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ASSESSMENT OF CHEMICAL DEGRADATION OF SELECTED SOIL PROPERTIES AS INDUCED BY COPPER, ZINC AND HYDROGEN

OCENA CHEMICZNEJ DEGRADACJI WYBRANYCH WŁAŚCIWOŚCI GLEB POD WPLYWEM MIEDZI, CYNKU I WODORU

Abstract: The concept of this study was based on the evaluation of the impact of copper (Cu), zinc (Zn) and hydrogen protons (H^+) on selected chemical characteristics of two arable soils: light loamy sand (No. 1) and silty soil (No. 2). The targeted chemical alterations of the soils concerned pH changes, water soluble forms of Cu and Zn and displaced alkaline cations as induced by Cu, Zn and H incorporation. Preliminarily, the amounts of exchangeable alkaline cations ($ExAC = Ca_{ex} + Mg_{ex} + K_{ex} + Na_{ex}$) were extracted by using 1 M CH_3COONH_4 , pH 7.0 and these amounts were used for calculating amounts of Cu, Zn and H to be incorporated as follows: copper as $CuSO_4 \cdot 5H_2O$, zinc as $ZnSO_4 \cdot 7H_2O$ and hydrogen in the form of HCl at spiking rates corresponding to 0, 5, 10, 30, 60, 100, 150, 200, 300, 400, 500 and 1000 % of ExAC. Treatments were incubated for 16 weeks at 18 °C and kept at 75–85 % WHC (water holding capacity).

Copper, zinc and hydrogen effects on soil chemical properties can be first observed throughout pH changes, which were more pronounced for H treatments as compared with Cu and Zn ones. The amounts of water extractable Ca (ie displaced) at Cu and Zn spiking rates of 1000 % ExAC are 25 and 21 times higher, respectively, for the soil No. 1 (light loamy sand), whereas for the soil No. 2 (silty soil), 44 and 38 times higher, as compared with the control treatment. The impact of H is intermediate and represents 24 and 35 times, for the soils No. 1 and No. 2, respectively. Results reported in the paper drive specific attention on the destructive effects of Cu, Zn and H, separately. The joint impact of these metals along with protons is the core of agroenvironmental concern. The chemical degradation established on the basis of water extractable alkaline cations (WEAC) follows the range: $H > Cu > Zn$.

Keywords: copper, zinc, hydrogen cations, alkaline cations, arable soils, chemical degradation

The chemical degradation of soils is induced by several chemical compounds of which organic and mineral are most frequently reported. Their negative impacts ie bio(phyto)toxicity, depend on the chemical forms and persistence [1]. If organic

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contaminants are recognized to be biodegradable [2] unfortunately this can not account for mineral ones, such as trace elements, which persist in the environment. Among these, copper (Cu) and zinc (Zn) draw specific attention due to their dualistic classification: firstly as micronutrients (agricultural environments) and, secondly, toxic metals (severely contaminated soil environments). The most frequently encountered classification in terms of environmental concern is the second one, which intrinsically focuses on the occurrence of potential toxicity of metals due both to their elevated content in the soil and the strengthened mobility [3, 4].

Since most Cu and Zn geochemical processes proceed *via* exchange reactions, therefore it should be expected the occurrence of direct exchange mechanisms between Cu and Zn ions and alkaline cations (Ca^{2+} , Mg^{2+} , K^+ and Na^+) within soils sorptive complex [5, 6]. The magnitude of this phenomenon is closely related to the level of Cu and Zn incorporation into soils in one hand, and to the “*stability*” of soil fertility expressed by the bulk content of exchangeable alkaline elements on the other hand [7].

Throughout exchange mechanisms, hydrogen cations (H^+) may potentially displace alkaline cations from soil colloids, a process increasing their concentrations in the soil solution [8]. This process is boosted by the specifically high affinity of H^+ for phenolic and carboxylic groups of humic acids, by forming strong chemical bonds [9]. Under such conditions alkaline cations undergo mostly leaching, which consequently enhances the negative impact of protons over the soil sorptive complex [7].

The purpose of the study was to evaluate the impact of copper, zinc and hydrogen ions induced chemical changes in two arable soils and the resulting consequences for soil quality.

Materials and methods

Origin of soil samples

Soils used in the study were composite samples made by 20 subsamples collected in 2005 at the depth 0–30 cm from two sites: Swadzim (52°26' N and 16°44' E, Poland), an Experimental Station belonging to the University of Life Sciences in Poznan, designated here and after as soil No. 1, and Wrzesnia (52°19' N and 17°35' E, Poland), an agricultural farm leading intensive crop production (winter wheat, sugar beet and oilseed rape), as soil No. 2.

Physical and chemical soil analyses

Prior to chemical analyses, both soils were air-dried and crushed to pass a 1.0 mm screen. Particle size composition was determined according to the aerometric method of Bouyoucos-Casagrande [10] and organic carbon (organic C) by the Walkley-Black method as reported by Nelson and Sommers [11]. The pH was determined potentiometrically (*w/v*, 1:5) according to Polish Standard [12] in 0.010 M CaCl_2 . Exchangeable alkaline cations ($\text{ExAC} = \text{Ca}_{\text{ex}} + \text{Mg}_{\text{ex}} + \text{K}_{\text{ex}} + \text{Na}_{\text{ex}}$) were extracted by using 1 M $\text{CH}_3\text{COONH}_4$, pH 7.0 according to Thomas [13] and the electrical conductivity (EC)

was determined conductimetrically as described by Jackson [14]. Selected soil analytical data are reported in Table 1.

Table 1

Selected physical and chemical characteristics of soils used in the study

Soil	Silt	Clay	organic	EC	pH ^c	Ca _{ex}	Mg _{ex}	K _{ex}	Na _{ex}	ExAC ^d
	0.05–0.002	< 0.002	C							
No. 1 ^a	332	160	7.6	99.3	5.6	380.8	62.7	216.6	22.7	682.8
No. 2 ^b	412	480	6.2	77.5	4.9	612.9	107.3	182.0	23.3	925.5

^a light loamy sand; ^b silty soil; ^c in 0.010 M CaCl₂; ^d Ca_{ex} + Mg_{ex} + K_{ex} + Na_{ex}

Experimental design

Soils No. 1 and No. 2 were spiked with copper (CuSO₄ · 5H₂O), zinc (ZnSO₄ · 7H₂O) and hydrogen ions (HCl) at rates corresponding to 0, 5, 10, 30, 60, 100, 150, 200, 300, 400, 500 and 1000 % of ExAC (ie the sum of exchangeable alkaline cations) as listed in Table 2.

Table 2

Set of volumes of HCl and bidistilled water elaborated for H treatments

% of ExAC ^a	No. 1			No. 2		
	mmol H ⁺ · kg ⁻¹	5 mmol HCl [cm ³]	bidist. H ₂ O [cm ³]	mmol H ⁺ · kg ⁻¹	5 mmol HCl [cm ³]	bidist. H ₂ O [cm ³]
5	1.6	0.31	99.69	2.2	0.45	99.55
10	3.2	0.62	99.38	4.2	0.90	99.10
30	9.6	1.85	98.16	13.2	2.70	97.30
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^a Ca_{ex} + Mg_{ex} + K_{ex} + Na_{ex}

In the case of H-treatments, H⁺ was added as described in Table 1: ExAC were converted to mmol(+) · kg⁻¹ and a solution of 5.0 mmol HCl · cm⁻³ (ie 1 cm³ contains 5 mmol H⁺) was diluted with adequate amounts of bidistilled water to give a final solution of 100 cm³ (Table 2), which were added to air-dried soils (1.0 kg).

Copper, zinc and H-spiked soils were incubated for 16 weeks at 18 °C and kept at 75–85 % WHC (water holding capacity). All treatments were triplicated and a composite sample (mean of three) was prepared at the end of the incubation, air-dried and analyzed in duplications for pH in 0.01 M CaCl₂, water soluble Cu and Zn and displaced alkaline cations (Ca²⁺, Mg²⁺, K⁺ and Na⁺). Graphs and computations were made by using Excel[®] Sheet.

Results and discussion

Soils pH changes

Soil physical and chemical characteristics reported in Table 1 show that both soils are acidic, mostly the silty one (No. 2) characterized by the highest content of silt and clay for 412 and 480 $\text{g} \cdot \text{kg}^{-1}$, respectively. The soil No. 1 (light loamy sand) exhibits a higher salinity level ($\text{EC} = 99.3 \mu\text{S} \cdot \text{cm}^{-1}$), as compared with the soil No. 2, but the organic carbon content of both soils was relatively low. One of the key characteristics of soils is the pool of exchangeable alkaline cations (ExAC) responsible for the regulation and maintenance of soil pH and other geochemical processes such as exchange mechanisms. As it can be observed, exchangeable calcium (Ca_{ex}) represented alone *ca* 56 and 66 % of all alkaline cations, respectively for soils No. 1 and No. 2. The same applies for exchangeable potassium (K_{ex}), with *ca* 32 and 20 %, respectively. Both Ca_{ex} and K_{ex} represent 88 and 86 % of the exchange potential of the studied soils, which implies that the lability of alkaline cations of these soils is significantly high. Acidic conditions could be partly responsible for this state.

The concept of this study is based on the evaluation of the impact of copper (Cu), zinc (Zn) and hydrogen ions (H^+) on selected soil chemical characteristics of two arable soils. The targeted chemical alterations concern pH changes, water soluble forms of Cu, Zn and displaced Ca^{2+} , Mg^{2+} , K^+ and Na^+ as induced by Cu^{2+} , Zn^{2+} and H^+ incorporation. As reported in Table 3, the amounts of Cu, Zn and H incorporated into soils were different and varied by a factor of 1.36 between soils No. 1 and No. 2 in the case of Cu^{2+} , Zn^{2+} , and by 1.47 for H^+ , respectively.

Table 3

Amounts of Cu, Zn and H^+ incorporated into soils on the basis of the amounts of exchangeable alkaline cations (ExAC)

% of ExAC ^a	$\text{Cu}^{\text{b}}, \text{Zn}^{\text{c}}$ [$\text{mg} \cdot \text{kg}^{-1}$]		H^{d} [$\text{mmol H}^+ \cdot \text{kg}^{-1}$]	
	No. 1	No. 2	No. 1	No. 2
5	34.0	46.0	1.6	2.2
10	68.0	92.5	3.2	4.2
30	205.0	277.5	9.6	13.2
60	409.5	555.0	18.4	26.6
100	682.5	925.5	30.8	45.2
150	1024.0	1388.0	46.0	67.8
200	1365.5	1851.0	61.4	90.2
300	2048.0	2776.5	92.2	135.4
400	2731.0	3702.0	122.8	180.6
500	3413.5	4627.5	153.6	225.6
1000	6827.5	9255.0	307.0	451.4

^a $\text{Ca}_{\text{ex}} + \text{Mg}_{\text{ex}} + \text{K}_{\text{ex}} + \text{Na}_{\text{ex}}$; ^b as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; ^c as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$; ^d as HCl

Copper, zinc and hydrogen effects on soil chemical properties can be first observed throughout pH changes (Fig. 1).

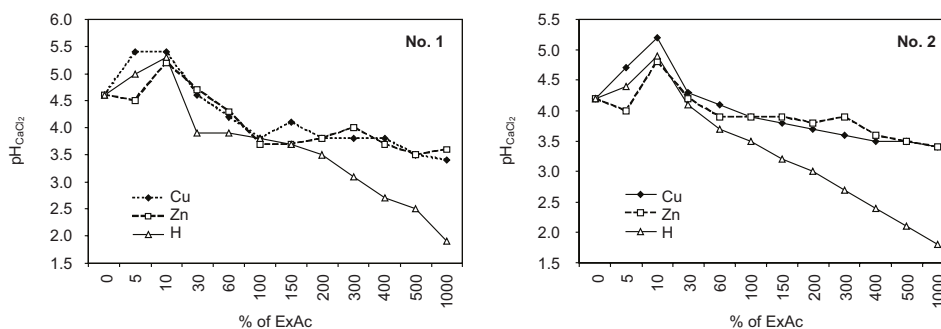
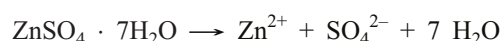


Fig. 1. Effect of Cu^{2+} , Zn^{2+} and H^+ spiking rates [% of ExAC] on pH changes for soils No. 1 and No. 2

The patterns of pH decrease are similar for both soils and are more pronounced for H ions treatments as compared to both Cu and Zn ones. Unexpectedly a raise of pH occurred at Cu, Zn and H ions spiking rates of 5 and 10 % ExAC. Processes involved in the chemical reactions of incorporated Cu, Zn and H concern preponderantly exchange mechanisms (retention and release). Therefore one may assume that the retention of Cu, Zn and H induced a simultaneous displacement and release into the ambient soil solution of equivalent units of Ca, Mg, K and Na, which in turn undergo hydrolysis reactions [6, 15]. The latter ones have been most specifically responsible for such unexpected pH raise at these two spiking rates.



which means 1 eq Cu or Zn = SO_4^{2-} = H^+ .

For the 5 % ExAC, 34.0 mg Cu have displaced 152.3 mg of all alkaline cations per kg of the soil No. 1. Therefore 34.0 mg Cu have induced 34.0 mg H^+ whose acidifying power was totally neutralized by 152.3 mg of all displaced alkaline cations. The same applies for the soil No. 2, where 46.0 mg Cu have displaced 151.0 mg of all displaced alkaline cations per kg of soil. This explained the gradual and progressive pH decrease along with increasing Cu spiking.

In the case of zinc, the exchange process at 5 % ExAC proceeded as follows:

a) 34.0 mg Zn have displaced 166.5 mg of all alkaline cations per kg of the soil No. 1;

b) 46.0 mg Zn have displaced 150.8 mg of all alkaline cations per kg of the soil No. 2.

A similar approach may be applied for H-spiked soils as below:



Therefore 1 meq H^+ = 1 mmol H^+ .

For the 5 % ExAC, 1.6 mmol H^+ have displaced 2.3 mmol(+) of Ca per kg of the soil No. 1. Therefore 1.6 mmol H^+ were totally neutralized by 2.3 mmol(+) of Ca, *alone*. The same applies for the 10 % ExAC, ie 3.2 mmol H^+ were neutralized by 3.67 mmol(+) of Ca, *alone*.

This geochemical evaluation elucidates the observed pH raise at the initial exchange process. Copper, zinc and H rates from 30 % ExAC and beyond, generated stronger acidification, which has not been neutralized by more and more displaced alkaline cations. In the current study, the highest amounts of incorporated H^+ amounted to 307.0 and 541.4 mmol $H^+ \cdot kg^{-1}$, respectively for soils No. 1 and No. 2 and were significantly lower as compared with *ca* 730.0 mmol $H^+ \cdot kg^{-1}$ incorporated yearly between 1975–1989 [16], as a result of ammonium sulphate, ammonium nitrate(V) and urea application to arable lands. The impact of such high fertilizers-generated H^+ may last for years and needs huge amounts of aglime or other neutralizing agents. Thus in most soils that are used in agriculture, acid rain does not appear to be a serious practical problem.

Water extractable Cu and Zn and their potential lability

Amounts of water extractable Cu and Zn (Fig. 2) are low as compared with those of Cu and Zn incorporated into soils and vary for the soil No. 1 within the ranges 0.6–52.1 % and 1.3–65.7 %, respectively for Cu and Zn. This corresponds to an extremely and relatively high amounts of Cu and Zn retained by the soil No. 1, ie from 99.4 to 47.9 % for Cu and from 98.3 to 34.3 % for Zn. Quite similar ranges were observed for the soil No. 2, where the amounts of Cu and Zn retained varied respectively from 99.2 to 58.5 % and 98.6 to 36.9 %. Such strong Cu and Zn partition to the solid phase may be attributed to three factors: Cu and Zn specific affinity to soil colloids [16], the relatively high level of silt and clay (Table 1), and the aqueous pH of Cu, Zn-spiked soils, as illustrated by the Fig. 2.

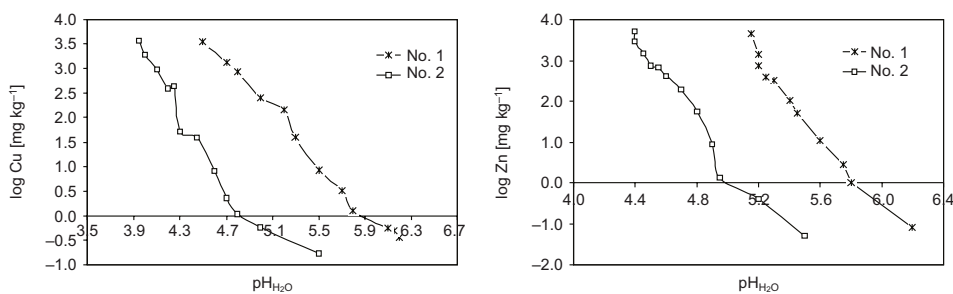


Fig. 2. Relationships between the amounts of water extractable Cu and Zn and aqueous pH of the investigated soils

According to Abd-Elfattach and Wada [18], the electronegativity values of Cu and Zn are 1.9 and 1.6, respectively. These physicochemical properties, greater for Cu as compared with Zn, express the affinity of both metals to soil colloids. The retention of

both metals is in line with data obtained in the current work, ie, more copper was partitioned to both soils than did Zn. The role of silt and clay was decisive for such Cu and Zn behaviour, which may be explained by electrostatic and inner-sphere surface complexation reactions [19, 20].

Concentrations and the activity of Cu and Zn in the soil solution are controlled by dissolved organic and mineral substances, but most specifically by the pH of the solution. Trends illustrated in the Fig. 2 decidedly show, that both metals are very sensitive to pH changes and this sensitivity increases along with a raise of pH (steep slopes). Therefore, under such conditions, the emergence of easily hydrolyzed Cu and Zn forms takes place and this favors in turn the establishment of strong Cu and Zn partition to the solid phase. This effect induces chemical reactions, mostly exchange mechanisms leading to the displacement of significant amounts of alkaline cations.

Alkaline cations displacement and agroenvironmental consequences

Amounts of water extractable alkaline cations (WEAC) as influenced by Cu, Zn and H ions spiking to soils No. 1 (light loamy sand) and No. 2 (silty soil) are reported in Table 4 for selected spiking rates.

Table 4

Amounts of water extractable Ca, Mg, K and Na as influenced by Cu, Zn and H ions spiking rates (selected) for the soils No. 1 and No. 2

% of ExAC ^a	No. 1			No. 2		
	Cu	Zn	H	Cu	Zn	H
	WEAC (Ca) ^b			WEAC (Ca)		
	[Mg · ha ⁻¹]					
0	0.28 (0.10)			0.21 (0.09)		
5	0.46 (0.20)	0.50 (0.20)	0.35 (0.14)	0.45 (0.25)	0.45 (0.22)	0.75 (0.49)
10	0.42 (0.20)	0.50 (0.23)	0.46 (0.22)	0.37 (0.21)	0.33 (0.19)	0.60 (0.39)
60	0.98 (0.57)	1.12 (0.68)	2.02 (1.43)	1.25 (0.91)	1.20 (0.91)	2.05 (1.52)
100	1.50 (0.99)	1.29 (0.89)	2.26 (1.48)	1.80 (1.42)	1.86 (1.44)	3.20 (2.49)
150	1.90 (1.34)	2.01 (1.35)	2.95 (2.05)	2.67 (2.20)	2.62 (2.05)	4.36 (3.50)
500	3.18 (2.45)	2.60 (1.96)	4.57 (3.19)	4.60 (3.83)	4.50 (3.71)	5.01 (3.38)
1000	3.26 (2.49)	2.78 (2.11)	4.16 (2.43)	4.67 (4.00)	4.23 (3.38)	4.93 (3.19)

^a Exchangeable alkaline cations (ExAC); ^b Amounts of Ca, only (in brackets)

Acidic soils are generally reported to exhibit low exchangeable calcium contents. This could be expectable, since hydrogen and aluminum ions promote a direct alkaline cations displacement and further their leaching, a process which in turn intensifies acidification. The amounts of ExAC listed in Table 1 are assessed for 2.05 Mg · ha⁻¹, of which Ca_{ex} alone represents ca 56 % (ie, 1.14 Mg · ha⁻¹) for the soil No. 1, whereas in the case of the soil No. 2, respectively ExAC = 2.78 Mg · ha⁻¹ and ca 66 % of Ca_{ex} (ie, 1.84 Mg · ha⁻¹). This implies that Ca is the main “stabilizing” factor of the exchange capacities of these soils as demonstrated by Grzebisz and Maciejewska [21] and Królak

et al [22], who reported that exchangeable Ca was the first determinant of the cation exchange capacity at even 98 %, irrespective of soil pH.

Since alkaline cation displacement also took place in soil colloids, therefore exchangeability could be the intrinsic mechanisms. These reactions should operate throughout substitution or ionization of surface OH and COOH groups as suggested by Abd-Elfattah and Wada [18]. Interestingly, it should be mentioned that the direct impact of Cu, Zn and H ions over the soil buffering capacities was decidedly acute for H ion since just at 60 % (= 18.4 mmol H⁺ · kg⁻¹) and 100 (45.2 mmol H⁺ · kg⁻¹) % ExAC, respectively for soils No. 1 and No. 2, the amounts of water extractable Ca exceed those representing the ExAC (Table 1). In the case of Cu and Zn, the targeted spiking level for both soils is 150 % ExAC, which corresponds to 32.2 mmol Cu²⁺ · kg⁻¹ and 43.8 mmol Zn²⁺ · kg⁻¹.

Processes involved in the chemical reactions of incorporated Cu, Zn and H concern preponderantly exchange mechanisms (retention and release). Therefore one may assume that the retention of Cu, Zn and H ions induced the displacement and release of equivalent units of Ca, Mg, K and Na ions [6]. This process is the first step for soil chemical degradation by Cu, Zn and H ions and creates suitable, but only temporary, conditions for increased metals mobility and hence their potential uptake by crop plants [23] or leaching. Water extractable Ca, revealed that the amounts of Ca displaced at Cu and Zn spiking rates of 1000 % ExAC are 25 and 21 times higher, respectively, for the soil No. 1 (light loamy sand), whereas for the soil No. 2 (silty soil), 44 and 38 times higher, as compared with the control treatment. The impact of H ion was intermediate and represented 24.3 and 35 times, for the soils No. 1 and No. 2, respectively. Results reported in the paper drive specific attention on the destructive effects of Cu, Zn and H ions, separately. The joint impact of these metal ions along with hydrogen ions is the core of agroenvironmental concern. The chemical degradation established on the basis of water extractable alkaline cations (WEAC) follows the range: H > Cu > Zn.

Conclusions and statements

Investigated soils ie, light loamy sand (No. 1) and silty soil (No. 2), were characterized by an acidic pH. It was observed, that exchangeable calcium (Ca_{ex}) represented alone *ca* 56 and 66 % of all extractable alkaline cations (ExAC), respectively for soils No. 1 and No. 2. The same applies for exchangeable potassium (K_{ex}), with *ca* 32 and 20 %, respectively. Both Ca_{ex} and K_{ex} represent 88 and 86 % of the exchange potential of the studied soils, which implies that the lability of alkaline cations of these soils is significantly high.

Amounts of water extractable Cu and Zn (Fig. 2) are decidedly low as compared with those of Cu and Zn incorporated into soils and vary for the soil No. 1 within the ranges 0.6–52.1 % and 1.3–65.7 %, respectively for Cu and Zn. This corresponds to an extremely and relatively high amounts of Cu and Zn retained by the soil No. 1, ie, from 99.4 to 47.9 % for Cu and from 98.3 to 34.3 % for Zn. Quite similar ranges were observed for the soil No. 2, where the amounts of Cu and Zn retained varied respectively from 99.2 to 58.5 % and 98.6 to 36.9 %.

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OCENA CHEMICZNEJ DEGRADACJI WYBRANYCH WŁAŚCIWOŚCI GLEB POD WPLYWEM MIEDZI, CYNKU I WODORU

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Abstrakt: Koncepcja przedstawionych badań dotyczy oceny oddziaływania miedzi (Cu), cynku (Zn) i protonów (jonów wodorowych H⁺) na wybrane właściwości chemiczne dwóch gleb uprawnych: piasku

gliniastego lekkiego (gleba Nr 1) i iłu pylastego (gleba Nr 2). Badane zmiany dotyczyły pH, wodororozpuszczalnych form Cu, Zn oraz kationów alkalicznych wypartych z koloidów glebowych pod wpływem wniesienia do obu gleb jonów Cu, Zn i H. Wymienne kationy alkaliczne ($ExAC = Ca_{ex} + Mg_{ex} + K_{ex} + Na_{ex}$) ekstrahowano uprzednio przy użyciu roztworu 1 M CH_3COONH_4 przy pH 7.0, a uzyskane dane służyły do obliczenia ilości Cu, Zn i H do wniesienia do gleb w postaci: miedź jako $CuSO_4 \cdot 5H_2O$, cynk jako $ZnSO_4 \cdot 7H_2O$ i wodór w formie HCl. Dawki tych jonów odpowiadały 0, 5, 10, 30, 60, 100, 150, 200, 300, 400, 500 i 1000 % ExAC. Obiekty inkubowano przez 16 tygodni w temperaturze 18 °C oraz 75–85 % PPW (Polowej Pojemności Wodnej). Oddziaływanie jonów Cu, Zn i H na chemiczne właściwości gleb ujawniły się najpierw poprzez zmiany odczynu, które były znaczące dla obiektów z jonem wodoru w porównaniu z obiektami z Cu i Zn. Wodororozpuszczalne ilości Ca (tzn. wyparte) przy dawkach Cu i Zn wynoszących 1000 % ExAC są odpowiednio 25 i 21 razy większe dla gleby Nr 1 (piasku gliniastym lekkim), podczas gdy dla gleby Nr 2 (iłu pylastego), odpowiednio 44 i 38 w porównaniu z obiektem kontrolnym. Oddziaływanie H jest natomiast pośrednie, czyli 24 i 35 większe, odpowiednio dla gleby Nr 1 i Nr 2. Wyniki przedstawione w pracy zwracają szczególną uwagę na destrukcyjne działania jonów Cu, Zn i H stosowanych oddzielnie. Łączne oddziaływanie obu metali wraz z protonami wywołuje negatywne skutki w ekosystemach poddanych antropopresji. Szereg degradacji chemicznej oparty na ilościach wodororozpuszczalnych kationów alkalicznych (WEAC) kształtował się następująco: $H > Cu > Zn$.

Słowa kluczowe: miedź, cynk, protony wodorowe, kationy alkaliczne, gleby uprawne, degradacja chemiczna