J. Elem. s. 1119–1130

DOI: 10.5601/jelem.2014.19.2.332

CONTENT OF Fe, Mn, Cu AND Zn IN LIGHT SOIL AFTER INTRODUCING ANIONS IN THE FORM OF CALCIUM SALTS AND AFTER IRRIGATION

Marta Wojcieszczuk, Łukasz Chorągwicki, Teresa Wojcieszczuk

Institute of Soil Science
West Pomeranian University of Technology in Szczecin

Abstract

Mineral fertilisation pertains to the supply of cations and anions affecting the chemism of soil environment, which leads to changes in the solubility of chemical compounds, including Fe, Mn, Cu and Zn. The purpose of this research was to determine the effects of anions CO_3^{2-}, SO_4^{2}, NO_3^- applied in the form of calcium salts and of irrigation on the solubility of Fe, Cu, Mn and Zn compounds in light soil. In order to attain our objective, a soil column (PO no 54427) was used for laboratory examinations of irrigated soil. A two-factor laboratory experiment was set up with the method of complete randomisation in three replications, where the first factor was an anion coupled with calcium cations: I – 0, II – $CaCO_3$, III – $CaSO_4$, IV – $Ca(NO_3)_2$; and the second one was the soil depth: a – 0-10, b – 10-20, c – 20-30 cm. Soil material was collected from the humus accumulation horizon of brown-rusty soil (0-10 cm). It was characterised by very acid reaction and the amount of ø<0.02 mm fraction lower than 13%. The calcium salt dose was determined on the basis of the soil's hydrolytic acidity and its grain-size distribution. Soil was placed in a soil column and irrigated. After the water sprinkling, the soil material was analysed for the content of chemical elements soluble in H_2O, HCl at the concentration 0.1 mol dm^{-3} and concentrated acids HNO_3+$HClO_4$. Calcium incorporated into the soil as well as the soil irrigation affected the soil reaction depending on the applied accompanying anion. The highest concentration of Mn forms measured in concentrated acids was found after applying $CaCO_3$, and the significantly lowest one was determined in response to $CaSO_4$. The content of the Cu forms soluble in concentrated acids was the largest in the soil supplied with $CaSO_4$. Calcium salts applied in the study modified differently the soil resources of Mn and Zn forms measured in 0.1 mol dm^{-3} HCl and the forms of Fe, Cu and Zn soluble in water.

Key words: sprinkling, anions, solubility, light soil.

mgr inż. Łukasz Chorągwicki, Institute of Soil Science, West Pomeranian University of Technology in Szczecin, J. Słowackiego 17, 71-434 Szczecin, Poland, e-mail: lchoragwicki@zut.edu.pl

ZAWARTOŚĆ Fe, Mn, Cu I Zn W GLEBIE LEKKIEJ PO WPROWADZENIU ANIONÓW W POSTACI SOLI WAPNIA I NAWADNIANEJ

Abstrakt

Nawożenie mineralne gleby polega na dostarczeniu kationów oraz anionów wpływających na chemizm środowiska glebowego, co prowadzi do zmiany stopnia rozpuszczalności związków chemicznych, w tym także Fe, Mn, Cu i Zn. Celem badań było określenie wpływu anionów CO_3^{2-}, SO_4^{2-}, NO_3^- zastosowanych w formie soli wapnia i nawadniania na rozpuszczalność związków Fe, Cu, Mn i Zn w glebie lekkiej. Do realizacji celu badań wykorzystano urządzenie kolumnowe do laboratoryjnych badań gleby z nawadnianiem (PO nr 54427). Doświadczenie laboratoryjne 2-czynnikowe założono metodą kompletnej randomizacji w 3 powtórzeniach. Pierwszym czynnikiem był anion towarzyszący kationowi wapnia: I – 0, II – $CaCO_3$, III – $CaSO_4$, IV – $Ca(NO_3)_2$; natomiast drugim miąższość gleby: a – 0-10, b – 10-20, c – 20-30 cm. Materiał glebowy użyty w doświadczeniu pobrano z poziomu akumulacji próchnicy gleby brunatnej rdzawej (0-10 cm). Odznaczał się on bardzo kwaśnym odczynem i zawartością frakcji o ø<0.02 mm w ilości nie przekraczającej 13%. Dawki soli wapnia wyznaczono na podstawie wartości kwasowości hydrolitycznej z uwzględnieniem składu granulometrycznego gleby. Glebę umieszczono w urządzeniu kolumnowym i nawadniano. W materiale glebowym po nawadnianiu oznaczono zawartość form pierwiastków chemicznych rozpuszczalnych w H_2O, w HCl o stężeniu 0,1 mol dm^{-3} oraz w stężonych kwasach HNO_3+$HClO_4$. Wapń dodany do gleby i nawadnianie miały wpływ na odczyn gleby w zależności od anionu towarzyszącego. Największe stężenie Mn ogółem stwierdzono po zastosowaniu $CaCO_3$, a istotnie najniższą wartość – po dodatku $CaSO_4$. Zawartość formy ogólnej Cu była największa w glebie, w której zastosowano $CaSO_4$. Zastosowane w doświadczeniu sole wapnia odmiennie kształtowały zasobność gleby lekkiej w formy Mn i Zn oznaczone w 0,1 mol dm^{-3} HCl , a także w formy Fe, Cu, Zn rozpuszczalne w wodzie.

Słowa kluczowe: deszczowanie, aniony, rozpuszczalność, gleba lekka.

INTRODUCTION

Mineral fertilisation pertains to the supply of cations and anions affecting the chemism of soil environment, which leads to changes in the degree of solubility of chemical elements, including Fe, Mn, Cu and Zn. Water solubility of the above elements is negatively correlated with the increase in soil pH, whereas a growing amount of organic carbon has been observed to result in an increase in the concentration of Fe, Mn, Cu and Zn in the soil solution (ŁABĘTOWICZ, RUTKOWSKA 2002, RUTKOWSKA et al. 2004, JAKUBUŚ 2007). In the opinion of MARTÍNEZ and MOTTO (2000), H^+ ion activity affects the solubility of Cu and Zn. At pH = 6.2 for Zn and 5.5 for Cu, the soil content of these metals remains on a natural level, whereas below these pH values their solubility is increasing. Higher pH values and lower soil acidity are obtained by supplying the soil with calcium carbonate (PATRA, MOHANTY 1994, BADORA, FILIPEK 1999, KOWALENKO, IHNAT 2010), magnesium carbonate or bicarbonate of calcium and magnesium (BADORA, FILIPEK 1999).

BADORA and FILIPEK (1999) found higher pH in 0.01 $CaCl_2$ as affected by $Ca(NO_3)_2$ supplied with manure. In turn, pH values were reduced after fertilising light soil with $(NH_4)_2SO_4$ and KCl or $(NH_4)_2SO_4$ and K_2SO_4 or $(NH_4)_2SO_4$

with KCl, in comparison with manure fertilisation and $CaCO_3$. According to Błaziak (1998), $MgSO_4$ did not cause a change in pH, but significantly increased the values of soil exchangeable and hydrolytic acidity.

Agricultural practices lead to changes in the concentration, availability and mobility of anions in arable land. Jakubuś (2007) is of the opinion that the content of Fe, Mn, Cu and Zn soluble in DTPA solution depends on the share of grain crops in a rotation, the dose of nitrogen fertiliser and sprinkler irrigation.

Having been incorporated into soil, cation and anion forms of nitrogen fertiliser differentiate the yield and chemical composition of field crops. Nutrient uptake by plants depends on the kind of anion coupled with cation introduced into the soil (Warchołowa, Mroczkowski 1982, Michałek 2000). Small differences in copper desorption from very acid grey-brown podsolic soil developed from slightly loamy sand and silt loam by Mg^{2+} and NH_4^+ cations with accompanying Cl^- anion were found by Paszko et al. (2000) and Paszko (2000). In their opinion, anions introduced into soil with fertilisers may have a greater influence on the Cu depletion from the soil.

The purpose of this research was to determine the effects of anions CO_3^{2}, SO_4^{2-}, NO_3^- coupled with calcium cations on the solubility of Fe, Cu, Mn and Zn in light soil after sprinkling.

MATERIAL AND METHODS

In order to attain our objective, a soil column (PO no 54427) for irrigated soil examinations was used. Two-factor laboratory experiment was set up by the method of complete randomisation, in three replications, where the first factor was an anion coupled with calcium cations: I – 0, II – $CaCO_3$, III – $CaSO_4$, IV – $Ca(NO_3)_2$; and the second one was the soil depth: a – 0-10, b – 10-20, c – 20-30 cm.

Soil material for the experiment was collected from the humus accumulation horizon of brown-rusty soil (0-10 cm), in a field of Experimental Agricultural Station in Lipnik. It was characterised by very acid reaction and 13% share of ø<0.02 mm fraction. The calcium salt dose was determined on the basis of the soil's hydrolytic acidity and grain-size distribution. The data on the chemical properties of the soil material used in our laboratory experiment before sprinkling, and the quantities of applied calcium salts are presented in Wojcieszczuk and Wojcieszczuk (2009).

Soil material, placed in a soil column for laboratory investigations of irrigated soil, was sprinkled 8 times with deionised water. The water dose was the same for all fertiliser variants. After sprinkling, 36 soil samples were taken from columns for analysis. In total, 7.4 litres of water were used per one column during one irrigation cycle. Under the humid climatic conditions, this amount of water would soak through a soil column in more than 12 years (Levesque, Hanna 1966).

After irrigation, the soil material was analysed to determine the content of chemical elements Fe, Mn, Cu and Zn soluble in H_2O, in HCl at the concentration 0.1 mol dm^{-3} and in concentrated acids HNO_3+$HClO_4$. Physicochemical analyses were carried out by the methods described by Ostrowska et al. (1991). The concentration of metals was measured spectrophotometrically by the ASA methods.

The results obtained in laboratory investigations were verified statistically by two-factorial analysis of variance (Anova) with a software package Statistica 9 software at α=0.05. The significance of differences was estimated using the Newman - Keuls test.

RESULTS AND DISCUSSION

In the light, irrigated soil with $CaCO_3$ amendment, pH measured in 1 mol KCl dm^{-3} was higher than in the unfertilised treatment with the supplement of $CaSO_4$ or $Ca(NO_3)_2$ (Table 1). Wojcieszczuk and Wojcieszczuk (2009) give pH values in 1 mol KCl dm^{-3} for light, non-irrigated soil after the application of $CaCO_3$ within the range 6.34 - 6.45, whereas in unfertilised soil and in the soil with $CaSO_4$ and $Ca(NO_3)_2$, the values of pH_{KCl} ranged from 3.57 to 3.67. According to Kowalenko and Ihnat (2010), fertilisation of acid soil with $CaCO_3$ increases its pH in water and this effect is enhanced with growing amounts of the applied fertiliser. With time, pH was decreasing in successive years of experiments. Patra and Mohanty (1994) stated that $CaCO_3$ introduced into the soil flooded with deionised water, under rice cover, caused an increase of pH measured *in situ* from 5.2 to pH 7.0-7.2. These researchers noticed that in the inundated soil without fertilisers, pH (6.0) was also higher prior to the studies. In our investigations, soil irrigation widened the range of pH_{KCl} from 3.53 to 3.88 in unfertilised objects with the amendment of $CaSO_4$ and $Ca(NO_3)_2$ – Table1. As a result of sprinkling and calcium carbonate application, the values of pH_{KCl} decreased by 1.48-1.69 units in comparison with the non-irrigated soil (Wojcieszczuk, Wojcieszczuk 2009). Moto-

Table 1

Soil pH values measured in 1 mol KCl dm^{-3} after the application of calcium salts and irrigation

Property	Soil depth (cm)	Form of calcium salt				Mean
		I – control	II – $CaCO_3$	III – $CaSO_4$	IV – $Ca(NO_3)_2$	
pH_{KCl}	0-10	3.53	4.97	3.60	3.57	4.42
	10-20	3.73	4.76	3.73	3.80	4.27
	20-30	3.74	4.65	3.80	3.88	4.20
Mean		3.68	4.82	3.72	3.77	

wicka-Terelak and Dudka (1991) also found that supplementing the soil developed from sand with elemental sulphur caused acidification of humus (0-20 cm), from pH_{KCl} 4.2 to pH_{KCl} 3.7 in bare soil at the 0-10 cm depth and from pH_{KCl} 4.0 to pH_{KCl} 3.8 at the 11-20 cm depth. Due to the leaching of chemical elements in the 21-40 cm layer of bare soil, the authors recorded higher pH_{KCl}, since pH_{KCl} was in the range of 5.0-4.3 in the 21-30 cm depth, but higher pH_{KCl} values were found at the depth of 31-40 cm (pH_{KCl} 5.3-5.8).

We obtained a similar distribution of pH_{KCl} values in the unfertilised variants with the supplement of $CaSO_4$ and $Ca(NO_3)_2$; in the soil supplied with $CaCO_3$, the highest pH_{KCl} was found in the 0-10 cm layer, was decreasing with depth. Wojcieszczuk et al. (2004) report that the hydrolytic acidity of light soil after sprinkling was decreasing with depth. In our studies, increasing pH_{KCl} values in deeper soil layers were observed in unfertilised soil with the amendment of $CaSO_4$ and $Ca(NO_3)_2$; in turn, in the soil enriched with $CaCO_3$, the highest pH_{KCl} was in the 0-10 cm layer, again decreasing with depth.

In the conducted laboratory experiment, sprinkling affected the solubility of various forms of chemical compounds and their mobility in soil. Compared to non-irrigated soils (Wojcieszczuk, Wojcieszczuk 2009), sprinkling reduced the content of Fe and Cu compounds soluble in concentrated acids, whereas their content in 0.1 mol dm^{-3} HCl increased. It was only the sprinkling treatment of the soil fertilised with $CaCO_3$ that reduced the amount of Fe and Cu compounds soluble in H_2O.

The mean content of the Mn forms soluble in 0.1 mol dm^{-3} HCl significantly depended on the depth from which the soil material was taken, but his was not observed in the case of the Mn forms soluble in concentrated acids and in water (Tables 2 and 3). Soil material from the 0-10 cm layer was characterised by a lower mean content of Mn measured in 0.1 mol dm^{-3} HCl than that one from the 10-30 cm depth (Table 4). In the topsoil supplied with NO_3^-, a considerably lower amount of Mn forms soluble in 0.1 mol dm^{-3} HCl was detected than in unfertilised soil from the 20-30 cm layer.

Solubility of Mn compounds determined in concentrated acids varied and depended on both the kind of an anion and the depth. A markedly higher amount of total Mn was found in the 0-10 cm layer in the soil with $CaCO_3$ in comparison with the content determined in all layers of the soil with $CaSO_4$ and $Ca(NO_3)_2$ – Table 2. At the depth of 10-30 cm, substantially higher amounts of Mn forms soluble in concentrated acids were found under the influence of carbonate anion rather than sulphate.

In contrast to non-irrigated soil (Wojcieszczuk, Wojcieszczuk 2009), sprinkling lowered the mean content of Mn compounds soluble in concentrated acids from 123.4-126.5 mg kg^{-1} to 102.4-116.7 mg kg^{-1}. The only exception was the variant with calcium carbonate, where the mean value was higher by 14.5 mg kg^{-1} after water application. Water treatment of the soil contain-

Table 2

Content of Fe, Mn, Cu and Zn forms soluble in concentrated acids HNO_3+$HClO_4$ in soil after irrigation depending on applied form of calcium salt (mg kg^{-1})

Chemical element	Soil layer (cm)	Form of calcium salt				Mean
		I – control	II – $CaCO_3$	III – $CaSO_4$	IV – $Ca(NO_3)_2$	
Fe	0-10	4939	5291	5803	5573	5402
	10-20	5096	5407	5373	5442	5330
	20-30	5056	5399	5219	5356	5258
Mean		5030	5366	5465	5457	
Mn	0-10	119.2^{abc}	139.3^{c}	105.7^{ab}	106.0^{ab}	117.6
	10-20	116.6^{abc}	136.7^{bc}	101.4^{a}	107.9^{ab}	115.7
	20-30	114.1^{abc}	135.6^{bc}	100.2^{a}	106.0^{ab}	114.0
Mean		116.7^{b}	137.2^{c}	102.4^{a}	106.6^{ab}	
Cu	0-10	5.10^{ab}	4.45^{a}	5.15^{ab}	4.92^{ab}	4.90
	10-20	4.70^{ab}	4.92^{ab}	5.24^{ab}	5.10^{ab}	4.98
	20-30	4.24^{a}	5.21^{ab}	5.97^{b}	5.64^{ab}	5.26
Mean		4.67^{a}	4.86^{a}	5.45^{b}	5.21^{ab}	
Zn	0-10	19.88	20.17	21.95	20.51	20.63
	10-20	19.61	21.36	21.86	20.66	20.87
	20-30	18.09	21.70	29.28	21.59	22.67
Mean		19.19	21.08	24.36	20.92	

Key: $^{a, b, c}$ – homogenous groups were obtained using the Newman - Keuls test at α=0.05.

ing calcium carbonate and nitrate forms increased the mean content of Mn in 0.1 mol dm^{-3} HCl by 4.6 and 3.1 mg kg^{-1}, respectively, in relation to the values presented by Wojcieszczuk and Wojcieszczuk (2009). Irrespective of the applied anion, the mean content of water soluble Mn was lower after sprinkling than in unfertilised soil. The concentration of Mn compounds soluble in water ranged from 0.328 to 0.860 mg kg^{-1}.

Supplying the soil with $CaCO_3$ lowers the solubility of manganese compounds (Badora 2001, Rutkowska et al. 2009, Wojcieszczuk, Wojcieszczuk 2009, Kowalenko, Ihnat 2010). On the other hand, amending the soil with nitrate or ammonium form of nitrogen increases the content of Mn^{2+} in the soil solution. Jakubuś (2007) recorded an increase in the amount of bioavailable Mn as a result of nitrogen fertiliser. This author also stated that there was more active Mn (extracted with DTPA) in the soil without sprinkling than in irrigated soil. In Błaziak's opinion (1998), a significantly higher content of active Mn (determined according to Schachtschabel) was found in excessively moist soil (moisture 33% volume), and the amendment of calcium and magnesium oxide brought about an over two-fold decrease in its content. Gondek (2009) claims that liming and watering heavy soil resulted in a lower concentration of mobile forms of Cu, Mn and Zn (soluble in NH_4NO_3 at the

Table 3

Content of Fe, Mn, Cu and Zn forms soluble in H_2O in soil after irrigation depending on the calcium salt applied (mg kg^{-1})

Chemical element	Soil layer (cm)	Form of calcium salt				Mean
		I – control	II – $CaCO_3$	III – $CaSO_4$	IV – $Ca(NO_3)_2$	
Fe	0-10	3.51	2.83	4.84	6.58	4.44
	10-20	3.74	5.03	10.32	10.26	7.34
	20-30	6.36	5.63	7.31	10.18	7.37
Mean		4.54^{a}	4.49^{a}	7.49^{ab}	9.01^{b}	
Mn	0-10	0.527	0.297	0.833	0.893	0.637
	10-20	0.930	0.370	0.480	0.857	0.659
	20-30	1.123	0.317	0.810	0.783	0.758
Mean		0.860	0.328	0.708	0.844	
Cu	0-10	0.300^{abc}	0.197^{a}	0.267^{ab}	0.327^{abc}	0.272^{a}
	10-20	0.297^{abc}	0.270^{ab}	0.307^{abc}	0.417^{cb}	0.322^{a}
	20-30	0.340^{abc}	0.380^{cb}	0.450^{c}	0.553^{d}	0.431^{b}
Mean		0.312^{a}	0.282^{a}	0.341^{a}	0.432^{b}	
Zn	0-10	0.150	0.093	0.183	0.160	0.147
	10-20	0.130	0.120	0.173	0.203	0.157
	20-30	0.187	0.130	0.163	0.227	0.177
Mean		0.155^{ab}	0.114^{a}	0.173^{b}	0.197^{b}	

Key: $^{a, b, c}$ – homogenous groups were obtained using Newman - Keuls test at α=0.05.

concentration 1 mol dm^{-3}) than the one found in soil without liming. Soil irrigation and the NPK [NH_4NO_3, $Ca(H_2PO_4)$ H_2O, KCl] and NPKS [(NH_4NO_3, $Ca(H_2PO_4)$ H_2O, KCl $(NH_4)_2SO_4$] fertilisation applied by Gondek (2009) increased the content of mobile Cu and Mn in the treatments without liming; in the case of Zn, the differences were significant in comparison with the unfertilised object.

In this research, the mean content of the forms of Cu soluble in concentrated acids was significantly higher in unfertilised soil with $CaSO_4$ than in unfertilised soil supplied with $CaCO_3$, whereas there was no significant difference in the soil with the amendment of $Ca(NO_3)_2$ – Table 2. After sprinkling, a significantly higher amount (5.97 mg kg^{-1}) of copper compounds soluble in concentrated acids was detected at the 20-30 cm depth after $CaSO_4$ application than in the same layer of unfertilised soil (4.24 mg kg^{-1}) and the 0-10 cm layer (4.45 mg kg^{-1}) of the soil supplemented with $CaCO_3$ (Table 2).

Anions coupled with calcium cations had no significant effect on the mean content of copper in 0.1 mol dm^{-3} HCl (Table 3). Considerable differences were observed in individual layers. In the topsoil, a markedly lower content of the forms of Cu soluble in 0.1 mol dm^{-3} HCl was found as a result of

Table 4

Content of Fe, Mn, Cu and Zn forms soluble in HCl at the concentration of 0.1 mol dm^{-3} in soil after irrigation depending on the calcium salt applied (mg kg^{-1})

Chemical element	Soil layer (cm)	Form of calcium salt				Mean
		I – control	II – $CaCO_3$	III – $CaSO_4$	IV – $Ca(NO_3)_2$	
Fe	0-10	275.8	273.9	290.9	281.1	280.4
	10-20	357.3	271.6	319.9	338.6	321.8
	20-30	368.2	272.9	348.8	372.9	340.7
Mean		333.8	272.8	319.9	330.9	
Mn	0-10	53.3^{ab}	57.7^{ab}	45.6^{ab}	40.5^{a}	49.3^{a}
	10-20	70.8^{ab}	54.6^{ab}	49.0^{ab}	58.5^{ab}	58.2^{b}
	20-30	74.8^{b}	56.7^{ab}	48.4^{ab}	61.8^{ab}	60.5^{b}
Mean		66.3^{b}	56.4^{ab}	47.7^{a}	53.6^{a}	
Cu	0-10	2.25^{ab}	2.32^{ab}	2.17^{ab}	1.87^{a}	2.15^{a}
	10-20	2.36^{ab}	2.08^{ab}	2.04^{ab}	1.99^{ab}	2.12^{a}
	20-30	2.52^{ab}	2.69^{b}	2.61^{ab}	2.68^{b}	2.62^{b}
Mean		2.38	2.36	2.27	2.18	
Zn	0-10	6.49^{ab}	5.76^{ab}	4.06^{a}	4.60^{a}	5.22^{ab}
	10-20	4.51^{a}	3.81^{a}	4.73^{a}	3.45^{a}	4.13^{a}
	20-30	6.80^{ab}	9.65^{b}	3.82^{a}	4.01^{a}	6.07^{b}
Mean		5.93^{ab}	6.41^{b}	4.20^{a}	4.02^{a}	

Key: ^{a,b,c} – homogenous groups were obtained using the Newman - Keuls test at α=0.05.

nitrate anion and water in comparison with the amount obtained in the soil material from the 20-30 cm layer in the same column and the soil with $CaCO_3$.

Our studies showed that irrigation and $Ca(NO_3)_2$ application resulted in higher mean values of the forms of Cu soluble in water in relation to the other fertiliser variants. The mean value of the content of Cu compounds soluble in water was substantially higher in the 20-30 cm layer (Table 3). The amount of this form of copper in particular layers of irrigated soil was affected by the anion coupled with calcium cation. The highest content of Cu compounds soluble in water was determined in the 20-30 cm layer in the soil with NO_3^-, whereas the lowest content of this copper form was determined in the topsoil with CO_3^{2-}. Soil fertilisation differentiated the content of copper compounds soluble in water within the distinguished layers. No significant differences were found only in unfertilised soil.

Hoch et al. (2011) think that the fertilisation of light soil with ammonium nitrate and potassium salt had a greater effect on the content of Cu in HCl at the concentration 1 mol dm^{-3}, whereas calcium amendment resulted in reducing the content of this form of copper. Rutkowska et al. (2009)

demonstrate that an increase in Cu content in the soil solution was caused by ammonium nitrate, which lowered pH values. According to Gondek (2009), irrigation of heavy soil and its fertilisation with NPK [NH_4NO_3, $Ca(H_2PO_4)\cdot H_2O$, KCl] and NPKS [(NH_4NO_3, $Ca(H_2PO_4)\cdot H_2O$, KCl $(NH_4)_2SO_4$] increased the content of the Cu mobile form (soluble in NH_4NO_3 at the concentration 1 mol dm^{-3}), whereas liming decreased its amount. This study shows that the content of Fe and Cu forms soluble in water was significantly lower in irrigated soil with $CaCO_3$ supplement than in soil with the amendment of $Ca(NO_3)_2$. In the opinion of Wojcieszczuk and Wojcieszczuk (2009), the content of the forms of Cu soluble in water was significantly smaller in the control object, although it did not vary significantly in the objects with $CaCO_3$, $CaSO_4$ and $Ca(NO_3)_2$.

The mean content of Zn in concentrated acids ranged from 19.19 to 24.36 mg kg^{-1}, but the differences were statistically insignificant (Table 2). Calcium carbonate and sprinkling raised the mean concentration of Zn compounds soluble in 0.1 mol dm^{-3} HCl. After water treatment of light soil supplemented with SO_4^{2-} and NO_3^-, there were significantly more Zn compounds soluble in water compared with the soil supplied with CO_3^{2-} (Table 3). The situation was reverse in the case of Zn determined in 0.1 mol dm^{-3} HCl, where its amount was higher in the soil with CO_3^{2-} than after the application of SO_4^{2-}, or NO_3^- (Table 4). Jakubuś (2007) states that the quantity of bioavailable Zn increased after nitrogen fertilisation and irrigation. Błaziak (1998) indicates that magnesium sulphate and soil moisture growing up to 23.5% and 33.0% volume significantly reduced the content of the Zn forms soluble in HCl at the concentration 0.1 mol dm^{-3}. Gondek (2009) recorded an increase in the content of the mobile Zn form after fertilising heavy soil with NPK and NPKS, and its decrease after liming. According to Rutkowska et al. (2009), reduced the amount of Zn in the soil solution by supplying the soil with $CaCO_3$. Also, Kowalenko and Ihnat (2010) demonstrate that carbonate anions lowered the amount of available Zn (extracted from soil by the Mehlich-3 method) in relation to the variant without $CaCO_3$. The results presented by Wojcieszczuk and Wojcieszczuk (2009) show that $CaCO_3$, $CaSO_4$ and $Ca(NO_3)_2$ contributed to a decline in the content of Zn determined in 0.1 mol dm^{-3} HCl in non-irrigated soil.

The mean content of the Zn forms soluble in 0.1 mol dm^{-3} HCl depended on the layer from which the soil material for analysis was separated after the completion of water treatment, but it did not significantly affect the amount of zinc compounds soluble in concentrated acids and water. The mean content of exchangeable zinc was considerably higher at the depth of 10-20 cm (Table 4). The concentration of zinc in 0.1 mol dm^{-3} HCl in particular layers was affected by anions introduced into the soil. The highest value (9.65 mg kg^{-1}) was obtained at 20-30 cm after the application of CO_3^{2-}, at the same time being significantly different from the lowest value determined in the same column at 10-20 cm (3.81 mg kg^{-1}). The values for Zn in

0.1 mol dm^{-3} HCl in all layers of the soil where SO_4^{2-} and NO_3^- were applied and from the 10-20 cm layer of unfertilised soil were considerably lower than those from the soil with CO_3^{2-} supplement at the depth of 20-30 cm.

There were no significant differences in the content of particular forms of iron depending on the depth. In our laboratory experiment, only the content of iron compounds soluble in water was significantly dependent on the form of calcium salt applied. A significantly higher amount of Fe compounds soluble in water was recorded in the soil with $Ca(NO_3)_2$ in comparison with its content in the soil without fertilisation and after the application of $CaCO_3$ (Table 3). Ammari and Mengel (2006) found that the soil content of Fe bound to organic complexes in aqueous extract ranged from 40-91% and its concentration was significantly correlated (r=0.77) with hydrogen ion activity. Wojcieszczuk and Wojcieszczuk (2009) found that in non-irrigated soil the content of Fe compounds soluble in water after the application of $CaSO_4$ and $Ca(NO_3)_2$ was 0.11 and 0.09 mg kg^{-1}, respectively. In our studies, sprinkling the light soil supplied with SO_4^{2-} and NO_3^- increased the solubility of Fe compounds in water up to 7.49 and 9.01 mg kg^{-1} (Table 3).

In the light soil subjected to sprinkling, the content of Fe in 0.1 mol dm^{-3} HCl ranged from 272.8 to 333.8 mg kg^{-1} (Table 3). Comparing these results with the amount of Fe compounds soluble in 0.1 mol dm^{-3} HCl in non--irrigated soil (Wojcieszczuk, Wojcieszczuk 2009), it was noticed that water treatment increased solubility of these compounds by 104.6-183.1 mg kg^{-1}. A smaller increase in irrigated soil versus non-irrigated one was observed after the application of CO_3^{2-}, and the highest one occurred after using NO_3^-. Jakubuś (2007) stated that nitrogen fertilisation resulted in the growing amount of bioavailable Fe in soil, and its content was increasing with higher doses of nitrogen fertiliser. The content of Fe in the soil solution rises under the influence of ammonium nitrate, whereas $CaCO_3$ reduces the content of iron (Rutkowska et al. 2009). The decrease in the amount of available iron (extracted from the soil by the Mehlich-3 method) affected by CO_3^{2-} was proven by Kowalenko and Ihnat (2010).

CONCLUSIONS

1. Calcium amendment and irrigation affected soil reaction depending on the accompanying anion applied.

2. CO_3^{2-}, SO_4^{2-}, NO_3^- anions introduced into light soil coupled with calcium cation and irrigation influenced differently the solubility of compounds of Fe, Mn, Cu and Zn in the soil.

3. The calcium salts and irrigation applied differentiated the mean content of Fe, Mn, Cu and Zn depending on the layer from which the soil material was collected. Statistically significant differences were found for the

amount of Mn, Cu, Zn compounds soluble in 0.1 mol dm^{-3} HCl and the form of Cu soluble in H_2O.

4. In the case of the content of Mn and Cu compounds soluble in concentrated acids, and amount of Mn, Cu, Zn compounds soluble in 0.1 mol dm^{-3} HCl as welll as the form of Cu soluble in water, there was an interaction between the activity of anions coupled with calcium cations and the depth from which the soil material was separated after irrigation.

5. Mineral fertilisation and irrigation should be adjusted to soil properties and plant nutrient requirements so as to reduce the loss of chemical elements in the plant root system. The results show that chemical element leaching is affected not only by cations but also by the anions introduced.

REFERENCES

Badora A., Filipek T. 1999. *Role of nitrogen and potassium fertilizers, liming and organic fertilization in aluminium mobilization*. Pol. J. Soil Sci., 32(1): 43-51.

Badora A. 2001. *Aluminum and manganese mobility in the soil*. Pol. J. Soil Sci., 34(1): 1-8.

Błaziak J. 1998. *The influence of calcium and magnesium application at various moisture conditions on the microelement content in soil*. Zesz. Probl. Post. Nauk Rol., 456: 183-186. (in Polish).

Gondek K. 2009. *The effect of fertilization on the content of mobile forms of selected microelements in soil and their leaching in a pot experiment*. Acta Agroph., 13(1): 89-101. www.old.acta-agrophysica.org/artykuly/acta_agrophysica/ActaAgr_166_2009_13_1_103.pdf. (in Polish)

Hoch M., Szulc W., Rutkowska B., Kuśmirek E. 2011. *Effect of unbalanced fertilization on the content of copper in soil and rye in a long term fertilization experiment*. Zesz. Probl. Post. Nauk Rol., 565: 77-82. www.zeszytyproblemowe.pan.pl/images/stories/Zeszyty/2011/565/8.pdf. (in Polish)

Jakubuś M. 2007. *The influence of agrotechnical factors on bioavaible contents of microelements in the humus horizon of soil*. Pol. J. Soil Sci., 40(2): 195-205. www.pjss.org/zeszyty

Kowalenko C. G., Ihnat M. 2010. *Effects of limestone applications on soil pH and extractable elements in a cauliflower field study*. Can. J. Soil Sci., 90: 655-665. DOI: 10.4141/CJSS09014

Levesque M., Hanna W.J. 1966. *Downward movement of phosphorus and iron in some Pozdzolic soils of New Jersey*. Can. J. Soil Sci., 46(1): 53-60. DOI: 10.4141/cjss66-008

Łabętowicz J., Rutkowska B. 2002. *Environmental factors effecting the concentration of microelements in the soil solution of polish arable soils*. Pol. J. Soil Sci., 35(1): 19-29.

Martínez C.E., Motto H.L. 2000. *Solubility of lead, zinc and copper added to mineral soils*. Environ. Pollut., 107: 153-158. www.elsevier.com/locate/envpol

Michałek W. 2000. *Accumulation of magnesium in lettuce leaves according to the aluminium form and dose in the substrate*. Biul. Magnezol., 5(1): 51-55. (in Polish)

Motowicka-Terelak T., Dudka S. 1991. *Chemical degradation of soils polluted with sulpheur and the influence of soil degradation on field crops*. IUNG Puławy, 284: 1-95. (in Polish)

Ostrowska A., Gawliński S., Szczubiałka Z. 1991. *Methods of analysis and assessment of soil and plant properties*. Catalogue, IOŚ. Warszawa. (in Polish)

Paszko T., Gąszczyk R., Muszyński P. 2000. *Effectiveness of Cu^{2+}, Co^{2+}, and Cr^{3+} desporption with NH_4^+ cations in acid mineral soils*. Biul. Magnezol., 5(1): 62-67. (in Polish)

Paszko T. 2000. *Desorption of Cu^{2+}, Co^{2+}, and Cr^{3+} with Mg^{2+}cations in Grey-Brown Podzolic soils*. Biul. Magnezol., 5(3): 186-191. (in Polish)

Patra B. N., Mohanty S. K. 1994. *Effect of nutriens and liming on changes in pH, redox potential, and uptake of iron and manganese by wetland rice in iron-toxic soil*. Biol. Fertil. Soils, 17(4): 285-288. DOI: 10.1007/BF00383983.

Rutkowska B., Szulc W., Łabętowicz J. 2004. *The effect of organic carbon in the soil on the chemical composition of the soil solution*. Pol. J. Soil Sci., 37(2): 105-112.

Rutkowska B., Szulc W., Łabętowicz J. 2009. *Influence of soil fertilization on concentration of microelements in soil solution of sandy soil*. J. Elementol., 14(2): 349-355.

Ammari T., Mengel K. 2006. *Total soluble Fe in soil solutions of chemically different soils*. Geoderma, 136: 876-885. DOI: 10.1016/j.geoderma.2006.06.013

Warcholowa M., Mroczkowski W. 1982. *The effect of nitrogen source on mineral composition of plants*. Pam. Puł., 78: 63-76. (in Polish)

Wojcieszczuk T. 1996. *The soil column for laboratory examinations of irrigated soil* (in Polish). PO nr 54427. WUP, 8. Wyd. Urzędu Patentowego RP, Warszawa.

Wojcieszczuk T., Wojcieszczuk M. 2009. *The impact of anions introduced to soil in the form of calcium salt on some chemical properties*. Zesz. Probl. Post. Nauk Rol., 538: 347-355. www.zeszytyproblemowe.pan.pl/images/stories/Zeszyty/2009/538/42-538.pdf. (in Polish)

Wojcieszczuk T., Niedźwiecki E., Meller E., 2004. *Effect of sprinkling and coal ash applied on chemical properties of light soil*. Rocz. Glebozn., 55(1): 249-255. (in Polish)