SOME NEW CONCEPTS ON THE PHYSICOCHEMISTRY OF HEAVY METALS IN SOILS

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A b s t r a c t. Basing on the concepts of the strongly acidic (TCA) and weakly acidic (TA) nature of the ionex-changers of soil colloids, the physicochemical behavior of heavy metals in soils is discussed. It is shown, that their physicochemical behaviour, depending on soil acidity passes through: 1) an ionic (toxic) mobilization in the case of incomplete neutralization of the strongly acidic ionexchanger by strong bases (Ca, Mg, K...) (soil pH <6.0); 2) a universal for plants acidic optimum, when the strongly acidic ionexchanger is fully neutralized by strong bases, while the weakly acidic ionexchanger is protonated (pH around 6.0) and 3) a hydroxide precipitation (immobilization), when the hydrolytically alkaline salt of the weakly acidic ionexchanger with adsorbed strongly basic cations is active (pH>6.0). On that basis, the permissible copper and zinc concentrations in soil are presented not as separate numbers, but as functions of soil acidity.

K e y w o r d s: heavy metals, acidic reactivity of soil colloids, soil acidity

INTRODUCTION

Heavy metals (Mn, Zn, Cu, Pb, U, etc.) naturally present in soil or added as a result of anthropogenic contamination possess as a main fundamental property - amphoteric behaviour in the chemical reactions. It follows, that their existence in the form of basic cations, insoluble in water hydroxides or weakly acidic anions is governed mainly by the acidity of the environment, i.e., the soil itself [2,5-8]. In acid soils, heavy metals are readily taken by plants, causing toxicity,while in neutral or weakly al-kaline soils (carbonate soils), they are less available to the agricultural crops and deficiency of some of them may cause physiological weakening of plants, known as chlorosis [1,3,9,12].

Just after the new chemical concepts on the acidic reactivity of soil colloids and their acidic systems were developed, it was possible to create a quantitative physicochemical theory about heavy metal behaviour in soils. The purpose of the present paper is to discuss the relations between soil acidity and heavy metals status in soils.

THEORETICAL CONSIDERATIONS

It is now generally accepted, that soil colloids (clay minerals and humic acids) behave as strong and weak acids in the processes of cation exchange and the neutralization of the strongly acidic (TCA) and weakly acidic (TA) ionexchangers of the clay and organic colloids with chemically different cations creates the whole variety of acidic and salt-like adsorbent systems resulting in the degree and forms of soil acidity [4-6], what is shown in Fig. 1.

For example, strongly basic cations (Ca^{2+}, Mg^{2+}, K^+) adsorbed on the weakly acidic io-nexchanger on the edges of clay minerals form a hydrolytically alkaline reaction of the soil
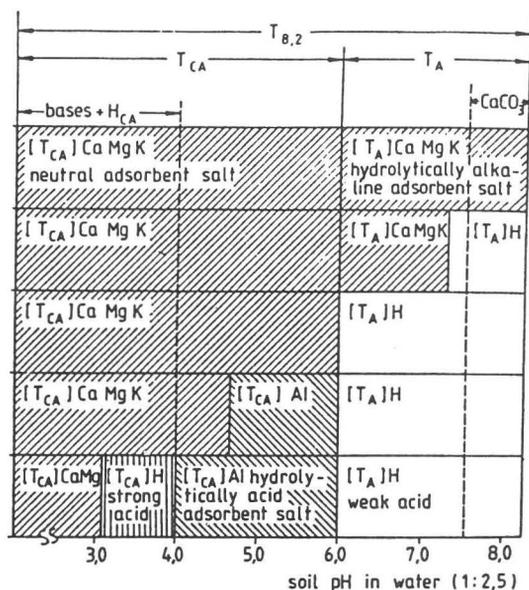
Fig. 1. Acidic and buffer systems of soils formed as a result of the different neutralization with strong bases of the strongly acidic (T_{CA}) and weakly acidic (T_A) ionexchangers of soil colloids.

(pH 7.4-8.4). Partial substitution of strongly basic cations at weakly acidic ionexchanger by H^+ ions, termed 'residual acidity' by the classical soil chemistry, leads to the formation of a buffer system, consisting of the remaining hydrolytically alkaline adsorbent salt and the newly formed free (protonated) weak acid (soil pH 7.4-6.0). When the strongly basic cations are adsorbed only on the highly acidic ionexchanger (i.e., the basal surfaces of clay minerals form a neutral adsorbent salt) and the weakly acidic ionexchanger is fully protonated soil pH is around 6.0.

The exchangeable desorption of strongly basic cations from the highly acidic ionexchanger by H^+ ions converts the soil adsorbent into a strong protonated acid (soil pH 3.0-4.0). Because of its aggressiveness, the destruction of the edge surfaces of the octahedral layer of clay minerals begins, followed by liberation of aluminum ions (podzolization process) occupying the highly acidic exchangeable sites. This results in the formation of a hydrolytically acidic adsorbent salt, consisting of the weakly basic aluminum cations and the highly

acidic ionexchanger of the soil adsorbent, forming soil pH of 6.0-4.8. This type of acidity, desorbable by a neutral unbuffered salt solution (KCl, $CaCl_2$, $BaCl_2$) has been termed 'exchangeable' acidity according to the classical views [5]. When free (protonated) organic acid is present in those acid systems, soil pH varies in the interval 5.0 to 4.0.

The sum of all adsorbed cations with acid functions at all adsorbing sites (ionexchangers) of the soil colloids, which is desorbable by a hydrolytically alkaline salt (e.g., Na-acetate) represents the total (general) acidity i.e., hydrolytic acidity according to the classical views. The neutralization of the total soil acidity by basic cations is reflected in the degree of base saturation. The latter is related to soil pH via the acidic nature of soil adsorbents. The correlations between the pH of soils and their percentage base saturation involving different portions of the highly acidic and weakly acidic ionexchangers are shown in Fig. 2.

It is well known that maximum crop yield with a best biological quality, is produced at pH around 6.0, i.e., at the acidic plant optimum
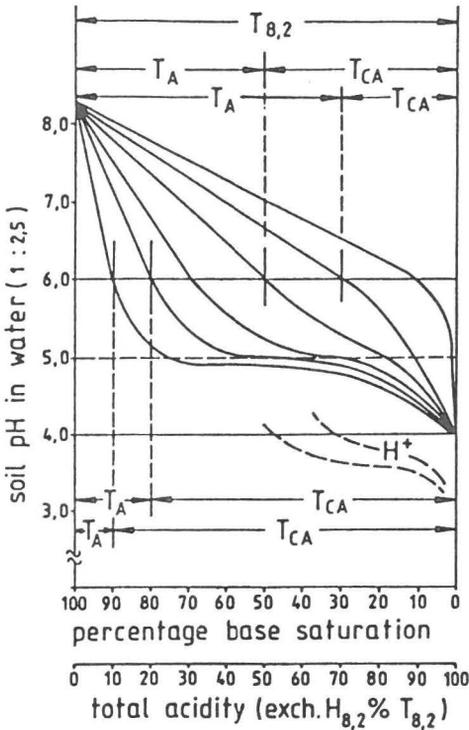
Fig. 2. Correlations between soil pH and percentage base saturation at different values of the strongly acidic (T_{CA}) and weakly acidic (T_A) ionexchangers of soil.

defined by the full neutralization of the highly acidic ionexchanger of the soil adsorbent with strong bases and the protonated form of the weakly acidic ionexchanger (bases =TCA; exch. H(8.2)=TA; exch. Al=0). And so the relationship yield - soil acidity neutralization passes through a maximum, characterized by these parameters what is exemplary shown in Fig. 3. The same yield-pH relation is valid for a situation of heavy metal pollution of soils (Fig. 4). Thus it is interesting to find some links between acidic conditions and heavy metal status in soils.

All the acidic, salt-like and buffer adsorbent systems in normal (salt-unaffected) soils can be well quantitatively and chemically determined and their chemical activity allows a quantitative description of heavy metal behaviour in soils in relation to their physicochemical properties [2,5,8].

Different heavy metals precipitate from solution as hydroxides at different pHs and in soils where acidic conditions are formed by both the strongly acidic and weakly acidic ionexchangers of the soil adsorbent and their neutralization by different cations, heavy metal behaviour may be somewhat different. It is traditionally accepted, that heavy metal cations
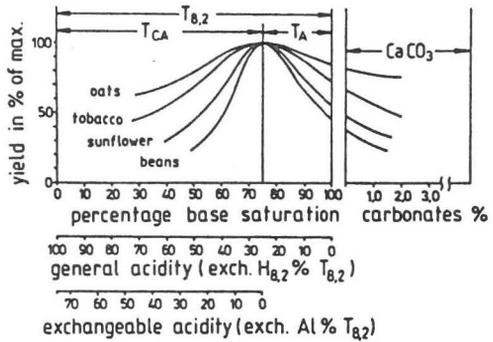

Fig. 3. Optimal soil acidity for plants defined with the maximum yield at the complete neutralization with strong bases of the strongly acidic ionexchanger (T_{CA}) and protonated weakly acidic ionexchanger (T_A) of soil colloids (pH= 6.0).
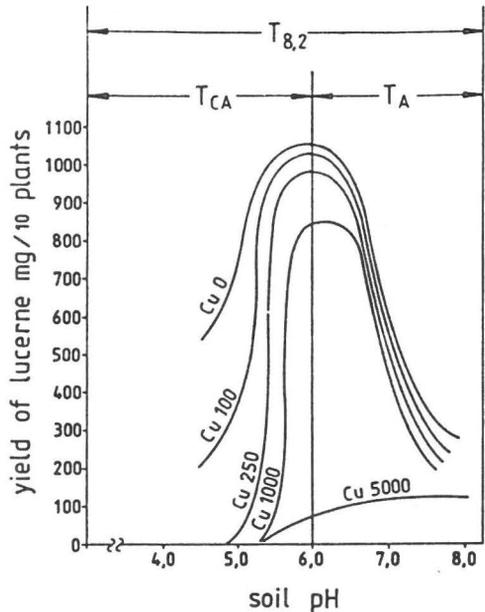

Fig. 4. Yield of lucerne (II cut) in relation to the neutralization of soil acidity at different copper pollution levels (mg/kg soil).

are present mainly as exchangeable adsorbed cations by different soil colloids, although the acidic boundary below which they are present as adsorbed cations and above which as precipitated insoluble hydroxides, has been usually treated not in general but related to the complexity of particular soil systems. That is why an irreversible chemisorption, called specific sorption has always been estimated. It is clear now, that only the strongly acidic ionexchanger acidity is successful in releasing heavy metal cations from their oxygen and hydroxyl coordination in soil minerals and can maintain their ionic state in soil preventing their hydrolysis to insoluble hydroxides. In the presence of the weakly acidic ionexchanger buffer systems, heavy metals are precipitated as insoluble hydroxides and deficiency takes place for those, which are necessary for the physiological needs of the plant organisms. It follows, that heavy metal behaviour in soils is determined by their ionic-hydroxide equilibrium at the surface of soil colloids [2,5].

It results in heavy metal cations being exchangeably adsorbed only at the strongly acidic ionexchanger of the basal clay mineral surfaces and not being adsorbed in an exchangeable state at the weakly acidic ionexchanger of the edge clay surfaces, because of their hydrolysis to insoluble hydroxides.

The described chemical behavior of heavy metals in soil determines to a great extent a universal acidic optimum for plants at pH of 6.0. It is fairly known, that a considerable part of heavy metals possess major biological functions in the enzyme apparatus of the plant organism. Consequently, the harmonious and disharmonious action of the main metabolic processes, the formation of crop yield, as well as the biological quality of production is dependent on the amphoteric microelement uptake by plants. For example, when the strongly acidic ionexchanger of the soil adsorbent is not completely neutralized by strong bases (pH<6.0), heavy metals in ionic form are taken up by plants in considerable excess, which is toxic for the organism and disturbs the growth. Oppositely, the neutralization of not only the

strongly acidic, but also of the weakly acidic ionexchanger of the soil by strong bases, heavy metals are fully precipitated as insoluble hydroxides and their plant uptake is inhibited to a large extent. It can take place only through a contact dissolution of the oxyhydroxides by H^+ ions, released by plant roots. Because of the presence of neutral and hydrolytically alkaline buffer adsorbent systems at these conditions (pH 6.5-8.4), the neutralization of the H^+ ions released by plant roots occur and their ability for a contact dissolution of the amphoteric hydroxides is also markedly suppressed. Only in the case of a full neutralization of the strongly acidic ionexchanger by strong bases together with the protonation of the weakly acidic ionexchanger (soil pH around 6.0) the plants can utilize physiologically optimal concentrations of heavy metals. In such conditions they are in general precipitated as hydroxides, which precludes the plant uptake of toxic amounts. Those hydroxides are not, however protected against acidic dissolution by the H^+ ions of the contacting plant roots, because of the lack of a hydrolytically alkaline system for proton neutralization. In that case, environmental factors do not introduce advantages or limitations for anyone of the heavy metals and the uptake is only dependent on the physiological needs of the plant organism [2,4,5]. Heavy metal ionization in soil, caused by the action of the strongly acidic soil adsorbent system brakes the soil internal bareer against their uptake by plants what results in the toxic accumulation in the plant organism. That is why heavy metal uptake depending on their contents in soil is described by a group of curves shifting to higher values with increasing soil acidity, which is illustrated in Fig. 5.

It means, that one and the same amount of heavy metals in soil can be accumulated by plants at different levels depending on soil reaction (pH). Because of this, in situations of soil pollution with heavy metals from transport, non-ferrous metallurgy, nuclear industry, etc., the permissible concentrations of these elements in soils can not be determined only
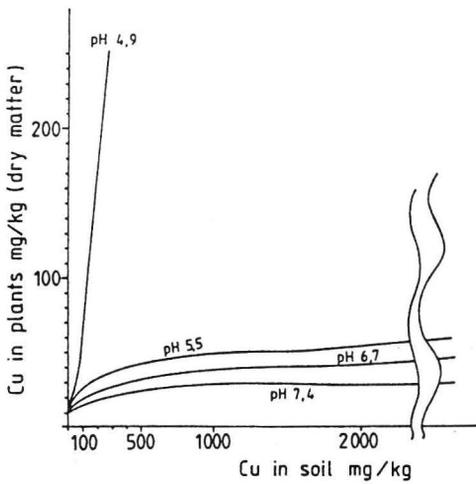
Fig. 5. Copper uptake in lucerne in relation to soil copper at different values of soil acidity.

by a certain critical harmless amount but should be defined as a function of soil acidity [10,11]. It follows, that heavy metal content 'curve' in soil has to be described by marking at different acidity levels the plant uptake at rates of negligible harmfulness (less, than the error of the biological experiment in the testing). As a result of the study of plant growth, and copper and zinc uptake in soils of different lime-managed acidity and pollution rates we present the respective curves in function of soil acidity (Figs 6 and 7). It is clear, that for example some tens of milligrams Cu per 1 kg soil can be very toxic for plants, when the strongly acidic ionexchanger of the soil colloids is active (soil pH<6.0) while plants can tolerate much higher concentrations (e.g., several hundreds of milligrams Cu per 1kg soil) in the case of a complete neutralization of the strongly acidic ionexchanger by strong bases when
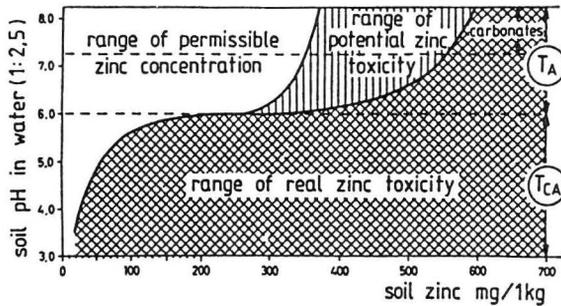

Fig. 6. Curve of permissible copper concentration in soils in relation to their acidity.
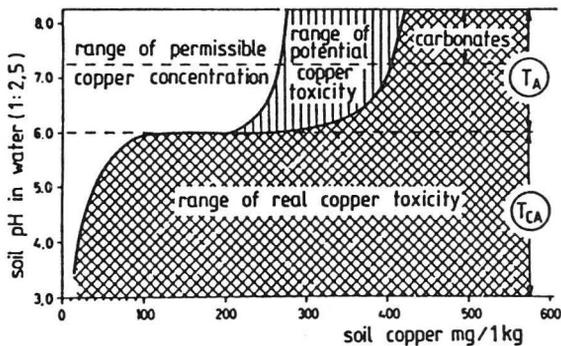

Fig. 7. Curve of permissible zinc concentrations in soils in relation to their acidity.

the neutral and hydrolytically alkaline buffer adsorbent system is active (pH>6.0). It confirms the understanding, that the permissible concentrations of heavy metals in soils can be defined only as function of soil acidity.

CONCLUSIONS

It must be concluded, that in relation to the great recent hazard of environmental pollution the intensive work in solving the practical problems must be carried out. The showed relations between soil acidity and heavy metals status in soils may be very helpful in this respect.

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