

Original papers

MUTUAL Cu, Fe AND Mn SOLUBILITY CONTROL UNDER DIFFERENTIATED SOIL MOISTURE STATUS

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Abstract

The effect of three different moisture statuses, i.e., 150, 200 and 300% FWC (Field Water Capacity) on copper (Cu), iron (Fe) and manganese (Mn) solubility and solution activity was investigated on soil samples characterised by different levels of copper contamination. Soils (200 g) were weighted into polyethylene containers (500 cm³) and amounts of bi-distilled water were properly added to reach the targeted moisture status of 150, 200 and 300% of the FWC. The incubation was held under laboratory conditions at the temperature of 19-20°C for a period of 30 days. Supernatants (10 cm³) were collected at given intervals of time, filtered and analysed for pH (potentiometrically) as well as for Cu, Fe, and Mn (spectrophotometrically).

It was found that the activity of Cu²⁺ ions decreased gradually with increasing pH of the solution, irrespective of the moisture status and that this process was more pronounced for 150 and 200% than for 300% FWC. The activity of Fe varied in a narrow range i.e. -5.0 and -6.0 mol_cdm⁻³ and was related to pH changes (in the range 4.0-7.5). The impact of increased moisture status on the solubility process was less pronounced. Further studies should be undertaken in order to elucidate such Fe behaviour. Manganese solution activity varied mostly between - 4.0 and -7.0 mol_cdm⁻³, and was found to be less sensitive to pH changes. But it must be pointed out that the effect of high pH on the increase of Mn activity was limited, which implied that Mn²⁺ activity was moisture-dependent, basically. Care should be taken to avoid any submersion of soils subjected to contamination or pollution by trace metals, since any excess of stagnant water (anoxic conditions) leads to increased solubility and simultaneous activity of trace metals in the solution. This process is greatly strengthened by significant amounts of soil-born Fe and organic matter.

Key words: copper, iron, manganese, solubility, solution pH, metal activity, soil moisture.

WZAJEMNA KONTROLA ROZPUSZCZALNOŚCI Cu, Fe I Mn W WARUNKACH ZRÓŻNICOWANEGO UWILGOTNIENIA GLEBY

Abstrakt

W pracy przedstawiono wpływ trzech różnych stanów uwilgotnienia gleby, tzn. 150, 200 i 300% PPW (polowej pojemności wodnej), na dynamikę rozpuszczalności oraz aktywność miedzi (Cu), żelaza (Fe) i manganu (Mn) w glebach o zróżnicowanym stopniu zanieczyszczenia miedzią. Próbkę gleb o masie 200 g umieszczono w polietylenowych pojemnikach (500 cm³), do których dodano odpowiednią ilość wody podwójnie destylowanej w celu zapewnienia właściwej wilgotności, tj. 150, 200 i 300% PPW. Zawartość pojemników inkubowano w warunkach laboratoryjnych w temp. 19-20°C przez okres 30 dni. W wyznaczonych odstępach czasu pobrano roztwory z gleby (10 cm³), przesączono i oznaczono w nich pH (potencjometrycznie) oraz Cu, Fe i Mn (spektrofotometrycznie).

Wykazano, że aktywność jonów Cu²⁺ malała stopniowo wraz ze wzrostem pH roztworów, niezależnie od stanu uwilgotnienia, z tym że ten proces zaznaczył się bardziej w przypadku 150 i 200% PPW w porównaniu z 300% PPW. Aktywność Fe wahała się w wąskim przedziale, tzn. -5.0 i -6.0 mol_cdm⁻³, i zależała od zmian pH między 4,0 a 7,5. Ponadto, należy zaznaczyć, że wzrost uwilgotnienia na jego rozpuszczalność był słabo zaznaczony. Dalsze badania powinny być przeprowadzone w celu wyjaśnienia takiego zachowania żelaza. Aktywność manganu w roztworze wahała się między -4,0 a -7,0 mol_cdm⁻³ i była mniej wrażliwa na zmiany pH. Należy podkreślić, że wpływ wysokiego pH na wzrost aktywności Mn był ograniczony, co oznacza tym samym zależność aktywności jonów Mn²⁺ od uwilgotnienia gleby. Należy ostrożnie postępować z glebami zanieczyszczonymi lub skażonymi pierwiastkami śladowymi w celu uniknięcia ich zatapiania, gdyż nadmiar stojącej wody (warunki beztlenowe) prowadzi do wzrostu rozpuszczalności i jednocześnie aktywności tych metali w roztworze. Ten proces jest zdecydowanie silniejszy w warunkach występowania znacznych ilości Fe i materii organicznej.

Słowa kluczowe: miedź, żelazo, mangan, rozpuszczalność, aktywność metali, uwilgotnienie gleby.

INTRODUCTION

As a result of increased input from industry, traffic and agriculture, the average trace metal content in soils worldwide is increasing considerably. This has become a major point of concern during the last few decades since metal contents have reached potentially toxic levels in urban as well as agricultural soils in the vicinity of mining and metallurgical industries, thus creating areas frequently depicted as *hot spots* (HELIOS-RYBICKA 1996). Metal solubility, toxicity and transfer away from the contamination point depend on many soil chemical and physical properties. However, risk assessment is still entirely based on the total soil metal content. Ecotoxicological studies revealed, however, that metal speciation in the solution phase is one of the key factors that regulate metal toxicity in soil subjected to contamination

(RENNER 1997, MEIBNER et al. 2008). Hence, metal toxicity (bioavailability) appears to be related closely to free metal activity in solution instead of the total soil metal content in the solid phase (HARE, TESSIER 1996). Consequently, changes in soil chemical conditions that control the concentration and free metal activity (pH, solubility, desorption) induce changes in the availability without apparent changes in the total metal content (SPURGEON and HOPKIN 1996, MCBRIDE et al. 1997). Soil parameters that affect metal solubility and speciation in the soil solution include moisture status, total metal content, pH, organic matter and clay content.

Soils may contain appreciable amounts of iron and manganese, which under conditions of water excess, activate redox processes of soils. GOTOH and PATRICK (1972, 1974) studied the distribution of different forms of Fe and Mn in water logged soil over a wide range of closely controlled potential and pH conditions. These researchers reported that increases in water-soluble and exchangeable iron were favoured by a decrease in both redox potential and pH. Moreover, they found that at pH 5 almost all of the soil manganese was converted from reducible into water-soluble plus exchangeable. SCHWAB AND LINDSAY (1983) plotted the Fe^{2+} activity as a function of pH and reported that the Fe^{3+} activity is controlled by FeCO_3 (siderite) at pH below 8 and by $\text{Fe}_3(\text{OH})_8$ (ferrosic hydroxide) at pH above 8. According to HASSAN (1990), the solubility of manganese was controlled by MnO_2 at the beginning of the flooding period, whereas MnCO_3 (rhodochrosite) controlled this solubility up to 15 weeks.

Some reports have pointed out that contaminated soils are becoming frequently subjected to flooding (HELIOS-RYBICKA and ADAMIEC 2001, SAHA and MANDAL 2000, KELLY et al. 2003).

This is of great concern since specific site contaminants are potentially dispersed into neighboring areas, thus creating some environmental threat. The monitoring of solubilized metals and their concentrations under flooding conditions is still a matter of great challenge due to several constraints (instability of bulk waters, continuous inputs of suspended organic and mineral particles, uncontrolled dilutions rates, etc.). Comprehensive investigations dealing with soil moisture status and how water excess induces the solubility and controls metal ion activity in the soil solution are still absent from scientific literature. Little is known about the effect of anoxic conditions on metal solubility and the subject has been less intensively studied because of experimental difficulties. With an increase in soil moisture, the solution concentration of most cationic metals and calcium tentatively increases due to strengthened solubility and desorption. But the commonly observed rise in solution pH leads to a decrease in metal concentration and ion activity in the solution due to adsorption processes (KABATA-PENDIAS 1993, DIATTA et al. 2004).

The purpose of the current study was to evaluate the impact of three soil moisture statuses, i.e., 150, 200 and 300% FWC (Field Water Capacity)

on mutual Cu, Fe, and Mn solubility and solution activity control of four soils under different levels of metal contamination, mainly that of copper. Another aim was to elucidate the effect of equilibrium pH on the activity of solubilized metals.

MATERIAL AND METHODS

Physical and chemical soil properties

Soil samples used in this study were collected (0-20 cm depth) from lands subjected to the Głogów Copper Smelter activity (N 51°41'03" and E 15°57'12", Poland). Prior to basic analyses, they were air-dried and crushed to pass through a 1 mm mesh sieve. Particle size distribution was determined according to the method of Bouyoucos-Casagrande modified by PRÓSZYŃSKI (rok). Organic carbon was determined by the dichromate wet oxidative method of Tiurin, in which soil organic carbon is oxidized with potassium dichromate in the presence of sulphuric acid. The unreacted potassium dichromate was back titrated with ferrous sulphate. Soil pH (in 0.01 mole CaCl_2) was potentiometrically measured in the soil solution (ratio 1:5), according to the Polish Standard (1994). Total dissolved solids (TDS) were determined conductively in supernatants collected during the incubation time and additionally in water extracts (soil/water ratio 1:5) at the end of the study. The specific surface area (SSA) was estimated by the ethylene glycol monoethyl ether (EGME) method as reported by CARTER et al. (1986). The cation exchange capacity (CEC) of the soils at their initial pH was determined by the barium chloride (0.10 mole BaCl_2) method as described by HENDERSHOT and DUQUETTE (1986), whereas the summation of exchangeable alkaline cations and acidity was done according to THOMAS (1982).

Experimental design and soils incubation

Prior to establishing the experiment, the water retention capacity of the soils was determined by the method of the capillary rise of soil moisture (LITYŃSKI et al. 1962). The method consists of filling in with a weighted soil a weighted metallic cylinder (diameter = 4 cm; length = 17 cm) supplied with a sieve located at 1 cm from the bottom of the cylinder, which is immersed in a crystallizer containing distilled water as shown below (Figure 1).

Once moisture appears on the surface of the soil, the cylinder containing the moist soil is taken out of the crystallizer and weighted after 1/2 to 1 hour. The difference between the moist and dry soil gives the amount of water the soil is able to retain.

The field water capacity (FWC) of soils used for the current experiment was as follows: 22.5% (No. 1 – slightly loamy sand); 31.0% (No. 2 – light

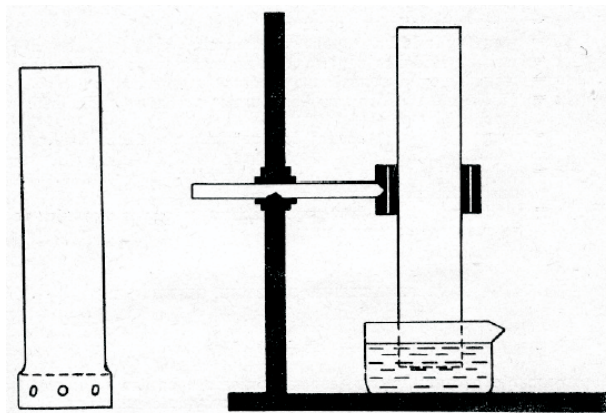


Fig. 1. Metallic cylinder and equipment used for the determination of the Field Water Capacity (FWC) of soils

loamy sand); 36.9% (No. 3 – light loamy sand) and 47.5% (No. 4 – silty medium loam). Soils (200 g) were weighted into polyethylene containers (500 cm³) and amounts of bidistilled water were properly added to reach the targeted moisture status of 150, 200 and 300% of the FWC. The incubation was held under laboratory conditions at the temperature of 19-20°C for a period of 30 days. All objects were duplicated.

Supernatant collection and analysis

Supernatants (10 cm³) were collected at given intervals of time, filtered and analysed for pH (potentiometrically) as well as for Cu, Fe, and Mn by the FAAS method (Flame Atomic Absorption Spectrophotometry, Varian 250 plus). The same amounts of bidistilled water (i.e., 10 cm³) were added back to polyethylene containers in order to keep the moisture status constant. Computation of the results and processing of the graphs were performed by the use of Excel[®] sheet facilities.

RESULTS AND DISCUSSION

Some of the properties of the four soils used in the current study are listed in Table 1. The soil reaction was mostly acidic to *ca* neutral and varied within the range 4.3-6.5, in contrast to the organic carbon content, which ranged widely from 2.1 to 31.5 g·kg⁻¹. The cation exchange (CEC) of soils varied accordingly from 11.3 to 29.7 cmol(+) kg⁻¹, which implied that the buffer properties were sufficiently developed and could probably affect

Table 1

Selected physical and chemical properties of investigated soils

Soil No.	Particle size (mm)			pH (0.01M CaCl ₂)	C-org. (g·kg ⁻¹)	SSA ^a (m ² ·g ⁻¹)	CEC ^b cmol (+) kg ⁻¹	Metals extracted by 6M HCl (mg·kg ⁻¹)		
	sand (1.0-0.05)	silt (0.05-0.002)	clay (<0.002)					Cu	Fe	Mn
1 ^c	680	250	70	4.3	2.1	7.8	11.3	45.5	1085.3	1118.3
2	660	220	120	5.6	11.7	9.8	14.1	2041.3	2503.7	223.7
3	700	180	120	6.5	14.7	19.9	23.9	114.3	3484.3	247.5
4	390	300	310	5.4	31.5	68.3	29.7	10710.0	18180.0	3555.0

a: specific surface area; *b*: cation exchange capacity; *c*: 1 – slightly loamy sand; 2 – light loamy sand; 3 – light loamy sand; silty medium loam

the solubility process. This could be related to a rather high level of both silt and clay contents, whose amounts ranged between 300 and 610 $\text{g}\cdot\text{kg}^{-1}$. The content of metals as listed in Table 1 varied significantly, e.g. from 45.5 up to 10 710 $\text{mg}\ \text{kg}^{-1}$ in the case of copper (Cu). According to the guidelines elaborated by KABATA-PENDIAS et al. (1993), copper contents can be classified as follows: Soil No. 1 – natural content (degree 0); No. 3 – slight contamination (degree II) and for soils No. 2 and No. 3 – strong contamination (degree V) and pollution (degree V), respectively. Under conditions of water excess (submerged soils), some complex interacting geochemical reactions could be expected which would reduce or enhance the solubility, desorption, diffusion of Cu, and interestingly iron (Fe) and manganese (Mn), basically (ROMKENS et al. 1996).

Copper solubility (activity) and solution pH at 150, 200 and 300% FWC

While most studies in environmental soil chemistry have focused on the adsorption or sorption of ions and molecules on soils, the solubility/desorption process is less studied but equally important. This is particularly true for soils that are subjected to (i) contamination or already contaminated and (ii) under conditions of temporary or permanent water excess. The results illustrated in Figures 2a, 3a, 4a for the respective moisture status 150, 200, 300 % FWC (Field Water Capacity) report the course of copper (Cu^{2+}) solubility expressed in terms of Cu^{2+} activity *versus* the equilibrium solution pH for the representative soils (No. 1, No. 2, No. 3 and No. 4). According to BARROW et al. (1981) and DIMIRKOU et al. (2002), the first Cu hydrolysis constant (pK_1) is about 8.0, (i.e., 7.2-8.1), which means that copper ions in the soil solution do not easily undergo hydrolysis process, which practically implies that the activity of Cu^{2+} ions should be significantly high throughout the pH values up to 8. This is particularly important since under a high contamination level and elevated moisture status, copper solubility, mobility and possible toxicity may gradually rise. Copper solubility shown in Figures 2a, 3a, 4a suggests that several ions and compounds may control its dynamics and activity in the soil solution. Most studies over the pH-dependence of copper solubility indicated that solubility and activity decreased with increasing pH (MA, DONG 2004). This can be illustrated by the copper solubility diagram reported by KABATA-PENDIAS and PENDIAS (1999), from which it could be deduced that up to pH *ca* 9.0, Cu^{2+} , CuOH^+ , CuO , $\text{Cu}_2(\text{OH})_2^{2+}$ and even CuCO_3 are the potential Cu forms and ions inducing copper solubility and solution activity. Some years ago HARTER (1983) assessed that at pH < 6.0, copper in solution was virtually present ($\approx 98\%$) as Cu^{2+} and at pH 4.0 about 0.01% of the copper ions should be present as CuOH^+ . This percentage may increase 10-fold as the pH is raised to 5.0. Thus, the effect of pH in depressing the activity of free ions in the soil solutions could also be attributed to an increase in the pH-dependent charges of organic matter and also of aluminium, iron and manganese oxides (ABD-ELFATTAH, WADA 1981, JARVIS 1981,

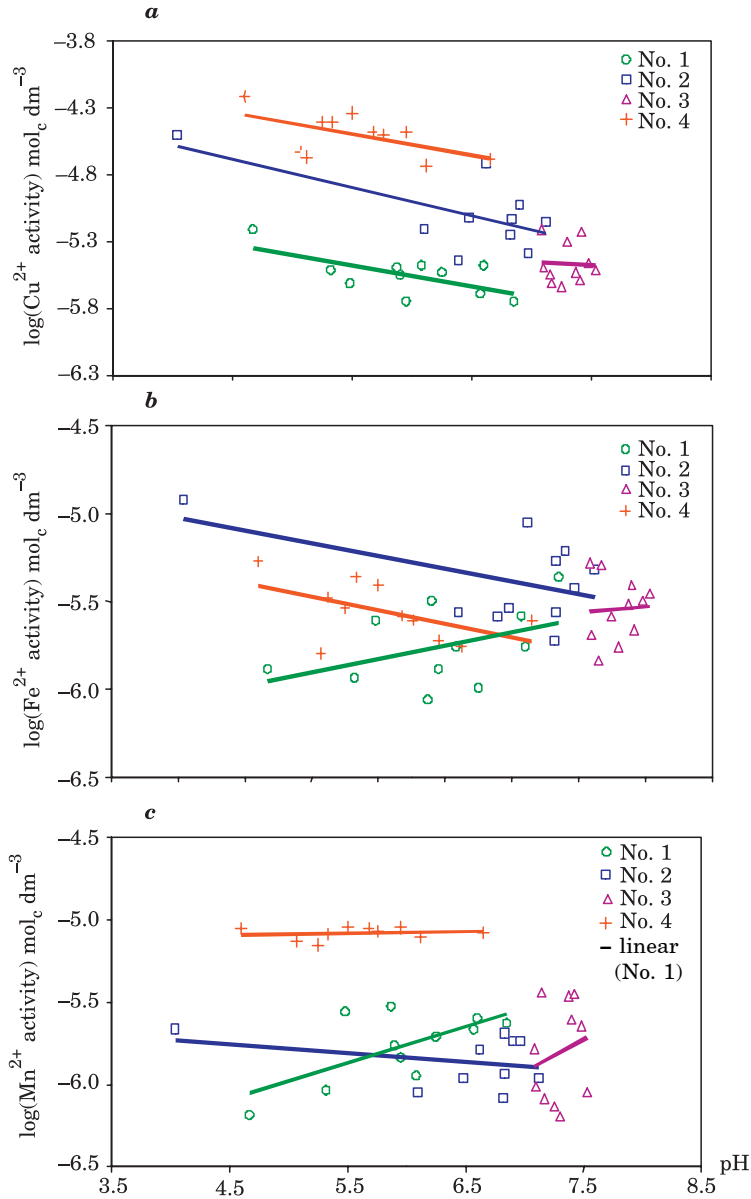


Fig. 2: Copper (a), iron (b) and manganese (c) activities in supernatants pH at 150% FWC (Field Water Capacity) for investigated soils (No. 1, No. 2, No. 3 and No. 4)

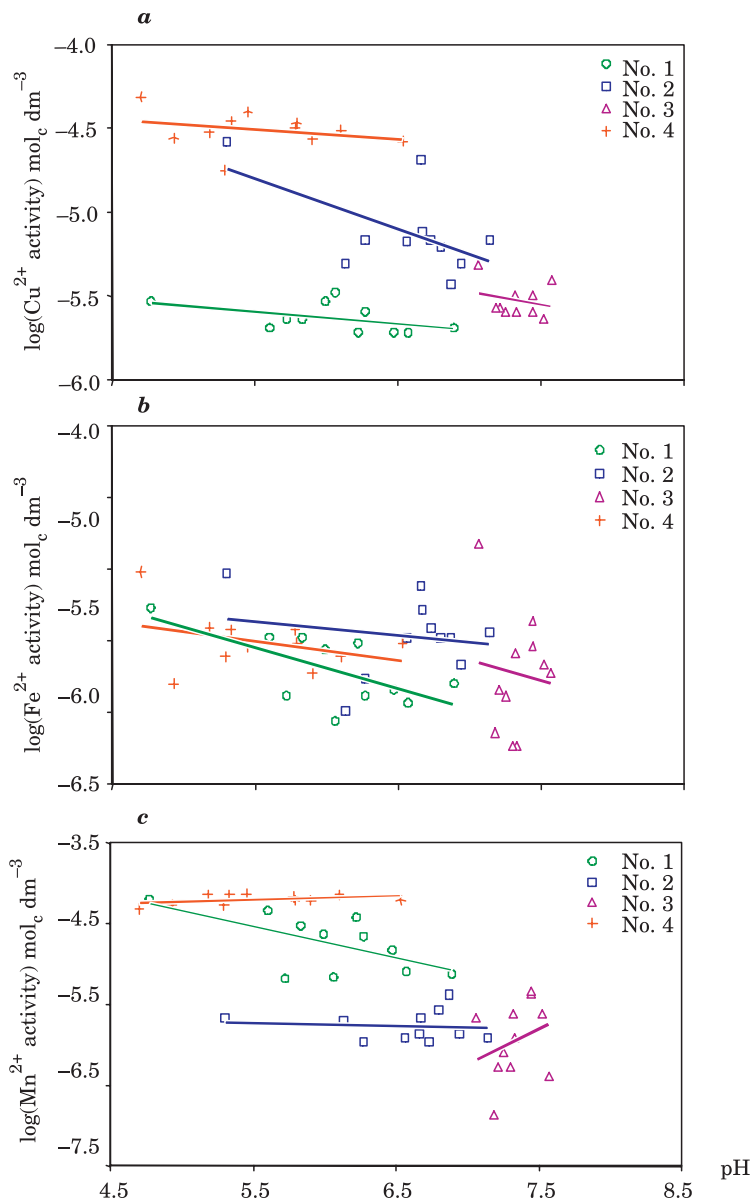


Fig. 3: Copper (a), iron (b) and manganese (c) activities in supernatants pH at 200% FWC (Field Water Capacity) for investigated soils (No. 1, No. 2, No. 3 and No. 4)

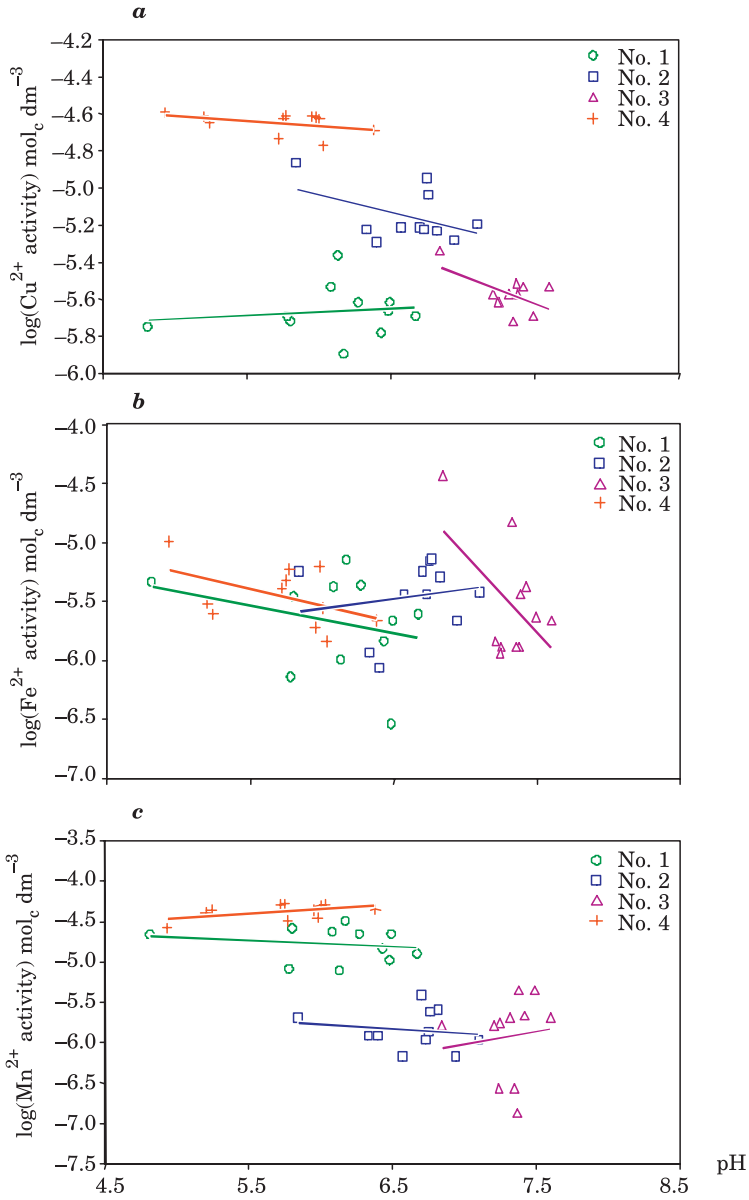
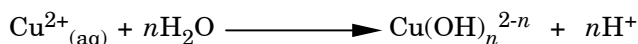
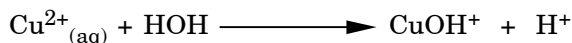


Fig. 4: Copper (a), iron (b) and manganese (c) activities in supernatants pH at 300% FWC (Field Water Capacity) for investigated soils (No. 1, No. 2, No. 3 and No. 4)

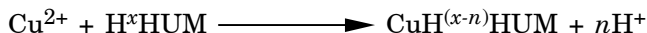
RITCHIE, JARVIS 1986, KING 1988). Therefore, if we assume that an increase of pH > 5.7 may lead to over 1.0% of copper ions hydrolyzing in a solution (SMITH, MARTELL 1976), then the mechanism that could be involved in the transformation can be presented as follows:



that is at $n = 1$, the hydrolysis may concern:



The activity of Cu^{2+} ions decreased gradually with an increasing pH of the solution, irrespective of the moisture status. This trend was more pronounced for the 150 and 200% than for the 300% FWC, for which the activity of Cu^{2+} in soil No. 1 increased slightly, mainly in the pH range from 4.5 to 6.5. Such copper behaviour was in close agreement with the fact that in extremely diluted media the activity of ions increases and this reaction is activated by a relatively low solution pH. The impact of pH on copper activity in the case of the soils No. 3 deserves particular attention. As listed in Table 1, this soil was characterised by the highest pH value (6.5) and acid soluble copper amount of $114.3 \text{ mg} \cdot \text{kg}^{-1}$. Theoretically, copper activity in this medium could be expected to be similar to that observed for soil No. 1, since the acid soluble Cu amount was only 3-fold higher. Unexpectedly and interestingly, the values of the $\log(\text{Cu}^{2+})$ fluctuated within a similar range (from -4.3 to $-5.8 \text{ mol}_c \text{ dm}^{-3}$) except that more than 95% of all Cu activity values were comprised within the pH interval 7.0-7.5, irrespective of the soil moisture status. At such high pH, the dissolution of organic compounds may take place and Cu complexation directly reduces Cu activity levels according to the following reaction:



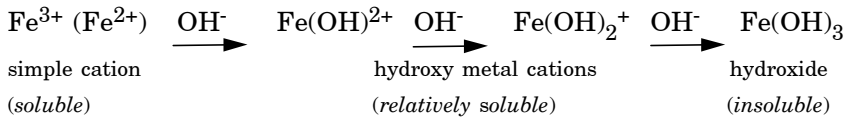
where HUM expresses the organic compound.

Copper forms stable complexes with dissolved organic compounds in solution and therefore higher levels will reduce the free ionic Cu^{2+} activity. According to ROMKENS and DOLFING (1998) at pH levels higher than 5 usually more than 99% of the total dissolved copper concentration is bound to dissolved organic compounds, which by developing their net negative surface charge acted as efficient carriers participating in copper solubility and mobility in soils, particularly under high moisture status. Copper activity of highly contaminated and polluted soils, i.e. No. 2 and No. 4, increased gradually along with an increasing moisture status. This could be attributed to the dilution effect, which practically strengthens Cu dissolution process and. Additionally, to the rise of pH along with an increase in the moisture

status, as shown in Table 2. Similar observations were pointed out by CHUAN et al. (1996), SAHA and MANDAL (2004), KELLY et al. (2003) and WANG and STAUNTON (2005), who stated that soil submersion (flooding) rapidly induced strongly reducing conditions, with a consequent increase in pH, which acts in a dual way: on the one hand, it tends to lower Cu activity in the solution and, on the other hand, simultaneously increases Cu solubility throughout its complexation by pH-dependent dissolution of organic compounds.

Iron (Fe) and Mn solubility (activity) versus solution pH at 150, 200 and 300% FWC

The solubility and further activity of Fe and Mn in soil solutions proceed throughout redox processes, which are practically controlled by the soil moisture status, the length of anoxic conditions (occurrence of ferric – Fe³⁺ and ferrous – Fe²⁺ compounds) and simultaneously mediated by pH, whose changes from acidic to alkaline reaction induce the following reactions of Fe with hydroxide ions:



As shown in Figures 2b, 3b and 4b respectively for the moisture status 150, 200 and 300% FWC (Field Water Capacity), Fe activity varied in a narrow range i.e. -5.0 and -6.0 mol_cdm⁻³, which implied that Fe transformations under current anoxic conditions could be related to more factors than to moisture status, basically. Solution reaction (pH) was one of the fundamental factors which decidedly influenced Fe solubility and activity. According to ATTA et al. (1996) the Fe reduction rate increased along with decreasing pH and was more pronounced at pH significantly below 7.0. This finding agrees well with the results illustrated in Figures 2b, 3b and 4b, which report the gradual decrease of Fe activity with increasing pH mainly for soils No. 1, No. 2 and No. 4 for pH values varying roughly between 5.55 and 6.63 (Table 2). The data included in Table 2 unequivocally show that anoxic conditions induced a slight rise in pH, which in turn could act as a limiting factor for Fe activity. This confirms that the more acidic the soil becomes, the more ferrous ions build up. As a consequence, larger ferrous iron concentrations after submergence are to be expected in more acidic soils since the hydrogen ion activity increases. This results in more iron being released from the crystalline or amorphous forms, which are present in the soil as free iron oxides, as earlier pointed out by PONNAMPERUMA (1986). Interestingly, pH changes recorded in the case of soil No. 3 (Table 2) deserve special attention, since they varied in a specifically close range i.e. 7.30-7.33, respectively for the soil moisture status 150-300% FWC. Importantly, Fe activity occurred at solution pH *ca* 7.5 (Figures 2b, 3b and 4b),

Table 2

Mean concentrations of soluble Cu and pH changes of soils incubated for 30 days at 150, 200 and 300% FWC (Field Water Capacity)

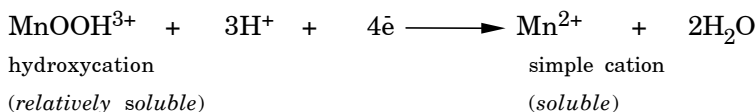
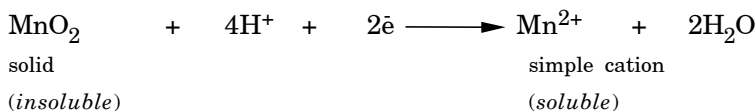
Soil No.	Moisture status (% of FWC – Field Water Capacity)					
	150		200		300	
	Cu concentrations (mg·dm ⁻³) and solution pH					
	Cu	pH	Cu	pH	Cu	pH
No. 1*	0.234 ± 0.094	5.96	0.186 ± 0.039	6.04	0.178 ± 0.064	6.10
No. 2	0.773 ± 0.641	6.46	0.724 ± 0.564	6.55	0.578 ± 0.222	6.63
No. 3	0.283 ± 0.108	7.30	0.231 ± 0.065	7.33	0.216 ± 0.055	7.42
No. 4	2.603 ± 0.985	5.55	2.489 ± 0.624	5.54	1.772 ± 0.216	5.72

*1 – slightly loamy sand; 2 – light loamy sand; 3 – light loamy sand; 4 – silty medium loam

which implied that under alkaline conditions Fe solubility may occur but with a slightly lower Fe activity. This could be attributed to the formation of less soluble compounds such as hydroxides, and – with higher pH – carbonates. This observation is in line with the results reported by SCHWAB and LINDSAY (1983), who plotted the Fe²⁺ activity as a function of pH and pointed out that Fe³⁺ activity was controlled by FeCO₃ (siderite) at pH below 8.0 and by Fe₃(OH)₈ (ferrosic hydroxide) at pH above 8. Based on these statements, it can be deduced that Fe activity was less dependent on the moisture status but more on pH changes, which controlled the extent of Fe solubility. Siderite was most probably the main compound regulating Fe concentrations in the water solution of soils, since the pH did vary up to ca 7.5. The fact that Fe activity did not vary much (practically between –5.0 and –6.0 mol_cdm⁻³) for solution pH between 4.0 and even 7.5 was strikingly unexpected. Further studies should be undertaken in order to elucidate this Fe behaviour.

The geochemical transformation of manganese (Mn) is by essence more complex than in the case of iron, due to the fact that the spectrum of Mn redox potential involves several steps i.e. from Mn⁷⁺ up to Mn²⁺ (KABATA-PENDIAS, PENDIAS 1999). According to BRADY (1984) in well-oxidized soils the manganic (Mn⁴⁺) form is dominating whereas under waterlogged conditions the reduced manganous form (Mn²⁺) prevails. The results reported in Figures 2c, 3c and 4c for the moisture status 150, 200 and 300% FWC (Field Water Capacity), respectively, are basically quantitative, therefore the Mn²⁺ was considered to represent the overall reduced forms of Mn under anoxic conditions of the current trial. Manganese solubility expressed in terms of its solution activity (logMn²⁺) varied mostly between –4.0 and –7.0 mol_cdm⁻³, irrespective of the effect of the moisture status and was found to be significantly sensitive to pH changes. On the other hand manganese solubility depended additionally on the soil-born manganese content (extracted in

6 moles HCl), since soils characterized by highest content (i.e. No. 1 and No. 4, Table 1) exhibited higher Mn activity, which gradually decreased along with the pH increase as observed for the soil No. 1. Interestingly, manganese solubility and activity course developed in the case of the soil No. 4, seemed to be more complex and may not be related to its soil-born content solely. A slight increase in Mn activity with a raise of pH was even unexpected, since the equilibrium solution pH of this soil did not exceed the pH value of 6.5. Two assumptions may be formulated: i) the extremely high Fe content detected in the soil No. 4 could be a substantial source of electrons, which acted as efficient Mn reducing agents in one hand and ii) the significantly high organic matter content ($31.5 \text{ g}\cdot\text{kg}^{-1}$) as a potential precursor of electrons, which could additionally strengthen Mn reduction, on the other hand. This finding is in line with the data reported by ATTA et al. (1996) who pointed out that the enrichment of submerged soils with organic matter induced an increase in the water-soluble Mn fractions by simultaneously decreasing the content of the residual Mn pool. According to HASSAN (1990), the solubility of manganese was controlled by MnO_2 at the onset of flooding, whereas the MnCO_3 (rhodochrosite) controlled this solubility in prolonged periods of water logging, i.e., up to 15 weeks. In the current study, the suggested Mn solubility and activity could have been mediated by the following reactions:



Manganese geochemical transformations observed for soil No. 3, as illustrated in Figures 2c, 3c and 4c, operated basically within pH ranges 7.0 and 7.6, similarly to those reported earlier for Fe. Interestingly, Mn^{2+} activity in a soil solution tended to increase along with pH increase, in contrast to the trends reported in many studies. Besides, it acted opposite to Fe. At such slightly alkaline pH of the solution, the hydroxy manganese forms could prevail, hence controlling the solubility as well as activity processes. The high-pH inducing manganese solubility and activity observed in the current study, which was characteristic for the slightly alkaline soil No. 3, agreed with the data reported by ATTA et al. (1996) and WANG and STAUNTON (2005). But it should be pointed out that the effect of high pH on the increase of Mn activity was limited, which implied that this activity was basically moisture-dependent. The occurrence of MnCO_3 (HASSAN 1990) as a manganese solubility/activity controlling factor was less probable under the current experimental conditions.

CONCLUSIONS AND STATEMENTS

1. The activity of Cu^{2+} ions decreased gradually with increasing pH of the solution, irrespective of the moisture status. This trend was more pronounced for the 150 and 200% than for 300% FWC (Field Water Capacity). This was attributed to the dilution effect, which practically strengthened the Cu dissolution process and, additionally, to the rise of pH along with the increased moisture status.

2. The activity of Fe varied in a narrow range i.e., -5.0 and $-6.0 \text{ mol}_c\text{dm}^{-3}$, which implied that its transformations under current anoxic conditions was related more strongly to the solution pH than to the moisture status. The fact that the Fe activity did not vary greatly for a solution pH between 4.0 and 7.5 was strikingly unexpected. Further studies should be undertaken in order to elucidate such Fe behaviour.

3. Manganese solubility and solution activity varied mostly between -4.0 and $-7.0 \text{ mol}_c\text{dm}^{-3}$, and was found to be less sensitive to pH changes. But it should be decidedly pointed out that the effect of high pH on the increase of Mn activity was limited, which implied that Mn^{2+} activity was moisture-dependent, basically.

4. Care should be taken to avoid any submersion of soils subjected to contamination and polluted by trace metals, since any excess of stagnant water (anoxic conditons) leads to increased solubility and simultaneously higher activity of trace metals in the solution. This process is evidently strengthened by significant amounts of soil-born Fe and organic matter.

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