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Petr ŠKARPA[1]

MONITORING THE CHANGES IN TOTAL CONTENTS OF MANGANESE, COPPER AND ZINC IN SOILS FROM LONG-TERM STATIONARY EXPERIMENTS

MONITORING ZMIAN CAŁKOWITYCH ZAWARTOŚCI MANGANU, MIEDZI I CYNKU W GLEBACH PODDAWANYCH DŁUGOTERMINOWYM DOŚWIADCZENIOM ROLNICZYM

Abstract: The objective of the long-term stationary experiment was to discover the effect of the year, production region, soil kind and soil type on total contents of micronutrients (Mn, Cu and Zn) in the soils. In the years 1982 to 1998 the soil was sampled in 7 selected localities. Analyses and extractions determining the total content of metals were carried out by means of mineralization in the HF – H_2O_2 – HNO_3 open system. The AAS method was used to determine the contents of the micronutrients. The content of manganese ranged between 296.2 and 978.6; copper between 6.1 and 25.7 and zinc between 29.5 and 99.8 mg · kg^{-1} of soil. During the experimental period 1982–1998 the total content of Mn and Zn decreased (by 7.9 % and 3.6 %, respectively), but was not statistically significant ($p < 0.05$). During the 15 years of the experiment the total amount of copper in the soil increased by 7.0 %. In comparison with the potato growing region the contents of all the micronutrients in the sugar-beet growing region were higher. The highest and statistically highly significant difference ($p < 0.001$) was that of copper (45.6 % increase). In terms of the soil kind the lowest contents of Mn and Cu were monitored on light soil. The total content of zinc on light soil and medium-heavy soil was comparable. With an increasing proportion of clay particles in the soil the contents of the micronutrients increased significantly ($p < 0.001$). In comparison with light soil, in heavy soil the contents of the metals increased; Mn by 38.9; Cu by 48.2 and Zn by 19.4 %. The levels of Cu and Zn were also affected by the soil type. The contents of these micronutrients were statistically ($p < 0.001$) the highest in chernozem (24.6 and 71.1 mg · kg^{-1} of soil, respectively). The content of Mn was the highest in brown soil (714.3 mg · kg^{-1} of soil). Graded rates of fertilisers did not have a significant ($p < 0.05$) effect on the total contents of metals. The differences were more marked in the treatment where liming was not carried out; here we monitored the greatest decrease in the contents of Mn, Cu and Zn, ie by 7.3, 23.8 and 9.4 %, respectively, compared with the control.

Keywords: long-term experiment, total zinc, total manganese, total copper

Soil is characterised as the most complicated, most dynamic and most reactive component on Earth [1]. Soil is a key part of the environment and irreplaceable source

[1] Department of Agrochemistry, Pedology, Microbiology and Plant Nutrition, Mendel University in Brno, Zemědělská 1, 613 00 Brno, Czech Republic, phone: + 420 545 133 345, email: petr.skarpa@mendelu.cz

of most of the bio-chemically active micronutrients influencing human beings through plants and animals. Important biogenic microelements are manganese, copper and zinc [2, 3]. Their total levels in the soil are based particularly on the mineral composition of the soil, soil type, content of clay particles (soil kind), content of organic matter in the soil, soil reaction etc [4–7]. The content of micronutrients in the soil is considerably affected by anthropogenic activities. An important source of micronutrients which increases their levels in the soil are indisputably fertilisers (particularly nitrogenous and phosphorus), calcareous matter, farmyard manure, slurry, pesticides and others [4, 8, 9].

The aim of this study was to evaluate changes in total content of manganese, copper and zinc in soil in long-term experiment.

Material and methods

The experiment was established in 7 localities of potato growing regions (altitude 400–650 m a.s.l., annual average temperature 5–8 ^{o}C, annual average precipitation 550–900 mm, predominate cambisols) and sugar-beet growing regions (altitude 250–350 m a.s.l., annual average temperature 8–9 ^{o}C, annual average precipitation 500–650 mm, predominate chernozems and haplic luvisols) as a long-term small-plot stationary trial by the Central Institute for Supervising and Testing in Agriculture between 1982 and 1998. Table 1 gives the characteristics of the localities.

Table 1

The characteristic of localities

Locality	Growing regions	Altitude m a.s.l.	Annual average		Reference soil groups	Soil textural class
			temperature [^{o}C]	precipitation [mm]		
Horazdovice	potato	470	7.4	573	Cambisols	sandy
Svitavy	potato	460	6.5	624	Cambisols	sandy
Chrastava	potato	345	7.1	798	Luvisols	loamy
Stankov	potato	370	8.3	443	Luvisols	clay
Puste Jakartice	sug.-beet	295	8.0	640	Luvisols	loamy
Uhersky Ostroh	sug.-beet	196	9.2	551	Luvisols	loamy
Zatec	sug.-beet	247	8.3	451	Chernozems	clay

Soil type (FAO soil taxonomy), soil textural class [10].

The experiment comprised 6 combinations of fertilization, in 4 replications. Table 2 shows the average contents of N, P and K, which were applied in organic fertilizers (farm manure) and mineral fertilizers at three levels (low – $N_1P_1K_1$, medium – $N_2P_2K_2$, high – $N_3P_3K_3$). Organic fertilizers were applied once every 4 years; 40 Mg ha^{-1} of farm manure was incorporated in the sugar-beet growing region to maize for silage and to sugar-beet and in the potato growing region to potatoes.

Table 2

Treatments of the experiment

Treatments of fertilization	Average content of nutrients in fertilizers [kg · ha^{-1} · year^{-1}]					
	Nitrogen		Nitrogen		Nitrogen	
	PGR[a]	SGR[b]	PGR	SGR	PGR	SGR
No fertilized	0	0	0	0	0	0
Farm. manure	25	25	8	8	35	35
Farm. manure + $N_1P_1K_1$	83	83	31	29	92	86
Farm. manure + $N_2P_2K_2$	113	112	43	41	125	116
Farm. manure + $N_3P_3K_3$	142	140	59	57	166	154
Farm. manure + $N_3P_3K_3$ without liming	142	140	59	57	166	154

[a] PGR – potato growing regions; [b] SGR – sugar-beet growing regions.

Soil was sampled in the localities in autumn 1982 and 1998. Soil samples were taken from 0–30 cm depth. Samples were dried naturely. The total content micronutrients (manganese, copper and zinc) of the soil in its dry state was estimated by the method of Houba et al [11] with the soil extracted in the mixture of HF – H_2O_2 – HNO_3 and measured by atomic absorption spectrometry (AAS) on the ContrAA 700 spectrometer (Analytic Jena).

The results of chemical soil analyses were computer-processed and set up using the Microsoft Excel editor. The Statistica 7.1 programme was used for the determination of the overall characteristics. Arithmetic means were calculated when evaluating the results. To elaborate the significance of differences among the arithmetic means of each characteristic we used the mono-factor and two-factor analysis of variance followed by testing at a 95% ($p < 0.05$) level of significance using Tukey test.

Results and discussion

Manganese. Manganese is the tenth-most abundant element on the surface of the earth [2]. Its natural content in soils of the Czech Republic ranges between 80 and 2220 mg · kg^{-1} of soil [12]. Bohn et al [13] reported that the average amount of total Mn ranges between 850 and 1000 mg · kg^{-1}. In our experiment the content of manganese ranged between 296.2 and 978.6 mg · kg^{-1}. During the experiment the total content of Mn decreased by 7.9 %, but this decrease was not statistically significant [$F (1; 164) = 3.312$; $p = 0.071$] (Table 3). The reason of the statistically insignificant effect of the production region on the Mn content in the soil [$F (1; 164) = 3.646$; $p = 0.058$] were significant differences in the Mn content among the individual localities. Nonetheless its average value in the sugar-beet growing region was by 9.1 % higher than in the potato-growing region (Table 4). Only the factor of the soil kind was statistically significant [$F (2; 163) = 26.536$; $p < 0.001$]. A significant difference was discovered between light soil and the medium-heavy and heavy soils (Table 5). Katyal a Sharma

[14], Trebichavsky et al [12], Raji et al [15], Rinaudo [16] reported that due to the content of clay particles the total content of Mn increased. In terms of the soil type the highest statistically significant content of Mn was detected in brown soil [F (2; 163) = 52.607; p < 0.001]. We compared the soils and discovered that the content of manganese was the lowest in cambisols; in chernozem it was by 11 % higher (Table 6). Wang et al [17] reported the highest content of Mn in chernozem. The total amounts of manganese in the soil after the respective fertiliser treatments did not significantly differ [F (5; 160) = 0.165; p = 0.975]. Podkolzin et al [18] presented similar conclusions. By contrast Kurakov et al [19] reported that the Mn content increased due to long-term application of fertilisers. Table 7 shows that the content of Mn was the highest in the treatment with no fertilisers (treatment 1) and the lowest where the highest amount of mineral fertilisers was applied without liming (treatment 6).

Copper. The total content of copper in non-contaminated soils ranges between 2 and 200 mg · kg^{-1} of soil [6, 13]. The average contents are quoted to range between 10 and 50 mg · kg^{-1} of soil [4, 20, 21]; in the Czech Republic the average Cu content is 26 mg · kg^{-1} of soil [12]. In our experiment the amount of Cu ranged between 6.1 and 25.7 mg · kg^{-1} of soil, an equivalent to the lower half of its natural content reported by these authors. As Table 3 shows during the experiment the content of copper increased by 7 %, but not statistically significantly [F (1; 164) = 1.412; p = 0.236]. However, the influence of the production region on the copper content was statistically significant [F (1; 164) = 56.401; p < 0.001]**.** In the sugar-beet region the content of copper was by 45.6 % higher than in the potato-growing region (Table 4). According to Trebichavsky et al [12], Kabata-Pendias, Pendias [4] and Yu et al [22] the soil kind also significantly affects the content of copper in the soil and confirms that the level copper in the soil increases due to the increasing amount of clay particles [F (2; 163) = 23.576; p < 0.001]. While the copper content on medium-heavy soil was by 7.3 % higher, the significantly highest content was monitored on heavy soil (Table 5). Likewise Wang et al (2003) reported a positive correlation between the copper content and clay particles. Another factor affecting the copper content was the soil type. The statistically significantly highest level of copper was detected in chernozem [F (2; 163) = 60.237; p < 0.001]. In brown soil and cambisol the content was lower by 39.8 and 44.3 %, respectively (Table 6). Barker and Pilbeam [2] also reported that the level of copper was the highest in chernozem soils. Graded rates of fertilizers had no statistically significant effect on the total amount of soil copper [F (5; 160) = 1.052; p = 0.389] (Table 7). Erhart et al [23] arrived at the same conclusions. In the experiment its amount gradually decreased with increasing rates of nutrients contained in the applied organic and mineral fertilisers. Much like Mn, also the copper content was the lowest in treatment 6.

Zinc. Trebichavsky et al [12] reported that the average total content of zinc in agricultural soils of the Czech Republic ranges between 10 and 244 mg · kg^{-1} of soil (82 mg · kg^{-1}) and that the worldwide average ranges between 50 and 60 mg · kg^{-1} [13]. The total content of zinc in our experiment ranged between 29.5 and 99.8 mg · kg^{-1} of soil. Much like manganese the average zinc content decreased during the experiment (Table 3), however not statistically significantly [F (1; 164) = 0.874; p = 0.351]. When compared with the other monitored micronutrients the effect of the production region on the zinc content was the same as on Mn (Table 4). The zinc supply was higher in the sugar-beet growing region (by 5.1 %) [F (1; 164) = 1.696; p = 0.195]. In our experiment the contents of zinc on light soil and on medium-heavy soil were comparable. The level of zinc on heavy soil (Table 5) significantly differed from the above soil kinds [F (2; 163) = 11.369; p < 0.001]. Moreno et al [24], Kparmwang et al [25], Valladares et al [26] and Menezes et al [27] also discovered that the effect of clay on the content of soil zinc was significant. The effect of the soil type was similar as in the case of copper

Table 3

Total contents of microelements in soil [mg · kg^{-1} d.m. soil] – Factor: year

Year	Mn	Cu	Zn
1982	636.6 a	15.7 a	61.4 a
rel. %	*100.0*	*100.0*	*100.0*
1998	586.0 a	16.8 a	59.2 a
rel. %	*92.1*	*107.0*	*96.4*

p < 0.05 – statistical significance at a 95% level of significance. Variants with identical letters express statistically insignificant differences.

Table 4

Total contents of microelements in soil [mg · kg^{-1} d.m. soil] – Factor: growing regions

Growing regions	Mn	Cu	Zn
Potato growing regions	587.2 a	13.6 a	59.0 a
rel. %	*100.0*	*100.0*	*100.0*
Sugar-beet growing regions	640.8 a	19.8 b	62.0 a
rel. %	*109.1*	*145.6*	*105.1*

p < 0.05 – statistical significance at a 95% level of significance. Variants with identical letters express statistically insignificant differences.

Table 5

Total contents of microelements in soil [mg · kg^{-1} d.m. soil] – Factor: soil textural class

Soil textural class	Mn	Cu	Zn
Sandy soil	471.0 a	13.7 a	56.7 a
rel. %	*100.0*	*100.0*	*100.0*
Loamy soil	676.2 b	14.7 a	56.6 a
rel. %	*143.6*	*107.3*	*99.8*
Clay soil	654.3 b	20.3 b	67.7 b
rel. %	*138.9*	*148.2*	*119.4*

p < 0.05 – statistical significance at a 95% level of significance. Variants with identical letters express statistically insignificant differences.

Table 6

Total contents of microelements in soil [mg · kg^{-1} d.m. soil] – Factor: reference soil groups

Reference soil groups	Mn	Cu	Zn
Cambisols	471.0 a	13.7 a	56.7 a
rel. %	*100.0*	*100.0*	*100.0*
Luvisols	714.3 b	14.8 a	58.5 a
rel. %	*151.7*	*108.0*	*103.2*
Chernozems	525.3 a	24.6 b	71.1 b
rel. %	*111.5*	*179.6*	*125.4*

$p < 0.05$ – statistical significance at a 95% level of significance. Variants with identical letters express statistically insignificant differences.

Table 7

Total contents of microelements in soil [mg · kg^{-1} d.m. soil] – Factor: Fertilization

Variant of fertilization	Mn	Cu	Zn
No fertilized	626.1 a	17.2 a	62.7 a
rel. %	*100.0*	*100.0*	*100.0*
Farm. manure	618.5 a	16.7 a	60.5 a
rel. %	*98.8*	*97.1*	*96.5*
Farm. manure + $N_1P_1K_1$	601.6 a	16.5 a	59.9 a
rel. %	*96.1*	*95.9*	*95.5*
Farm. manure + $N_2P_2K_2$	613.4 a	16.4 a	60.2 a
rel. %	*98.0*	*95.3*	*96.0*
Farm. manure + $N_3P_3K_3$	605.1 a	16.1 a	59.8 a
rel. %	*96.6*	*93.6*	*95.4*
Farm. manure + $N_3P_3K_3$ without liming	580.1 a	13.1 a	56.8 a
rel. %	*92.7*	*76.2*	*90.6*

$p < 0.05$ – statistical significance at a 95% level of significance. Variants with identical letters express statistically insignificant differences.

(Table 6). In cambisol and brown soil 56.7 and 58.5 mg Zn · kg^{-1}, respectively, were detected, whereas the significantly highest Zn content was monitored in chernozem [$F (2; 163) = 11.247$; $p < 0.001$]. The results of Wang et al [17] also support this fact. Table 7 shows that fertilisation did not significantly affect the content of Zn or the contents of the other micronutrients [$F (5; 160) = 0.345$; $p = 0.884$]. The level of Zn was the lowest when fertilised with the highest rate of mineral fertilisers without liming (treatment 6) and was the highest when not fertilised; the difference was 9.4 %.

Podkolzin et al [18] also reported that long-term application of organic and mineral fertilisers had no marked effect on the content of soil Zn.

Conclusions

The results of a long-term stationary experiment showed that during the 17 years of the experiment the total contents of Zn and Mn decreased and the amount of Cu increased, but not significantly. The levels of all the micronutrients were higher in the sugar-beet region than in the potato-growing region and only Cu was significantly higher (by 45.6 %). In terms of the soil kind the levels of the micronutrients were the lowest in light soil. The levels of metals increased significantly with the increasing content of clay particles in the soil. In heavy soil the contents of Mn, Cu and Zn were by 38.9, 48.2 and 16.4 %, respectively, higher than the amounts monitored on light soil. The differences among the soil types were significant. The contents of Cu and Zn were the highest in chernozem; the significantly highest content of Mn was detected in Luvisol. Graded rates of organic and mineral fertilisers did not affect the total content of metals.

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Katedra Agrochemii, Gleboznawstwa, Mikrobiologii i Żywienia Roślin
Uniwersytet im. G. Mendla w Brnie

Abstrakt: Celem wieloletniego stacjonarnego doświadczenia było określenie wpływu roku, rejonu produkcji oraz typu i rodzaju gleby na całkowitą zawartość mikroelementów (Mn, Cu i Zn) w glebie. W latach 1982–1998 pobrano próbki gleby z 7 wybranych miejsc. Całkowite zawartości metali oznaczono po wcześniejszej mineralizacji w otwartym systemie HF – H_2O_2 – HNO_3. Zawartości mikroelementów oznaczano metodą AAS. Zawartość manganu wahała się w zakresie od 296,2 do 978,6 mg · kg^{-1}, miedzi od 6,1 do 25,7 mg · kg^{-1} i cynku od 29,5 do 99,8 mg · kg^{-1} gleby. W okresie doświadczalnym 1982–1998 zmniejszyły się całkowite zawartości Mn (o 7,9 %) i Zn (o 3,6 %), jednak nie były to różnice statystycznie istotne ($p < 0,05$). Całkowite zawartości miedzi w glebie w ciągu 17 lat trwania doświadczenia wzrosły o 7 %. Stwierdzono, że zawartości wszystkich badanych mikroelementów w rejonach uprawy buraka były wyższe niż w rejonach uprawy ziemniaka. Największą, statystycznie istotną różnicę ($p < 0,001$) zaobserwowano w przypadku miedzi (wzrost o 45,6 %). Biorąc pod uwagę rodzaj gleby, najniższe zawartości Mn i Cu zarejestrowano w glebie lekkiej. Natomiast całkowite zawartości cynku były porównywalne w glebach lekkiej i średniej. Wraz ze wzrostem udziału frakcji ilastych w składzie granulometrycznym gleby znacząco ($p < 0,001$) wzrastała w badanych glebach zawartość mikroelementów. W porównaniu z glebami lekkimi w glebach ciężkich zawartości metali wzrosły: Mn o 38,9 %, Cu o 48,2 % i Zn o 19,4 %. Zawartości Cu i Zn zależały od typu gleby. Statystycznie ($p < 0,001$) najwyższy poziom tych mikroelementów stwierdzono w czarnoziemie (odpowiednio 24,6 i 71,7 mg · kg^{-1} gleby). Najwyższą zawartość manganu stwierdzono w glebach brunatnych (714,3 mg · kg^{-1} gleby). Wzrastające dawki nawozów nie miały istotnego wpływu ($p < 0,05$) na całkowite zawartości metali w glebach. Różnice zaznaczyły się wyraźniej w wariantach, w których nie stosowano wapnowania; w tym przypadku zaobserwowano największe spadki zawartości Mn, Cu i Zn, odpowiednio o 7,3, 23,8 i 9,4 % w porównaniu z obiektem kontrolnym.

Słowa kluczowe: wieloletnie doświadczenie, cynk, mangan i miedź, całkowite zawartości