially reduced (Table 2).

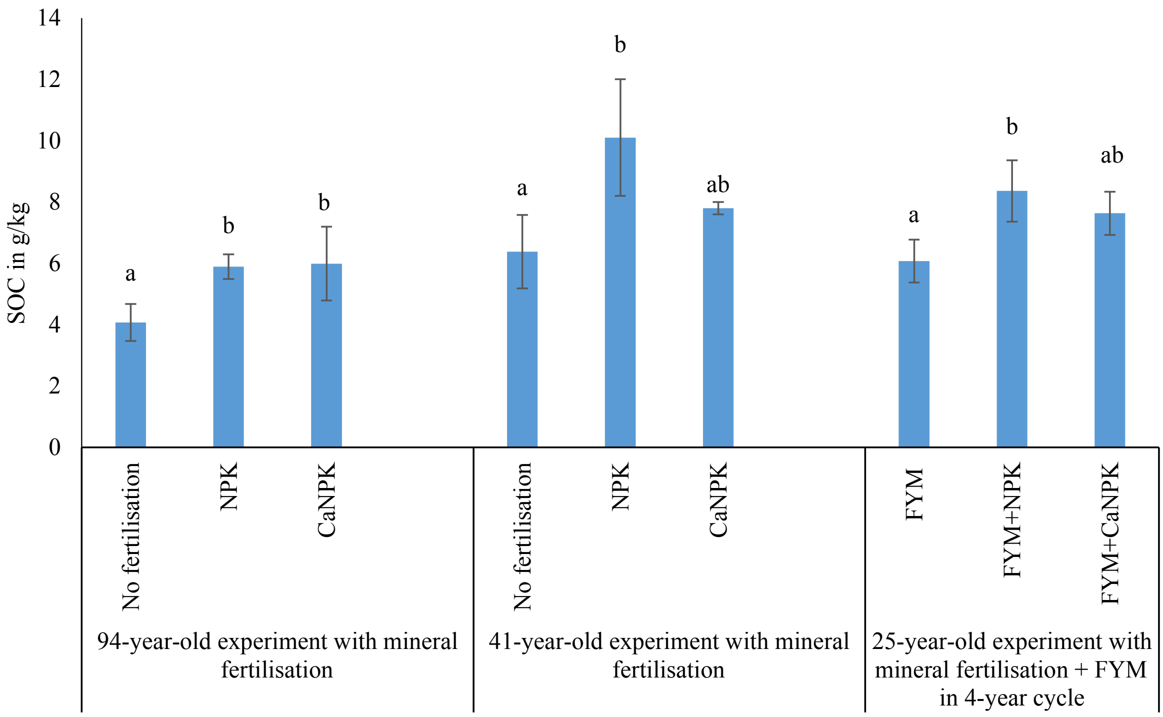

Figure 3. Effect of fertilisation on SOC in long-term experiments

Different letters (a, b) between columns indicate that treatment means are significantly different at $P < 0.05$ according to *LSD* test.

Correlation coefficients between sorption parameters, particle-size distribution and SOM parameters are shown in the Table 3. It is likely that the fertilisation period might be responsible for stronger correlation between the soil sorption parameters and SOM as well as clay content, however, our data cannot confirm this conclusively. The highest number of relationships was determined in the 41-year-old experiment, followed by the 94- > 25-year-old experiment. In the 94-year-old experiment, only Bs values positively correlated with C_L on the one hand, and negative with HS, HA, Q_{HS} and Q_{HA} on the other. This indicates that the labile fraction of SOM, but also humus stability, are responsible for observed saturation of the sorption complex. Overall, all sorption parameters were positively affected through higher stability of humic substances. Humus stability has positive effects on soil properties (Stevenson 1994; Lorandi 2012). In the 41-year-old experiment, higher sand content decreased Ha and CEC, but higher silt and SOC content increased the values of Ha and CEC. Grain size, together with SOM, are the key factors of soil sorption capacity (Stevenson 1994; Šimanský & Polláková 2014). A higher content of HS resulted in a decrease of Ha and an increase of SBC. Higher humus quality in the soil caused higher decreases in the hydrolytic acidity and improves sorption parameters at the same time. In addition, soil sorption complex was fully saturated due to better humus quality. The lower the values of colour quotient of humic substances and humic acids, the more improved soil sorption parameters in the 41-year-old experiment. These results support the fact that the application of mineral fertilisers can increase SOM quality (Fröberg *et al.* 2013). SOM quality is associated with higher soil sorption capacity (Foth 1990; Šimanský & Polláková 2014). In the shortest experiment, the sand content negatively correlated with SBC and CEC, however the silt content positively correlated with values of SBC and CEC. Clay content did not show statistically significant effects on sorption parameters (Table 3), which was surprising based on literature data (e.g. Ding *et al.* 2014). Negative effects of higher con-

T a b l e 2

Statistical evaluation of soil sorptive parameters

Treatments	Ha	SBC	CEC	Bs
94-year-old experiment with mineral fertilisation				
No fertilisation	27.40 ± 0.52[b]	7.31 ± 1.51[a]	34.7 ± 1.48[a]	20.9 ± 3.47[a]
NPK	19.10 ± 7.85[b]	20.50 ± 7.56[a]	39.6 ± 2.41[a]	51.9 ± 18.6[b]
CaNPK	3.15 ± 1.11[a]	77.60 ± 19.10[b]	80.8 ± 18.5[b]	95.9 ± 2.15[c]
P-value	*0.0018*	*0.0008*	*0.0037*	*0.0005*
41-year-old experiment with mineral fertilisation				
No fertilisation	20.2 ± 2.65[a]	25.5 ± 4.00[a]	45.7 ± 1.90[a]	55.6 ± 6.94[b]
NPK	66.5 ± 5.26[b]	11.3 ± 4.47[a]	76.8 ± 6.73[b]	14.4 ± 4.98[a]
CaNPK	34.9 ± 15.95[a]	22.2 ± 12.5[a]	57.0 ± 7.46[a]	39.8 ± 25.5[ab]
P-value	*0.0032*	*0.1535*	*0.0019*	*0.0459*
25-year-old experiment with mineral fertilisation + FYM in 4-year cycle				
FYM	6.18 ± 1.53[a]	31.7 ± 4.54[a]	37.9 ± 3.56[a]	83.5 ± 5.00[b]
FYM+NPK	25.4 ± 4.20[b]	18.2 ± 5.80[a]	43.6 ± 3.65[a]	41.4 ± 10.9[a]
FYM+CaNPK	10.4 ± 2.38[a]	73.6 ± 19.5[b]	84.0 ± 17.7[b]	86.9 ± 5.62[b]
P-value	*0.0005*	*0.0032*	*0.0034*	*0.0006*

Ha – hydrolytic acidity; SBC – sum of basic cations; CEC – cation exchange capacity; Bs – base saturation Different letters (a, b, c) between lines indicate that treatment means are significantly different at $P < 0.05$ according to *LSD* test tents of extracted humic substances mainly fulvic acids indicate the correlations between HS and Ha (r = 0.776, P < 0.01) also between FA and Ha (r = 0.808, P < 0.01) and between HS and Bs (r = –0.752, P < 0.01) as well as between FA and Bs (r = –0.690, P < 0.05). In the soil, fulvic acids are more aggressive and it had a higher mobility in the soil in comparison to humic acids (Tate 1987; Stevenson 1994). Organic matter after FYM application is decomposed – except mineralization through humification process. In soils with low biological activity such as sandy soils, FA are accumulated as a result of the humification process (Tate 1987), with negative effects on the sorption parameters (Table 3). Low humus quality due to long-term application of mineral fertilisation but as well as its combination with FYM in these experiments was also observed (Šimanský *et al.* 2019).

CONCLUSIONS

The results of this study showed that higher humus stability is the important agent for improving soil sorption capacity in the 41- and 94-year old experiments. In the 25-year-old experiment, this relationship was not observed. The strongest relationships between grain size distribution, SOM parameters and sorption parameters were determined in the 41-year-old

T a b l e 3

Correlation coefficients between particle-size distribution, SOM and humus parameters and soil sorption parameters with depend on fertilisation

	Clay	Sand	Silt	SOC	C_L	C_{HS}	C_{HA}	C_{FA}	C_{HA}:C_{FA}	Q_{HS}	Q_{HA}
94-year-old experiment with mineral fertilisation											
pH	n.s.	n.s.	n.s.	n.s.	n.s.	–0.774^{+}	–0.666^{+}	n.s.	n.s.	–0.772^{+}	–0.737^{+}
Ha	n.s.	n.s.	n.s.	n.s.	n.s.	0.734^{+}	n.s.	n.s.	n.s.	0.701^{+}	0.744^{+}
SBC	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	–0.827^{++}	n.s.
CEC	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	–0.844^{++}	n.s.
Bs	n.s.	n.s.	n.s.	n.s.	0.692^{+}	–0.778^{+}	–0.693^{+}	n.s.	n.s.	–0.683^{+}	–0.707^{+}
41-year-old experiment with mineral fertilisation											
pH	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.727^{+}	–0.734^{+}	n.s.
Ha	n.s.	–0.674^{+}	0.799^{++}	0.811^{++}	n.s.	n.s.	–0.733^{+}	n.s.	–0.895^{++}	0.865^{++}	0.838^{++}
SBC	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.735^{+}	n.s.	0.819^{++}	–0.713^{+}	n.s.
CEC	n.s.	–0.841^{++}	0.919^{+++}	0.825^{++}	n.s.	n.s.	n.s.	n.s.	0.807^{++}	–0.825^{++}	–0.889^{++}
Bs	n.s.	n.s.	n.s.	–0.687^{+}	n.s.	n.s.	0.728^{+}	n.s.	0.903^{+++}	–0.773^{+}	–0.714^{+}
25-year-old experiment with mineral fertilisation + FYM in 4-year cycle											
pH	n.s.	n.s.	n.s.	n.s.	n.s.	–0.686^{+}	n.s.	n.s.	n.s.	n.s.	n.s.
Ha	n.s.	n.s.	n.s.	n.s.	n.s.	0.776^{++}	n.s.	0.808^{++}	n.s.	n.s.	n.s.
SBC	n.s.	–0.839^{++}	0.830^{++}	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
CEC	n.s.	–0.891^{++}	0.891^{++}	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
Bs	n.s.	n.s.	n.s.	n.s.	n.s.	–0.752^{++}	n.s.	–0.690^{+}	n.s.	n.s.	n.s.

SOC – soil organic carbon; C_L – labile carbon; C_{HS} – content of humic substances carbon; C_{HA} – content of humic acids carbon; C_{FA} – content of fulvic acids carbon; C_{HA}:C_{FA} – humic acids carbon to fulvic acids carbon ratio; Q_{HS} – colour quotient of humic substances; Q_{HA} – colour quotient of humic acids; Ha – hydrolytic acidity; SBC – sum of basic cations; CEC – cation exchange capacity; Bs – base saturation.
n.s. $P > 0.05$; $^{+}P < 0.05$; $^{++}P < 0.01$; $^{+++}P < 0.001$

experiment, followed by the 94- > 25-year-old experiment.

This research provides information for farmers on optimizing soil management practices in sandy soils and on improving soil ecological functions and stability to avoid environmental degradation due to application of mineral fertilisers to the soil. The results of this study emphasize the importance of organic matter quantity and quality in relation to sorption capacity, especially in sandy soils under long-term mineral fertilisation.

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