

COPPER IN SOILS AND PLANTS

J.F. Lonergan
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Edited by

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PREFACE

Fifty years ago, the first definitive evidence for the essentiality of copper for the growth of higher plants was published. The burst of research activity which followed established copper deficiency as a limiting condition for plant growth and animal production on numerous soils in all continents.

The last ten years has seen a renaissance of that early interest in copper in agricultural systems. It has also seen a growing awareness of copper toxicity to plants and animals of pollutants from mine and sewage wastes. Furthermore, changing technology has exacerbated problems of deficiency and toxicity. The resulting research activity has expanded our understanding of the behaviour of copper in many processes. It therefore seemed timely for workers in relevant fields to meet and review this new information and to try and relate it to the behaviour of copper in soils and plant systems.

The Golden Jubilee of the recognition of copper as an essential element for plant growth provided an appropriate time for such a review. The scheduling in 1981 of the "Fourth International Symposium on Trace Element Metabolism in Man and Animals" in Western Australia, where so much research on copper has been done, provided an appropriate venue.

We wish to record our thanks to the Australian Academy of Technological Sciences for sponsoring the Symposium, to the organisations (p. xv) which provided financial support, and to members of the Organising Committee (p. xv). Our special thanks go to Dee Cahill and to Derek Plaskett for assistance in preparing the proceedings of the Symposium for publication.

We also wish to pay a tribute to the late Professor Alan Posner whose untimely death in the early stages of planning the Symposium deprived us of a valued friend and colleague. Alan Posner was an outstanding soil scientist whose work had included the study of processes involving the behaviour of copper in soils. We will miss his lively mind at the Symposium discussions but in the work reviewed we will remember his many contributions to this subject and to soil science generally.

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INTRODUCTION: THE CHEMISTRY OF COPPER

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COPPER MINERALS

Copper is widely distributed geographically and geologically. Deposits have been formed throughout geological time. However, copper ore bodies are rare and occupy only a very small fraction of known rock formations. The average amount of copper in the earth's crust is about 70ppm (Hodgson, 1963).

Copper frequently occurs as the metal and in the Lake Superior region of the USA masses weighing several tonnes have been found. More frequently copper occurs as a primary sulfide mineral, such as bornite (Cu_5FeS_4) or chalcopyrite (CuFeS_2). The secondary copper sulfide minerals such as chalcocite (Cu_2S) and covellite (CuS) are forms of copper which have been leached and precipitated. Oxidised copper minerals are formed by weathering of sulfides and occur as oxides, hydroxides, carbonates, chlorides and silicates (Butts, 1964). Copper and sulfur form sulfides in which copper is in the +1 rather than +2 oxidation state. The so-called "cupric sulfide", CuS , is more usefully thought of as copper(I) disulfide, Cu_2S_2 . Cu^+ (Vaughan and Craig, 1978). Copper(II) and sulfide ions are not compatible since copper (II) is reduced and sulfide is oxidised when these species are in contact in solution, in melts and in the gas phase.

Most copper sulfide minerals possess semi-conductor properties. In the natural state copper sulfide crystals contain impurities and defects, so they are good conductors (Vaughan and Craig, 1978). Whether it is long term weathering or short term leaching with bacteria, ferric sulfate or

ferric chloride, the oxidation of copper sulfide is an electrochemical or corrosion process (Parker *et al.*, 1981). Many sulfide ore bodies are gigantic electrochemical cells which have cathodic (reductive) sites at the oxygen-rich ground level and anodic sites (oxidation) deeper down near the water table. Thus weathering and oxidised zones are sometimes found at depth in copper ore bodies. Familiarity with semiconductors and electrochemical properties (Vaughan and Craig, 1978) is recommended for those interested in naturally occurring copper, be they mineralogists, extractive metallurgists or soil scientists.

ATOMIC AND PHYSICAL PROPERTIES (Cotton and Wilkinson, 1972)

Copper of atomic number 29 is the first element of subgroup 1B (the first transition series) of the periodic table. Copper has very little relation to the main group I elements, such as sodium and potassium, and is noticeably different from silver and gold. The electronic structure of the free copper atom is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$. The single $4s$ electron is outside a filled $3d$ shell. The filled $3d^{10}$ shell is much less effective than is a noble gas shell (e.g. $3p^6$ of potassium) in shielding this electron from the positive nuclear charge. Thus the $4s$ electron is rather difficult to remove from copper. Copper's first ionization potential (7.72 eV) reflects this greater energy for electron removal than does the first ionization potential of the alkali metals (e.g. $K = 4.34$ eV for example). Like all elements of the first transition series (e.g. Cr, Mn, Fe, Co, Ni) and unlike Li, Na, K, Rb, of Group I, two electrons are removed relatively easily from copper atoms (20.29 eV) in the gas phase to form Cu^{2+} (copper II). This ion is quite stable in water, but unlike any other elements in the transition series, the second ionization potential of copper is sufficiently higher than the first and the effects of the ions environment is such as to allow a variety of stable copper(I) species to also exist. Whether copper exists as copper(I) rather than copper(II) depends very much on the physical environment (i.e. crystal lattice, melt, gas phase, solution), the solvent, the concentration and what ligands (bases) are present. Thus copper(I) is stable in water containing excess halide ions, acetonitrile, pyridine, or cyanide ions, in anhydrous acetonitrile, ammonia, or pyridine, and as solid $CuCl$, $CuCN$, CuI , $CuSCN$, Cu_2O , Cu_2S , etc. However, in water, copper(I) disproportionates (eq.1) as the sulfate, nitrate,

or perchlorate, when attempts are made to prepare 10^{-1} - 10^{-2} M Cu_2SO_4 , CuNO_3 or CuClO_4 solutions in water. The hydrated Cu^+ ion is not a stable species in water at the concentration normally used by chemists.

An interesting aspect of copper in wet soils (Lindsay, 1979), as distinct from the aqueous copper salt solutions normally encountered by chemists, is that in very dilute solution (10^{-6} M - 10^{-7} M) copper(I) is moderately stable with respect to its disproportionation into copper metal and Cu^{2+} . The equilibrium constant K for (1) is 10^6M^{-1} at 25° in water, so that in "chemical solutions" (10^{-2} - 10^{-3} M), very little copper(I) is present.



However, since the average concentration of dissolved copper in copper-rich moist soils is 10^{-6} - 10^{-7} M, that copper could be present as 1×10^{-7} M Cu^{2+} and 3×10^{-7} M Cu^+ , for example. Hydrated Cu^+ would be the predominant copper species. This mathematical curiosity arises of course because of the squared $[\text{Cu}^+]$ term in $K = [\text{Cu}^{2+}] / [\text{Cu}^+]^2$.

The isotopes of copper are Cu^{63} (69%) and Cu^{65} (31%). The highly active Cu^{64} , of half life 12.8 hours, is the most suitable for tracer work. Decay of Cu^{64} leads to Zn^{64} or Ni^{64} by electron or positron emission respectively (Fronsbeyn and Firminhac, 1954).

CHEMISTRY OF COPPER IONS IN DIFFERENT ENVIRONMENTS

Standard reduction potentials at 25° for various forms of copper(I) and copper(II) in aqueous solutions, sometimes containing other bases, are in Table 1. The Table shows the electron accepting tendencies of these copper species under the conditions specified. The more positive the reduction potential, the more readily electrons are accepted by the copper containing species to the left of the reduction equation. Equally of course, Table 1 shows the ability of copper metal or copper(I) (i.e. species to the right of the reduction equation) to donate electrons to suitable electron acceptors in various environments. The more negative the reduction potential, the more readily does the copper or the copper(I) species on the right donate electrons (i.e. the more readily is the copper oxidised). For reasons associated with the poor shielding of the copper nucleus by its d^{10} electrons, as discussed above for the gas phase processes,

TABLE I. Electron Acceptor Tendencies^a (i.e. Reduction Potentials (nhe)) of Copper(I) and Copper(II) Systems in Water at 25°

Reduction Equation	E^0 volt nhe
$\text{Cu}_2\text{S} + 2\text{e}^- \rightarrow 2\text{Cu} + \text{S}^{2-}$	-0.95
$\text{CuS} + 2\text{e}^- \rightarrow \text{Cu} + \text{S}^{2-}$	-0.76
$\text{Cu}_2\text{O} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{Cu} + 2\text{OH}^-$	-0.36
$\text{CuSCN} + \text{e}^- \rightarrow \text{Cu} + \text{SCN}^-$	-0.27
$\text{CuI} + \text{e}^- \rightarrow \text{Cu} + \text{I}^-$	-0.19
$\text{Cu}(\text{NH}_3)_2^+ + \text{e}^- \rightarrow \text{Cu} + 2\text{NH}_3$	-0.11
$\text{Cu}(\text{NH}_3)_4^{2+} + 2\text{e}^- \rightarrow \text{Cu} + 4\text{NH}_3$	-0.05
$\text{CuBr} + \text{e}^- \rightarrow \text{Cu} + \text{Br}^-$	+0.03
$\text{Cu}(\text{NH}_3)_4^{2+} + \text{e}^- \rightarrow \text{Cu}(\text{NH}_3)_2^+ + 2\text{NH}_3$	+0.06
$\text{CuCl} + \text{e}^- \rightarrow \text{Cu} + \text{Cl}^-$	+0.12
$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+_{\text{aq}}$	+0.17
$\text{Cu}(\text{An})_3^+ + \text{e}^- \rightarrow \text{Cu}^0 + 3\text{CH}_3\text{CN}$	+0.18
$\text{CuS} + \text{e}^- \rightarrow \frac{1}{2}\text{Cu}_2\text{S} + \frac{1}{2}\text{S}^{2-}$	+0.19
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}^0$	+0.34
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}^0$	+0.52
$\text{Cu}^{2+} + \text{Cl}^- + \text{e}^- \rightarrow \text{CuCl}$	+0.57
$\text{Cu}^{2+} + \text{I}^- + \text{e}^- \rightarrow \text{CuI}$	+0.88

^a The more positive the reduction potential, the more readily electrons are accepted by the copper containing species to the left of the reduction equation to form the species shown to the right of the equation.

copper is a noble metal from which an electron is donated with difficulty to species dissolved in water. This is despite the strong solvation of the relatively small Cu^+ and Cu^{2+} ions, which form on oxidation of copper. In other than pure water however, as shown in Tables 1-3, the electron acceptor tendencies of copper ions and the electron donor properties of copper metal, depend very much on the environment of the copper ions, i.e. solid or liquid phase, nature of solvent, nature of copper-bases, etc. (Cotton and Wilkinson, 1972).

The term copper-base refers to any electron pair donor, e.g. NH_3 , H_2O , Cl^- , $(\text{NH}_2)_2\text{C}=\text{S}$, amino acid, hydroxy species, thiol, etc., which forms complexes with Cu^+ or Cu^{2+} . One uses the expression "copper-base" rather than simply "base" because relative base strengths towards copper ions (copper-basicity) often have little relation to base strengths towards hydrogen ions (proton-basicity). Thus the pK_b of bases in water (Table 2) is not necessarily an indication of the relative strengths with which the same bases form complexes with Cu^+ or Cu^{2+} (Ahrland *et al.*, 1958; Edwards, 1964; Sillen and Martell, 1964). For example, $\text{Cl}^-(\text{aq})$ or various $\text{RO}^-(\text{aq})$ species are stronger bases towards $\text{H}_3\text{O}^+(\text{aq})$ than are $\text{I}^-(\text{aq})$ and $\text{RS}^-(\text{aq})$ species, but $\text{I}^-(\text{aq})$ and $\text{RS}^-(\text{aq})$ are much stronger bases towards $\text{Cu}^+(\text{aq})$ than are $\text{RO}^-(\text{aq})$ or $\text{Cl}^-(\text{aq})$ (Tables 1 and 2). Ammonia is a very much stronger base towards H_3O^+ than is acetonitrile in water (Table 2) and is also a very much stronger base towards Cu^{2+} than is acetonitrile (Table 1). However, ammonia in water is only stronger by a factor of 10^6 as a base towards Cu^+ than is acetonitrile (Table 2). Indeed the term copper-base is itself inadequate, because one should compare bases in terms of their copper(II)-base strengths and their copper(I)-base strengths. The two properties are often different.

As a general rule, bases whose basic centre is an oxygen or nitrogen atom, or especially a chelating centre involving both these atoms, are strong copper(II)-bases, whereas those bases whose basic centre is a halide ion, a sulfur, phosphorus, arsenic, or selenium atom, or multiply-bonded nitrogen or carbon, are strong copper(I)-bases (Sillen and Martell, 1964; Cotton and Wilkinson, 1972). Examples are in Tables 1-3.

The disproportionation equilibrium of Cu^+ (eq.1) well illustrates the electron acceptor properties of Cu^{2+} and Cu^+ and the electron donor properties of Cu^+ and Cu^0 in various environments. Values of the equilibrium constant, K , for Cu^+ disproportionation differ by 10^{50} through different chemical environments in solution, as shown in Tables 2 and 3