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CALCIUM AS A FACTOR MITIGATING NEGATIVE IMPACT OF HEAVY METALS ON SOIL AND PLANT

I. SOIL CHEMICAL CHANGES AS INDUCED BY CALCIUM-BEARING COMPOUNDS

WAPŃ JAKO CZYNNIK ŁAGODZĄCY UJEMNE DZIAŁANIE METALI CIĘŻKICH NA GLEBĘ I ROŚLINĘ

I. ZMIANY CHEMICZNE GLEB WYWOŁANE ZWIĄZKAMI ZAWIERAJĄCYMI WAPŃ

Słowa kluczowe: zanieczyszczenie metalami, łagodzący wpływ Ca, wapno palone, fosforyt, wapno jeziorne, wapno krzemianowe.

Key words: metal contamination, Ca mitigation effect, quicklime, phosphate rock, lacustrine lime, silicate lime.

Głównym założeniem przy przygotowaniu niniejszego doświadczenia było wykazanie celowości stosowania wapnia jako pierwiastka przeciwnego do metali ciężkich na glebach nimi zanieczyszczonych. W tym celu zastosowano następujące związki zawierające wapń (CaBC): wapno palone (QL), fosforyt (PR), wapno jeziorne (LL) i wapno krzemianowe (SL), na glebę kwaśną ($pH_{CaCl_2} = 5,5$), bardzo zanieczyszczoną przez hutę miedzi. Związki zawierające wapń (CaBC), po uprzednim oznaczeniu ich ogólnej zasadowości (CaO), dodawano do gleby na podstawie kwasowości hydrolitycznej gleb (0,5 i 1,0 HA). Każdy obiekt (CaBC x HA) składał się z 600 g gleby i powtórzony był czterokrotnie. To samo dotyczyło obiektu kontrolnego. Całkowity czas inkubacji trwał 28 tygodni, próbki gleb pobierano co 7 tygodni. Oceny zawartości wapnia w obiektach dokonano na podstawie ekstrakcji wodą (Ca wodnorozpuszczalny) i 1 mol CH_3COONH_4 , pH 7,0 (Ca wymienny). Metale ciężkie ekstrahowano przy użyciu chemicznych testów 0,10 mol $NaNO_3$ (biodostępny) i 0,005 mol DTPA, pH 7,3 (chelatowany). Wyniki doświadczenia wykazały, że dodanie do gleby CaBC doprowadziło do zmniejszenia stężeń metali w roztworze glebowym wraz z upływem czasu, przy czym najbardziej fosforytu (PR) przy obu dawkach 1,68 i 3,36 g na 600 gleby od-

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powiednio do 0,5 i 1,0 HA oraz wapna krzemianowego przy dawce 0,74 g na 600 gleby (czyli 1,0 HA). Ten ostatni był mniej skuteczny w porównaniu do fosforytu przy dawce 1,68 g na 600 gleby (0,5 HA). Miedź występująca w największej ilości w badanej glebie była silnie związana przez kompleks sorpcyjny gleby, na równi z ołowiem, którego ilość w glebie w dużym stopniu zmniejszyło zastosowanie CaBC. Zastosowanie związków zawierających wapń na podstawie kwasowości hydrolitycznej okazało się niedostatecznym czynnikiem do skutecznego złagodzenia negatywnego działania metali na gleby, zwłaszcza w stosunku do miedzi.

1. INTRODUCTION

The natural capacity of soils usually develops for counteracting and mitigating threatening substances and chemicals is a resultant of interactions of a bulk of mineral as well as organic colloids. These along with the soil reaction (pH) create a specific buffering power, whose efficiency has been frequently ascribed to the prevailing levels of alkaline *versus* acid ions. Several decades ago, Graham [1959] has introduced the concept of 'ideal soil', where he suggested, that 65 per cent of the exchange complex should be occupied by calcium (Ca), 10 per cent by magnesium (Mg), 5 per cent by potassium (K), and 20 per cent by hydrogen (H). In the same way Liebhart [1981] relaxed the optimum specific ratios by proposing, that 65 to 85 percent of the cation exchange complex should be occupied by Ca, 6 to 12 percent by Mg, and 2 to 5 percent by K. Later on, Eckert [1987] defined normal values for the exchangeable cations as 60 to 80% for Ca, 10 to 20% for Mg, and 2 to 5% for K. The order reported for these alkaline elements explicitly reveals, that calcium should be considered as the real factor responsible geochemical exchange processes. Thus the magnitude of these processes is strictly related to the substantial fact, that its level predominates in the exchange complex [Crittter and Airoidi 2003].

The progressive loadings of heavy metals into agricultural and forest ecosystems may affect the soil chemistry of alkaline cation, basically. Several studies [Abd-Elfattah and Wada 1981; Gao 1997; Diatta et al., 2003] have been carried out on heavy metal inputs into soil ecosystems, their reactions (adsorption-desorption) with soil colloids and possible environmental concerns. The direct negative impact of heavy metals in soils as well as to living biota (i.e. the fauna and flora) is a resultant of the capacity of soils to mitigate the harmful effect *via* processes boosting the buffering capacity [Atanassova and Okazaki 1997; Diatta et al., 2000]. Soils are an important sink for heavy metals due to their high or relatively high retention capacities. In many cases, much of these metals in soils is not present in readily available fractions, which may vary from <1 to 10% for Pb, for instance [Boruvka et al. 1997; Kabala and Sing 2001]. Therefore their persistence and mobility in soils should be dictated by the extent to which their are retained to solid phases. This par-

ticularity is a function of reactions affecting surface charge and ion density [Sokołowska 1989; Diatta 2002].

Since metals contained in soils may be released simultaneously as a result of chemical and microbial processes, it is then expectable that their competitive and selective retention by soils may be of major importance in determining their phytoavailability [Berti and Jacobs 1996; Fontes et al. 2000]. Hence understanding mechanisms of metals, particularly Cu and Pb retention in soils is particularly important as these reactions dictate the strength of the metal-soil surface interaction. On a relative basis, exchange reactions may render these metals most labile, whereas inner sphere complex formation and coprecipitation with soils surface cause Cu and Pb to be retained strongly and in many cases nearly irreversible [McBride 1989].

Several factors are involved in the process of the mitigation of metal negative effects under conditions of contamination or even pollution. These are based on the natural capacity/power of metals impacted soils to neutralize or attenuate the labile i.e., active as well exchangeable metals forms [Mulligan and Yong 2004; Odenchantz et al. 2003; Brady et al. 2003]. In many cases the levels of labile metals forms become significantly high to be maximally buffered by soil colloids. Therefore the „strengthening” of buffer properties is assisted by the application of so-called stabilizer on the basis of primarily established criteria. However, the focus on the direct or indirect role of calcium, solely in the mitigation process is generally omitted. Some attempts have been undertaken through equilibrium studies [Diatta et al. 2000; Critter and Airoidi 2003], which in fact exhibit the role of calcium more at colloids interface level.

The purpose of the investigation was to evaluate the efficiency of calcium from calcium bearing compounds (CaBC) for mitigating the impact of copper and lead in a soil polluted by Cu smelter activity. The specific assumption was to exhibit the role of Ca as a counter element for metals earlier retained by the soil sorptive complex.

2. MATERIALS AND METHODS

Location of the soil sampling. The soil used in the current study was collected at 0–20 cm (500 m East from the main emitter) in 2002 within the area impacted by the Glogow Copper Smelter (51°39'32.6” N 16°04'49.9” E, Poland). The smelter was established in 1970's and the zone mostly contaminated by heavy metals (copper mainly) was taken out of agricultural utilization and afforested (poplars, maples) to create the so called the „Sanitary Belt”.

Physical and chemical analysis. Prior to basic analyses the soil sample were air-dried and crushed to pass through a 2.00 mm mesh sieve. Particle size distribution was determined according to the method of Bouyoucos-Casagrande modified by Prószyński

[Mocek et al. 2000]. Organic carbon was determined by the dichromate wet oxidative method according to Tiurin [Filipek 1999] and soil pH potentiometrically, according to Polish standard [1994]. The cation exchange capacity was obtained by summation of exchangeable alkaline cations and acidity according to Thomas [1982]. Iron (Fe) and manganese (Mn) were extracted by using both the citrate-bicarbonate-dithionite (CBD) and the acid-ammonium-oxalate (Ox) methods according to McKeague and Day [1966] and Mehra and Jackson [1960]. The assessment of the specific surface area was undertaken by applying the EGME saturation (Ethylene Glycol Monoethyl Ether) method as reported by Carter et al. [1986].

Heavy metals were assayed by using 6 moles $\text{HCl} \cdot \text{dm}^{-3}$ (extracted fractions designated as the „pseudo total” content) and additionally by the 0.005 moles $\text{DTPA} \cdot \text{dm}^{-3}$ method according to Lindsay and Norvell [1978], (chelated fractions). Unbuffered soil tests like 0.10 moles $\text{NaNO}_3 \cdot \text{dm}^{-3}$ [Gupta and Hani 1989] and deionized water were additionally used for extracting respectively bioavailable (Bio) and active (Act) metal fractions. Physical and chemical details of the investigated soil are listed in Tables 1 and 2.

Table 1. Selected physical and chemical characteristics of the investigated soil

Tabela 1. Wybrane właściwości fizyczne i chemiczne badanej gleby

Sand (2.0–0.02 mm)	Silt (0.02–0.002 mm)	Clay <0.002 mm	C_{org}	$\text{pH}_{\text{CaCl}_2}$	SSA^{a} ($\text{m}^2 \cdot \text{g}^{-1}$)	CEC^{b} $\text{cmol}_{(+)} \cdot \text{kg}^{-1}$
$\text{g} \cdot \text{kg}^{-1}$						
660	220	120	8.8	5.5	9.8	10.1

^a – Specific surface area; ^b – Cation exchange capacity.

Table 2. Metals extracted by different chemical tests from the investigated soil

Tabela 2. Metale ekstrahowane z badanej gleby przy użyciu różnych testów

Cu	Pb	Zn	Cd	S-SO_4	Fe		Mn	
6 moles $\text{HCl} \cdot \text{dm}^{-3}$					CBD ¹	Ox ²	CBD	Ox
$\text{mg} \cdot \text{kg}^{-1}$								
2041.3	540.0	68.7	0.80	76.0	2533	1931	171	194

¹ Citrate-Bicarbonate-Dithionite; ² Acid ammonium Oxalate.

Concept, experimental design and incubation process. It was assumed, that the low pH (tab. 1), i.e., high protons level favors metals activity and both may be counteracted by appropriated concentrations of calcium ions in the soil. Therefore calcium-bearing compounds (CaBC): quicklime (QL), phosphate rock (PR), lacustrine lime (LL) and silicate lime (SL) were incorporated into the acid soil on the basis of the hydrolytic acidity (HA). Prior to CaBC addition, their acid neutralizing capacity was determined and converted to CaO. Table 3 resumes basic information dealing with these details.

Table 3. Amounts of CaBC-based CaO incorporated to the investigated soil on the basis of hydrolytic acidity (HA)**Tabela 3.** Ilości związków zawierających wapń (CaBC) dodane w oparciu o CaO do badanej gleby na podstawie kwasowości hydrolitycznej (HA)

Calcium-bearing compounds (CaBC)	CaO (%)	Amount of CaBC added on the basis of			
		0.5 HA*	1.0 HA	0.5 HA	1.0 HA
		g CaBC 600 g ⁻¹ ·soil		t CaBC·ha ⁻¹	
Quicklime (QL)	83.7	0.18	0.36	0.905	1.81
Phosphate rock (PR)	9.0	1.68	3.36	8.39	16.78
Lacustrine lime (LL)	40.7	0.38	0.76	1.86	3.71
Silicate lime (SL)	41.1	0.37	0.74	1.84	3.68

* Hydrolytic acidity (HA); for convenience, 0.5 HA and 1.0 HA are designated a and b, respectively in Graphs 1, 2, 3 and 4.

Each treatment (i.e. CaBC x HA) consisted of 600 g soil and was replicated 4 times. The same applies for the control. These treatments were kept moist at 75% FWHC (Field water holding capacity) and incubated for 28 weeks at 18±2°C. The whole incubation period lasted 28 weeks of which soil sampling (120 g) was performed at each 7 weeks time interval. The collected soil samples were chemically analysed as described in the sub-section „*Physical and chemical analysis*”. All performed chemical tests were run in duplication and metals as well as other elements were determined by the FAAS method (Flame Atomic Absorption Spectrophotometry, Varian 250 plus). Simple statistical evaluations were done by using the Statgraphics® software and Excel® sheet facilities.

3. RESULTS AND DISCUSSION

The investigated soil is classified as loamy sand [Soil Taxonomy – USDA 1975] and Dystric Gleysols according to WRB-84 [1998], which implies that its natural capacity for buffering cationic elements should be appreciable (Tab. 1). This is supported by the relatively high level of the sum: silt+clay amounting to 340 g·kg⁻¹ and the content of organic carbon, 8.8 g·kg⁻¹. These parameters are practically invaluable in creating and shaping the size of both the specific surface area (SSA) and cation exchange capacity (CEC), which in turn are the core of several geochemical processes involved in the alleviation of heavy metal (Cu, Pb and Zn among others) direct impact on soil as well as living organisms.

It should be mentioned, that the recorded soil reaction, i.e., pH 5.5 (in 0.01 mole CaCl₂) may be considered as acidic and then quite incompatible with the magnitude of SSA and CEC. In fact, the levels of Cu, Pb basically and Zn slightly (Tab. 2) may have been responsible for the low pH value. Additional care should be given to the significantly high level of sulphate (76.0 mg·kg⁻¹) originating from the processing of Cu ores. Therefore the cumula-

tive effect of both of Cu, Pb and S-SO₄ are directly concerned in this matter. Further geochemical interactions are intended to govern or modify the chemistry of Ca *versus* metals and these are mediated by the soil reaction.

Effect of calcium-bearing compounds (CaBC) on soil pH and Ca status. The incorporation of CaBC induced both pH changes in one hand and led to a raise in the content of labile Ca fractions accordingly to treatments (Fig. 1). It should be decidedly mentioned that pH varied along with CaBC rates, i.e., 0.5 HA and 1.0 HA and reached its highest value (pH = 6.2) in the treatment receiving phosphate rock (PR) at 1.0 HA. Amounts of Ca incorporated leveled at 215.4 and 430.8 mg·kg⁻¹ for the quicklime (QL) and 1090.7 and 2181.4 mg·kg⁻¹ for PR treatments, at 0.5 HA and 1.0 HA, respectively. This is explicitly outlined by the progressive increase, as compared to the control (O). The dynamics of labile forms of Ca reported by Critter and Airoidi [2003], has pointed out on the particular role of Ca in the so-called exchangeability and interference mechanisms *versus* other metallic ions. If we assume the water extractable Ca (Ca-H₂O) to play the interference role, therefore the ammonium acetate Ca (Ca-Exch) decidedly should be involved in the second process.

The chemical composition of CaBC relies by essence on the fact, that calcium is not the sole element to be taken under consideration, otherwise the dominating one (71.4% in CaO; ca 40% Ca and 19.5% P in Ca₃(PO₄)₂; Lacustrine lime (LL), 28.8%, ca 35% Ca and 24% Si in CaSiO₃). In the case of PR treatments, calcium release may be related chemically to the concentration of phosphates ions [Ma and Rao 1999] and the latter ones to be indirectly and intermediately involved in the reaction with heavy metals. The chemical efficiency of phosphates ions seems to be substantially hampered due to the high levels of labile Ca forms as reported in Figure 1.

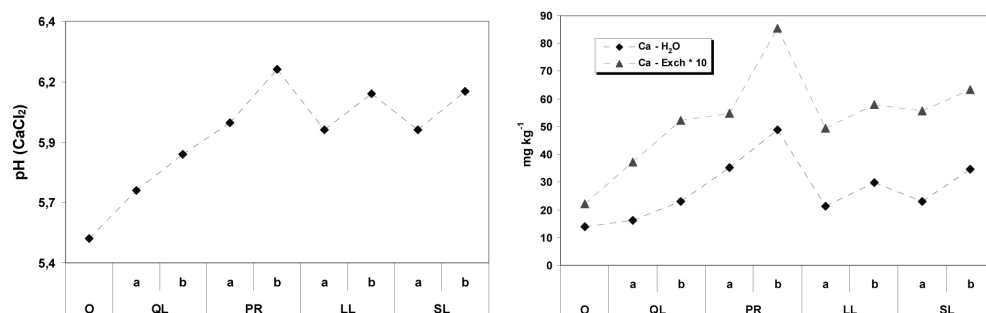


Fig. 1. Effect of calcium-bearing compounds (CaBC) on pH changes and calcium status of treatments; 0.5 HA = a, 1.0 HA = b, (More details, see Table 3)

Rys. 1. Wpływ związków zawierających wapń (CaBC) na zmiany pH oraz stan wapnia w obiektach; 0,5 HA = a, 1,0 HA = b (więcej szczegółów w tabeli 3)

Ca aqueous and exchangeable versus Cu bioavailable and chelated. Geochemical changes induced by Ca incorporation may proceed *via* hydrolysis reactions of the concerned metal species (Ca, Cu and Pb) and most frequently are decidedly dictated by the levels of the so-called labile forms, i.e., aqueous, bioavailable, exchangeable and chelated. Under conditions of the current study, it should not be omitted the physical and chemical feature of metals, which seems to be pertinently decisive in assessing the role of Ca in the direct or intermediary alleviation of Cu, and Pb negative effect on soils. According to Sanderson [1983], the electronegativity of the above mentioned metals varies as follows: Ca – 1.0, Cu – 1.90 and Pb – 2.33, which implies, that lead and copper are decidedly strongly attracted by soil colloids [Abd-Elfattach and Wada 1981; Christophi and Axe, 2000; Diatta et al. 2003] as compared to Ca. Therefore the levels of Ca in contaminated or polluted soil must be higher enough to counteract investigated contaminants.

Data reported in Figure 2, explicitly showed the direct quantitative effect of Ca source on its labile as well as exchangeable forms in the soils. The mitigation process may be formulated as follows:

- Ca water extractable (Ca-H₂O) *versus* biological (Cu – Bio) and chelated (Chel – Cu),
- Ca exchangeable (Ca-Exch) *versus* biological (Cu – Bio) and chelated (Chel – Cu).

The Ca-mitigation assessment based on the first case is particularly interesting due to the fact that Ca-H₂O occupies the intermediary position, i.e., between Chel – Cu and Cu – Bio. This implied that, irrespective of CaBC rates, the level of Ca-H₂O was sufficient enough to control only active Cu forms, hence to reduce their resorption to the soil phase.

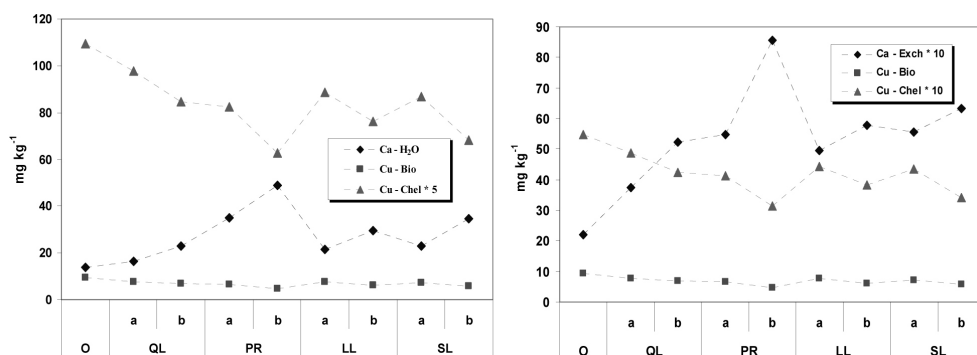


Fig. 2. Changes of Ca aqueous (Ca-H₂O) and exchangeable (Ca-Exch) levels and Cu bioavailable (Cu-Bio) and chelated (Cu-Chel) as induced by CaBC incorporation

Rys. 2. Zmiany w ilości Ca wodnorozpuszczalnego (Ca-H₂O) i wymiennego (Ca-Exch) oraz Cu biodostępnego (Cu-Bio) oraz schelatowanego (Cu-Chel) pod wpływem CaBC

Such interactions of Ca-Cu in extremely polluted soils have been a topic of detailed equilibrium/kinetic study [Diatta et al. 2000]. Authors have reported that the presence of Ca shaped Cu sorption/ retention by soil colloids *via* non-specific processes and the higher the Ca levels the strongest the processes become. The practical significance of these mechanisms relies on the efficient competitiveness of Ca for retention sites under its high levels. Then, the displaced or desorbed Cu ions hardly are sorbed back and strongly interfere with Ca ions in the bulk solution, where the latter one undergoes hydrolysis reactions significantly decreasing the activity of Cu. The pertinence of the approach reported in the current study is supported by data of McBride [1989] and Critter and Airoidi [2003].

The evaluation made on the basis of Ca-Exch outlined the specific role of exchangeability processes in controlling quite the whole level of both Cu-Bio and Cu-Chel for all CaBC. Most importantly is the quantitative prevalence of Ca over Cu and the geochemical significance of this state. In fact the Cu-Chel fraction involves two sub-fractions, i.e. Cu-Biol and namely, exchangeable Cu (Cu-Exch). Reactions and interactions occurring at this level are of prime importance for further evaluation of Ca-based mitigation effect on copper and heavy metals, in general. According to Christophi and Axe [2000], the competition established between heavy metals for active colloid sites and the resulting impact on the whole chemical status of colloids may not be limited to the „pure” electronegativity feature, solely, but also the bulk amounts of exchangeable Ca. Data reported in Table 4 decidedly shows the difference in the amount of total Ca incorporated into particular treatments and their post effect in the system.

Table 4. Amounts of Ca incorporated to the investigated soil on the basis of hydrolytic acidity (HA)

Tabela 4. Ilości Ca wprowadzonego do badanej gleby na podstawie kwasowości hydrolytycznej (HA)

Calcium-bearing compounds (CaBC)	CaO (%)	Amount of Ca incorporated on the basis of:			
		0.5 HA*	1.0 HA	0.5 HA	1.0 HA
		mg Ca·600 g ⁻¹		kg Ca·ha ⁻¹	
Quicklime (QL)	83.7	120.0	240.0	601.2	1202.4
Phosphate rock (PR)	9.0	672.0	1344.0	3366.6	6733.2
Lacustrine lime (LL)	40.7	110.0	220.0	551.1	1102.2
Silicate lime (SL)	41.1	130.0	260.0	651.3	1302.6

* Hydrolytic acidity (HA).

It may be assumed, that the capacity of the investigated soil was significantly high to adsorb additional amounts of Ca, which in turn could be expected to control and shape Cu chemistry. The observed process may be summarized consequently as follows: the relatively weak attraction of Ca by soil colloids must be compensated strictly by its high amounts in order to control efficiently high Cu concentrations [Abd-Elfatah and Wada 1981; Atanassova and Okazaki 1997].

Ca aqueous and exchangeable versus Pb bioavailable and chelated. The degree of soil pollution by Pb was significantly lower as compared to copper, whose amounts were *ca* 4 times higher. This implies therefore, that any quantitative as well as qualitative calcium effect towards Pb may be more pronounced under conditions of the current study.

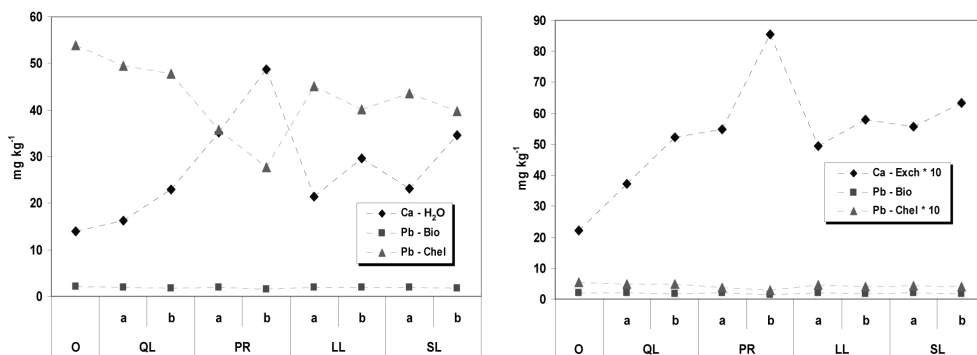
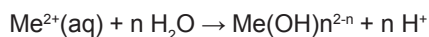


Fig. 3. Changes of Ca aqueous (Ca-H₂O) and exchangeable (Ca-Exch) levels and Pb bioavailable (Pb-Bio) and chelated (Pb-Chel.) as induced by CaBC incorporation

Rys. 3. Zmiany w ilości Ca wodnorozpuszczalnego (Ca-H₂O) i wymiennego (Ca-Exch) oraz Pb biodostępnego (Pb-Bio) oraz schelatowanego (Pb-Chel.) pod wpływem CaBC

Amounts of Pb bioavailable (Pb – Bio) as illustrated in the Fig. 3 explicitly show, that both Ca forms i.e., water extractable (Ca-H₂O) and exchangeable (Ca-Exch) efficiently controlled Pb chemistry in the investigated soil. This effect proceeded irrespective of the rates and the type of CaBC incorporated. Lead is reported to exhibit high affinity for most soil functional groups [McBride 1989; Diatta 2002] as a result of small hydrated radius (0.401 nm, electronegativity = 2.33) which in turn creates suitable conditions for electrostatic and inner-sphere surface complexation reactions [Rawat et al. 1990]. Processes involved in Pb sorption should be of two basic types: specific and nonspecific exchange reactions particularly. It was demonstrated by Schulthess and Huang [1990], that the first degree of hydrolysis of Pb²⁺ ions (Pb²⁺ → PbOH⁺) occurs at pH = 5.90. According to Altin et al. [1999], in neutral to alkaline soil conditions, amounts of hydrated metals at the first degree of hydrolysis increase, which simultaneously enhances metal adsorption/retention. The following reaction is generally suggested:



Most of soil solutions pH (Fig. 1) fluctuated between 5.5 and 6.2, particularly in treatments with phosphate rock (PR). Therefore it can be expected, that significant concentrations of Pb²⁺ may potentially undergo hydrolysis process to generate PbOH⁺ ions preferentially adsorbed over Pb²⁺ ones as pointed out by some researchers [Sauvé et al. 1998b].

This explains the complex role of Ca in processes leading to the mitigation of heavy metals, copper and lead among others.

Copper and lead mitigation: $\frac{Ca_{Exch}}{Cu_{Chel.}}$ and $\frac{Ca_{Exch}}{Pb_{Chel.}}$ ratios conceptual approach.

As reported above, exchangeable calcium and chelated copper as well as lead are those forms, which strongly interact and hence play the decisive role. Therefore any quantitative-based ratios should be of valuable information for classifying CaBC (Ca basically) in terms of their effect in controlling Cu and Pb in the soil. From data reported in Table 5, it appeared that the amounts of soil-born exchangeable calcium i.e., before CaBC incorporation, were not in position to alleviate the negative effect of Cu and Pb.

Table 5. Ratios of exchangeable Ca to chelated Cu and Pb for the particular treatments

Tabela 5. Stosunki Ca wymiennego do schelatowanych Cu i Pb dla poszczególnych obiektów

Calcium-bearing compounds (CaBC)	CaO (%)	0.5 HA*	1.0 HA	0.5 HA	1.0 HA
		$\frac{Ca_{Exch}}{Cu_{Chel.}}$		$\frac{Ca_{Exch}}{Pb_{Chel.}}$	
Control	–	0.40		4.09	
Quicklime (QL)	83.7	0.76	1.23	7.53	10.92
Phosphate rock (PR)	9.0	1.33	2.73	15.30	30.91
Lacustrine lime (LL)	40.7	1.12	1.51	10.96	14.41
Silicate lime (SL)	41.1	1.28	1.85	12.78	15.95

* Hydrolytic acidity (HA).

This is decidedly shown by the significantly low ratios values, 0.40 and 4.09 for $\frac{Ca_{Exch}}{Cu_{Chel.}}$ and $\frac{Ca_{Exch}}{Pb_{Chel.}}$, respectively. Tentative calculations have revealed, that the targeted ratio for efficient mitigation of Cu and Pb effects under conditions of this study vary between 11 and 15. None of the tested CaBC treatments has revealed such evidence towards copper, particularly. This means that the levels of Ca incorporated on the basis of hydrolytic acidity (HA) were far not sufficient. Therefore a potential phytotoxicity of Cu ions may be fully expected, contrarily to Pb, where only the control and QL treatment were found inappropriate for plant growth.

4. CONCLUSIONS

1. The incorporation of CaBC induced both pH changes and led to a raise in the content of labile Ca fractions accordingly to CaBC type. It should be decidedly mentioned that pH varied along with CaBC rates, i.e., 0.5 HA and 1.0 HA and reached its highest value ($pH_{CaCl_2} = 6.2$) in the treatment receiving phosphate rock (PR) at 1.0 HA.
2. The level of Ca water extractable (Ca-H₂O) was sufficient enough to control only active Cu forms, hence to reduce their resorption to the soil phase, irrespective of CaBC rates.

The evaluation made on the basis of Ca exchangeable (Ca–Exch) outlined the specific role of exchangeability processes in controlling quite the whole level of both Cu bioavailable (Cu–Bio) and Cu chelated (Cu–Chel) for all CaBC treatments.

3. Amounts of Pb bioavailable (Pb–Bio) explicitly show, that both Ca water extractable (Ca–H₂O) and exchangeable (Ca–Exch) efficiently controlled Pb chemistry in the investigated soil. This effect proceeded irrespective of the rates and the type of CaBC incorporated.
4. Tentative calculations have revealed, that the ratios $\frac{Ca_{Exch}}{Cu_{Chel}}$ and $\frac{Ca_{Exch}}{Pb_{Chel}}$ used for evaluating the efficient mitigation of Cu and Pb effects varied between 11 and 15. None of the tested CaBC treatments has revealed such evidence towards copper, particularly. This means, that the levels of Ca incorporated on the basis of hydrolytic acidity (HA) were far not sufficient.
5. The observed Ca *versus* Cu and Pb interactions may be summarized consequently as follows: the relatively weak attraction of Ca by soil colloids must be compensated strictly by its high amounts in order to control efficiently high Cu concentrations.

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