

CHEMICAL TIME BOMB – THE POTENTIAL RISK OF HEAVY METAL POLLUTION IN SOIL

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Abstract:

On two calcareous and three non-calcareous Hungarian soils, studies were made on the effect of the partial removal of organic matter by treatment with hydrogen peroxide on the sorption and desorption of Cu ion. Sorption was investigated after adding concentrations in the 0–10,000 mg kg⁻¹ range. The two-termed Langmuir isotherm was used to describe the sorption processes, and the calculated parameters were used to interpret the processes taking place. The adsorption of metal ions was found to involve two processes, one with higher and one with lower energy. The energetic constant of the higher energy process was 2 orders of magnitude higher than that of the lower energy process. The removal of organic matter had a decisive effect on the higher energy process taking place in the low concentration range, reducing the extent of adsorption taking place with this process. This was particularly pronounced in the case of the Cu A1 parameter, i.e. for the maximum amount of Cu which could be adsorbed on non-calcareous soils. The buffering capacity calculated for the C0 equilibrium concentration characterises this phenomenon in a single parameter. The Cu buffering capacity of non-calcareous soils, for example, dropped to a hundredth as the result of organic matter removal with hydrogen peroxide. Desorption studies carried out using the hot water percolation (HWP) method confirmed the role of soil organic matter in the adsorption of heavy metals. Not only were fewer heavy metal ion (Cu) adsorbed after the removal of organic matter, but the adsorption energy of the ions was also far smaller than prior to organic matter removal. On non-calcareous soils more heavy metal ions were desorbed from the fewer adsorbed ions in all cases than prior to organic matter removal.

Keywords:

Sorption, desorption, Cu, organic matter removal

1. INTRODUCTION

Chemical time bombs have been defined as possible chains of events responding to slow environmental alterations, resulting in the delayed and sudden occurrence of harmful effects due to the mobilization of chemicals stored in soils and sediments. Awareness of chemical time bomb phenomena requires the need for broad and imaginative analysis of the long-term risks of future, present and past practices related to the accumulation of chemical wastes in the environment [1]. The properties of soils, important natural chemical sinks that can control the capacity to retain potentially toxic chemicals. These properties are termed capacity controlling properties. The input of toxic substances into the environment results in the loading of chemical sinks. The major chemical sinks are the soil and surface sediments and these have been and will be subjected to chemical loadings for decades.

A chemical time bomb can occur when a toxic chemical is mobilized because the capacity of the sink containing it is either: exceeded by an excess of toxic chemical input, or diminished due to environmental changes influencing parameters that determine the sink capacity. Analogous to the

sorption characteristics, soil retention of soil chemical by precipitation into an immobile solid phase is also affected by capacity controlling properties. Changing a soil property (e.g., redox potential or pH) can increase the solubility of a solid and thereby cause a release of a toxic chemical to the mobile aqueous phase of the soil. However, the precipitation of a toxic chemical as a solid in environment is more favourable than sorption because the dissolved concentration of the toxin will remain fairly constant regardless of the total concentration of the solid. The problem comes when the solubility of the solid is altered by a change in a chemical factor such as redox potential or pH. The feature of the curve's shape that is most important for evaluating the chemical time bomb risk. For example, it is unlikely that a heavy metal will reach a level that exceeds the soil's maximum binding capacity. But, very small increases in dissolved metal concentration can make the metal dangerous to life: the shape of the isotherm at a sorbed metal concentration well below the maximum sorption capacity would be more important than the maximum capacity itself. Decreasing organic matter reduces the soil's maximum retention capacity for toxic compounds and can change the soil redox potential and drainage characteristics. Toxins might be mobilized through increased solubilisation and/or increased soil erosion.

Soils in a human environment may be polluted by heavy metals from various sources. As the result of regular pollution the heavy metal content of the soil may reach the toxic limit, while the solid phase of the soil becomes increasingly incapable of adsorbing fresh doses of heavy metals. The humus content of the soil plays a decisive role in preventing soil pollution and maintaining the buffering ability of the soil [2].

The paper discusses in what way typical Hungarian soils are able to adsorb increasing levels of toxic heavy metal pollution in the solid phase and what effect the removal of the most active component of the humus materials has on the heavy metal buffering ability of the soils.

2. MATERIALS AND METHODS

Five typical Hungarian soils were used in the adsorption and desorption studies. The most important characteristics of these soils are presented in Table 1.

Table 1: Chemical and physical properties of the soils

Soil	Treatment	Clay (%)	Humus (%)	CaCO ₃ (%)	CEC (meq/100g)	pH _{H2O}
Bak	untreated	21.8	1,16	-	16.8	6.07
	organic matter removed	-	0.96	-	14.4	-
Putnok	untreated	28.0	1.50	-	20.0	5.01
	organic matter removed	-	0.51	-	20.0	-
Nyírtelek	untreated	15.5	0.94	-	10.4	6.85
	organic matter removed	-	0.45	-	9.6	-
Iregszemcse	untreated	19.3	1.70	4,5	17.6	7.48
	organic matter removed	-	1.73	-	21.6	-
Görbeháza	untreated	35.5	3.04	traces	44.9	7.07
	organic matter removed	-	2.65	-	45.7	-

The soil samples were digested with 15 % H₂O₂: 500 g soil samples were treated with 3 times 50 cm³ H₂O₂, and then evaporated to dryness on a water bath.

The pH, humus content, clay content, cation exchange capacity, hydrolytic and exchange acidity and oxalate-soluble Fe content were determined in untreated samples. The mineral composition of the soils was determined using the X-ray diffraction method.

Five g samples of soil treated with H₂O₂ or untreated were passed through a 0.2 mm sieve and placed in centrifuge tubes, to which 50 ml solutions containing various concentrations of the heavy metal ions and 2 drops of sodium chloride were added. The heavy metal concentrations were as follows:

Cu: CuSO₄, 0-50-250-500-1000-2500-5000-7500-10000 mg Cu/kg soil

The soil suspensions were shaken on a rotary shaker for 17 hours, after which they were centrifuged at 5000 rpm. The decanted solution was filtered, and the ion quantities in the solution were measured using an atomic adsorption photometer.

Two-term Langmuir equation was fitted to the measured data:

$$q = \frac{A_1 \cdot b_1 \cdot c}{1 + b_1 \cdot c} + \frac{A_2 \cdot b_2 \cdot c}{1 + b_2 \cdot c}$$

where:

q is the amount of the adsorbed heavy metal, $mg \cdot kg^{-1}$

A₁ is the maximum amount of the sorbed heavy metal of high energy, $mg \cdot kg^{-1}$

A₂ is the maximum amount of the sorbed heavy metal of low energy, $mg \cdot kg^{-1}$

b₁ is the adsorption equilibrium constant of the first process

b₂ is the adsorption equilibrium constant of the second process

c is the equilibrium concentration, $mg \cdot l^{-1}$

Desorption studies were carried out on the soil of the 1000 mg/kg treatment. For this purpose 30 g air-dry soil was brought into equilibrium with a solution containing the required quantity of heavy metal. After 17 hours of shaking, the solid and liquid phases were separated by means of vacuum filtration. The solid matter was dried to air-dryness at room temperature. Desorption was carried out by means of hot water percolation (HWP) method [3]. In order to facilitate filtration 10 g quartz sand was mixed with 30 g treated soil. In the course of desorption, 10 times 100 cm³ fractions were collected. The metal ion quantities in the solution were determined using an atomic adsorption photometer.

First order kinetic equation was fitted to the measured description data:

$$y = A(1 - e^{-kv})$$

where:

y is the amount of desorbed heavy metal, $mg \cdot kg^{-1}$

A is the maximum amount of desorbed heavy metal, $mg \cdot kg^{-1}$

K is the rate constant

V is the volume, cm³

3. RESULTS AND DISCUSSION

The results of the adsorption studies are presented in Table 2 which contain the parameters (A_1 , b_1 , A_2 , b_2) of the 2-termed Langmuir isotherm function fitted to the results of metal ion adsorption experiments carried out on treated and non-treated soils, and the buffering capacity values calculated with the function for the C_0 equilibrium concentration.

Table 2 Cu sorption on five Hungarian soils, parameters of the two-term Langmuir equations

Soil	Treatment	A_1 (mg/kg)	b_1	A_2 (mg/kg)	b_2	BC_0 (l/kg)
Bak	untreated	1008	8.4×10^{-1}	2.7×10^3	7.2×10^{-3}	866
	organic matter removed	0	-	3.7×10^3	2.7×10^{-3}	9.9
Putnok	untreated	1151	4.2×10^{-1}	2.3×10^3	9.2×10^{-3}	512
	organic matter removed	0	-	1×10^3	4.8×10^{-3}	4.8
Nyírtelek	untreated	1064	8.8×10^{-1}	1.5×10^3	1.6×10^{-2}	968
	organic matter removed	28	3.6×10^{-1}	2.6×10^3	1.8×10^{-3}	15
Iregszemcse	untreated	7323	7.7×10^{-1}	$>5 \times 10^3$	3.9×10^{-3}	$>10^3$
	organic matter removed	7315	4.7×10^{-1}	$>5 \times 10^3$	1.1×10^{-2}	$>10^3$
Görbeháza	untreated	5642	9.6×10^{-1}	$>5 \times 10^3$	4.6×10^{-3}	$>10^3$
	organic matter removed	718	2×10^{-1}	$>5 \times 10^3$	3.1×10^{-3}	173

The discussion of the results will be begun with copper, since changes in the organic matter content of the soil had the greatest effect on the adsorption of this ion. The three non-calcareous soils (in Bak, Putnok and Nyírtelek) exhibited very similar behaviour during Cu adsorption and after the removal of organic matter.

In all three soils the maximum amount of Cu adsorbed in the course of A_1 , i.e. the process with greater energy ($b_1 \sim 10^{-1}$), was much the same without hydrogen peroxide treatment, while the quantity of Cu taking part in this process when the organic matter was partially removed became practically 0, i.e. the higher energy adsorption process ceased completely.

The course of the lower energy process ($b_2 \sim 10^{-3}$) was also interesting. In two soils (Bak, Nyírtelek) the Cu quantity originally adsorbed in the first process was partially added to that adsorbed by the lower energy process, resulting in an increase in the maximum quantity of Cu adsorbed in the latter process (Figures 1 and 2).

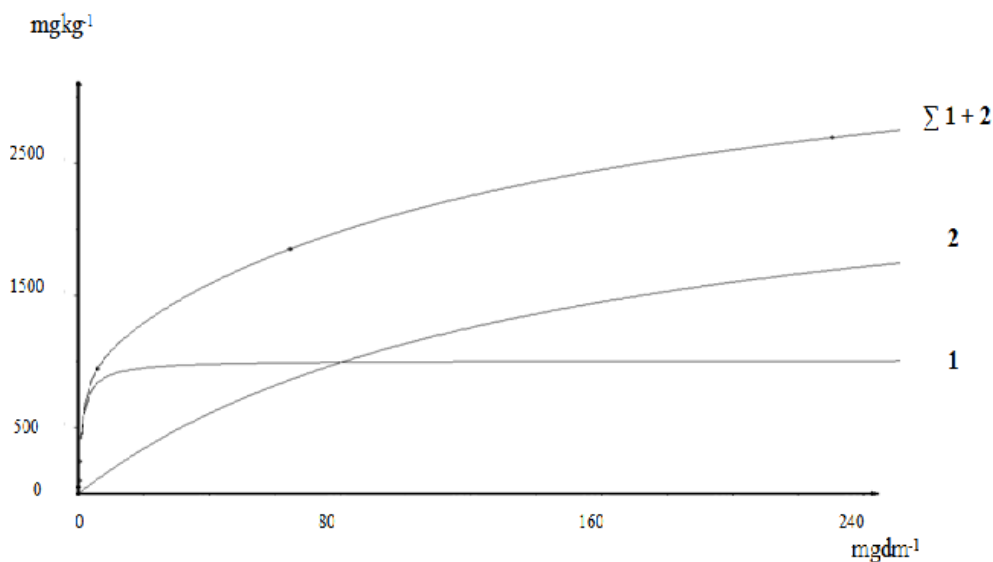


Figure 1: Cu adsorption on the untreated Bak soil
1: high energy process 2: low energy process

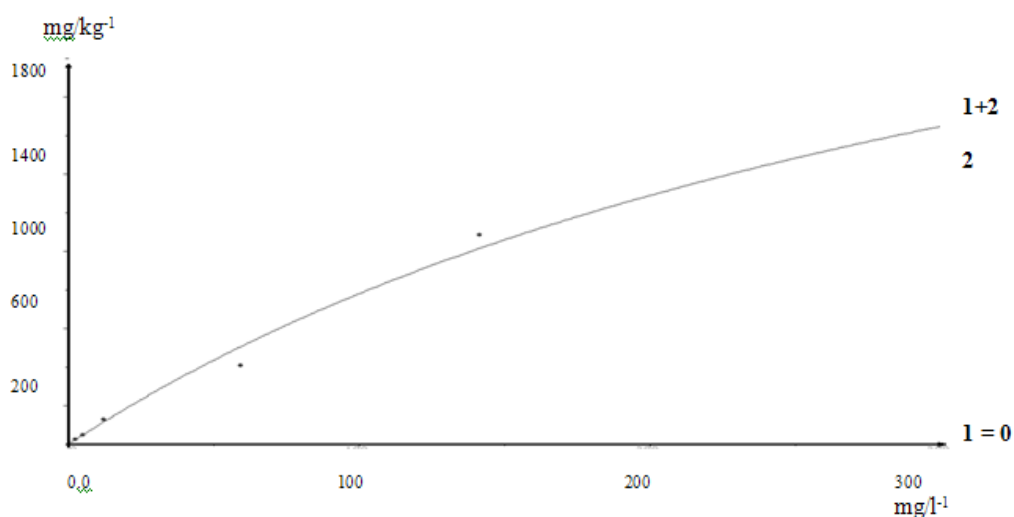


Figure 2: Cu adsorption on the Bak soil where organic matter was partially removed
1: high energy process 2: low energy process

In the calcareous soil in Iregszemcse the quantity of Cu adsorbed by the higher energy process was not reduced by the partial removal of the organic matter. A decrease could be seen in the quantity adsorbed at lower energy (A_2). Too much importance should not be attached to this, since the maximum value of A_2 is always far outside the measurement range if $b_2 < 10^{-2}$, making this value only

approximate. In the soil in Görbeháza, which contains traces of free CaCO_3 , there was a substantial decline in the Cu quantity adsorbed by the higher energy process when part of the organic matter was removed.

It can be seen from the buffering capacity values presented in Table 2 that these values were in accordance with the above. With the exception of the calcareous soil in Iregszemcse, the buffering capacity of the soil exhibited a considerable decrease when organic matter was removed. In the case of the Iregszemcse soil the high pH (>7) prevented a reduction in the extent of adsorption and thus in the buffering capacity.

The quantity of Cu adsorbed as the result of 1000 mg kg^{-1} treatment and then desorbed is presented in Table 3 in the form of the parameters of the first order kinetic equation.

On almost all the soils nearly all the Cu ions added were adsorbed (94–99 %). As shown by the adsorption studies, the removal of organic matter led to a considerable reduction in the proportion adsorbed. The results of desorption depict not only the maximum measured values of desorbed Cu, but also the maximum quantity calculated from the function. If the desorbed quantity falls far outside the measurement range, unrealistically high values may be obtained by extrapolation. At the same time, the value of the rate constant (k) will be extremely small.

In the case of copper, with the exception of the calcareous and thus very heavy soil in Iregszemcse, more Cu was desorbed in all cases from the H_2O_2 -treated soil, despite the fact that in general far less was adsorbed than on the untreated soil.

With one exception the measured values and those calculated from the function were in good agreement, indicating the effect of organic matter removal on the extent of Cu adsorption and the ease of desorption.

Table 3: Desorption of Cu with hot water (HWP) from 1000 mg kg^{-1} Cu treated soils

Soil	Treatment	Adsorbed mg kg^{-1}	Desorbed (measured) mg kg^{-1}	Desorbed calculated	
				A (mg kg^{-1})	k
Iregszemcse	untreated	996.4	7.00	7.44	2.4×10^{-3}
	treated with H_2O_2	996.4	4.93	9.02	7.6×10^{-4}
Görbeháza	untreated	996.4	8.76	4247	2×10^{-6}
	treated with H_2O_2	873.4	70.75	91.05	1.5×10^{-3}
Nyírtelek	untreated	954.5	32.33	57.07	7.9×10^{-4}
	treated with H_2O_2	317.0	138.64	135.99	5.1×10^{-3}
Putnok	untreated	941.1	14.03	19.04	1.3×10^{-3}
	treated with H_2O_2	224.8	184.39	242.09	1.7×10^{-3}
Bak	untreated	942.2	16.93	20.73	1.5×10^{-3}
	treated with H_2O_2	410.6	161.61	169.63	3×10^{-3}



An analysis of the parameters of the two-term Langmuir isotherm used for the description of sorption processes demonstrated that in the course of the adsorption of the Cu ion at least two, energetically quite distinct processes took place.

The basis for the separation is that the value of b_1/b_2 should be at least 10^2 , which means that the energetic constant of the first process should be two orders of magnitude greater than that of the second.

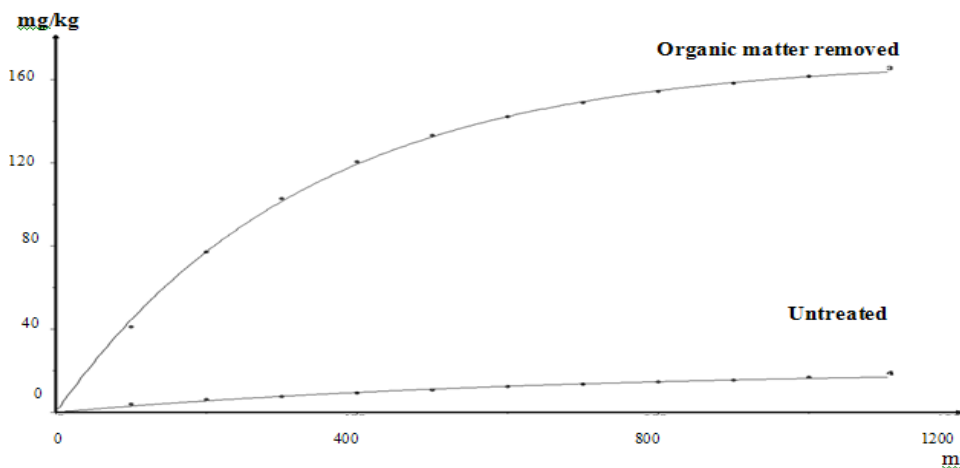


Figure 3: Cu desorption from the Bak soil equilibrated with 1000 mg kg^{-1} Cu

This separation was automatically carried out by the software utilised, although it did not contain this order of magnitude condition. In the majority of cases the breakdown into two processes satisfied this condition. If the adsorption isotherm was recorded at more frequent intervals, a further process would be clearly identifiable.

As can be seen in Figure 1, maximum adsorption took place at the lowest concentrations. In other words, the 2-term Langmuir equation could be expanded to include an adsorption process with additive constant (A_0) values, i.e. with the greatest energy at the lowest concentrations. The presence of this process can be assumed in all cases where $b_1 \sim 10^{-1}$. When organic matter was removed with H_2O_2 the quantity of ions adsorbed in the process characterised by the energetic constant b_1 , or in the hypothetical A_0 process with even greater energy, declined. The relatively small initial concentration, however, makes breakdown into three processes impossible; even the parameters of the lower energy process cannot be exactly determined.

The values of the initial and equilibrium concentrations, however, allow the 1st process to be distinguished fairly well and its parameters to be determined more accurately. The organic matter fraction which can be removed by H_2O_2 treatment obviously forms the less stable part of the soil humus content, but in most of the soils tested (i.e. in the non-calcareous soils) this can nevertheless be regarded as the most important of the soil components from the point of view of heavy metal adsorption.

This is most clearly perceptible in the case of the Cu buffering capacity of the non-calcareous soils in Bak, Putnok and Nyírtelek. The buffering capacity calculated at the C_0 concentration dropped to a hundredth when the organic matter was removed with hydrogen peroxide. The removal of organic matter thus had the greatest effect on the Cu buffering capacity.

If the extent to which the CEC decreased as the result of organic matter removal is compared with the reduction in the quantity of metal ions adsorbed by the higher energy process, it can be clearly seen that the role of the less stable organic matter fraction was far greater in the adsorption of heavy metals than in determining the CEC value. Naturally this was only true of the non-calcareous soils, since the presence of carbonate and the consequently higher pH is a factor of primary importance in the soil adsorption of the heavy metals investigated.

The desorption studies confirmed the existence of the processes found to take place as the result of organic matter removal in the sorption studies. On the one hand, far fewer heavy metal ions were adsorbed after the removal of organic matter, while on the other hand the adsorption energy of the adsorbed heavy metals was also far lower than prior to organic matter removal. Although less heavy metal was adsorbed on non-calcareous soils than before organic matter removal, more was desorbed in all cases.

The role of organic matter in sorption on soil in the case of Cu ion is far more important in non-calcareous soils than was previously thought. The role of soil organic matter is naturally the greatest in the case of Cu adsorption. The results indicate that the removal of organic matter has a similar effect to a reduction in the number of negative charges on the surface of soil colloids, to an increase in the number of positive charges, to a reduction in pH, or to soil pollution with a higher metal ion concentration.

4. REFERENCES

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