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Developments in Soil Science 5A

SOIL CHEMISTRY

A. Basic Elements

EDITED BY

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PREFACE TO THE SECOND EDITION

A number of irritating misprints, "dutchisms" and a few errors were removed: thanks are due to readers who pointed out some of these to us. After ample consideration the term Free Enthalpy was retained — in favor of the more ambiguous term Free Energy as still often used in Anglo-Saxon literature — when referring to the thermodynamic state function named Gibbs Energy or Gibbs Function in the I.U.P.A.C. recommendations.

Wageningen, 1978

G.H.B. and M.G.M.B.

fertilization with Cr-compounds has usually little effect even when using Cr salts of high solubility.

Necessity of Cr for plant growth has not been proved (Pratt, 1966). Toxicity of Cr at high concentration levels has been reported, especially on so-called 'serpentine' soils. These soils are rich in Cr, but also in other heavy metals like Ni and Co. The Cr content of most soils is usually limited to traces only but may reach values up to 46,000 ppm for 'serpentine' soils. Only a very minor part of the total Cr, however, is soluble (0.006 - 0.28% according to Soane and Saunder, 1959), thus strongly restricting plant availability.

The mobility of Cr within the plant is extremely low. It thus remains in that part where the uptake took place (Allaway, 1968). Turner and Rust (1971) assume that Cr is taken up by plants as chromate (Cr^{6+}), e.g. after addition of potassium chromate, K_2CrO_4 . This then would be the main reason why Cr is not a problem in soils, even not after disposal of Cr containing sludges. At the pH values and redox potentials prevailing in most soils, Cr^{6+} is readily reduced to Cr^{3+} , mainly occurring as the poorly soluble $\text{Cr}(\text{OH})_3$. Strijbis and Reiniger (1974) found in experiments with rice that also Cr^{3+} was taken up, although at considerably lower levels than Cr^{6+} . The uptake for both forms was lower under submerged conditions than at field capacity. This is in accordance with the decreased solubility at lower values of the redox potential.

10.4.5. Cu, copper

Prime use of Cu is as wire and brass, and as alloys with a number of different other metals. Most water supply systems consist of copper tubing. Copper in the form of CuSO_4 has been used as a fungicide for fruit crops and potatoes. Also in the form of copper sulfate Cu is sometimes used as an additive in swine and poultry feed in order to increase the feed efficiency. Such additions in feed can be made up to a level of 250 ppm Cu. Copper levels up to 750 ppm Cu have been reported for pig manure (Robinson et al., 1971) which means that disposal of this manure on land in excessive rates, or even the application at appropriate nitrogen fertilization levels, may induce an accumulation of Cu in soil.

The effects of high Cu contents of soil on the uptake of certain other micronutrients by plants are well known. High Cu levels may cause iron deficiency which is demonstrated as typical chlorosis features. Also an antagonism between Cu and Zn has been observed. The interaction between Cu and Mo has been described both for human and animal nutrition and for plant nutrition. In a comparable manner as Cu may inhibit Mo uptake, an abundant presence of Mo may in turn induce Cu deficiency, especially when the

last is present at relatively low amounts. The proper Cu-Mo balance is thus an important condition for proper plant nutrition.

High levels of Cu can be toxic to microorganisms. Its practical application to control microbial induced diseases is as old as 1882 when the so-called Bordeaux spray, CuSO_4 , was used for the first time as a fungicide. The presence of Cu in manures, as mentioned above, might thus considerably influence the rate of biodegradation of the organic constituents of these manures.

In view of sewage sludge disposal on land, Chumbley (1971) introduced the 'zinc equivalent factor', to be used as a relative indication of the toxicities of different metals. Very generally, it can be said that copper is about twice as toxic to plants as zinc, whereas nickel is about 8 times as toxic as zinc. The zinc equivalent factor is then defined as:

$$\text{Zn factor (in ppm)} = 1 \times \text{ppm Zn} + 2 \times \text{ppm Cu} + 8 \times \text{ppm Ni}.$$

Although this factor may be used for a rough relative toxicity indication, it must be kept in mind that the actual relative toxicity and tolerance is governed by these conditions and circumstances which determine the actual availability of Zn versus Cu or Ni; as such the organic matter, phosphate level and pH are the most important (Chaney, 1973).

With respect to crop production it is generally reported that an adverse influence on plant growth results if the Cu concentration in the soil solution exceeds 0.1 ppm. The Cu concentration in drinking water for human consumption is, according to drinking water standards, considered to be safe at levels not exceeding 1.0 ppm Cu. Sheep are known to be sensitive for high Cu levels; concentrations above 20 ppm Cu in feed and forage are reported to be toxic for sheep (Baker, 1974).

Normal Cu contents of soil are around 20 ppm with variations over the range 2 - 100 ppm. At pH values and oxygen pressures which usually prevail in most soils, the predominant ionic form of copper is as divalent cation.

Mobility and displacement of Cu in soils is low. It is strongly bound by organic matter, clay minerals, and even adsorption on pure quartz has been described. As a result of this bonding, downward movement of Cu in silty or clayey soils is almost nil. Even in sandy soils such movement is very small (Jones and Belling, 1967). Peat soils are famous for their copper fixation. After addition of 250 kg Cu per hectare to an acid peat soil only 0.2% was found to be removed from the top 5 cm layer in a time period of 5 years (Lundblad et al., 1949).

The cationic exchange between Cu^{2+} and Ca^{2+} on bentonite has been described by El-Sayed et al. (1970, 1971). Starting with a pure Ca-clay, it was found that the initial Cu-exchange was 'unfavorable', i.e. the clay exhibited as small preference for Ca-ions. With increasing Cu-adsorption, the ex-

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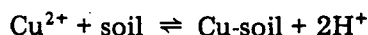
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change gradually shifted to 'favorable' exchange, i.e. with preference for Cu. This phenomenon was attributed by the above authors to a condensation of clay platelets with increasing Cu-adsorption, thus excluding a number of adsorption sites for the slightly larger Ca-ions.

Lindsay (1972) suggested for Cu, in a comparable way as for a number of other heavy metal cations, to summarize all Cu reactions in soil by the general equation:



According to Norvell and Lindsay (1969), the $\log K^{\circ}$ of this reaction amounts to -3.2. Such an approach may be useful in the construction of solubility diagrams as a function of pH. As the above equation covers all Cu-reactions that may pertain in soil, no information is gained about the bonding mechanism; this may as well be adsorption on clay minerals or other soil constituents, as precipitation of lowly soluble Cu-salts.

A large number of Cu complexes are known to occur in soils. As will be discussed later, Cu has also been studied intensively with respect to chelation.

10.4.6. Hg, mercury

Mercury is used in measuring and control instruments like thermometers, manometers, etc. It has an application as floating electrode in the electrolysis of chlorine and caustic soda. It is also used as a catalyst in the production of plastics. Agricultural use of mercury, mainly in the form of fungicides e.g. in seed dressings, amounts at present to 5% or less of total industrial mercury consumption. As a fungicide it is also applied for wood preservation and thus products of pulp and paper industry usually contain traces of mercury. Burning of coal and oil is the most important airborne source of Hg emission in the environment. As has been pointed out by Joensuu (1971) the annual natural discharge of mercury in the oceans as a result of chemical and physical weathering of Hg-containing rocks and minerals amounts to an estimated 230 metric tons on worldwide basis.

The hazardous effects of mercury attracted especially attention following the 1950's calamities of Minamata, Japan. Also Swedish researchers called specific attention on mercury behavior in the environment when it became clear that mercury accumulation occurred in food chains. One important Hg source was the use of alkyl mercury in seed dressings. There is a large difference in the toxicity of the different mercury compounds. The aromatic Hg compounds (e.g. phenyl-mercury) and the alkoxyalkyl Hg compounds (e.g. methoxyethyl mercury) are the least toxic. Then follow the inorganic salts of mercury and metallic mercury, Hg° , whereas the alkyl compounds (e.g. methyl and ethyl mercury) are the most dangerous. This is due to the