Functions and homeostasis of zinc, copper, and nickel in plants

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Abstract

Nutritional micronutrient deficiencies and exposure to pollutant metals threaten human health globally. Plant crops are at the beginning of a food chain that largely determines food metal contents. In order to survive, all organisms have to supply appropriate amounts of each micronutrient to the correct target apometalloproteins and at the same time avoid adventitious metal binding to non-target metal binding sites or other cellular compounds. This requires the operation of metal homeostasis networks, which orchestrate the mobilization, uptake, distribution, intracellular trafficking, chelation, and sequestration of all metal ions. Presumably as a result of time-dependent and local variations in bioavailable soil metal concentrations, plant metal homeostasis networks exhibit a remarkably high degree of plasticity and natural diversity. This is a review covering the current knowledge of metal-dependent processes and proteins, metal homeostasis and its regulation, and the molecular mechanisms underlying naturally selected metal hypertolerance and metal hyperaccumulation in higher plants.

1 Introduction

At all times in evolution, life forms have been exposed to chemical environments of often fluctuating compositions, from which available inorganic nutrients were eventually selected to perform essential biochemical functions (Fraústo da Silva and Williams 2001). The chemical composition of the biosphere varies locally and can change profoundly over time. The most notable change occurred when the Earth's atmosphere became oxygenic, which led to a radical change in the availability of a number of transition metal ions for life on Earth. This dramatically reduced the bioavailability of some transition metals – primarily iron - and made other transition metals more available – primarily copper. For the latter group, it can be postulated that the evolution of detoxification systems was dominant initially and that the use in biochemical functions evolved later. Indeed, the use of transition metal ions for biochemical functions has been extremely successful: about one third of all structurally characterized proteins are metalloproteins

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(Finney and O'Halloran 2003). Today several transition metals[1], namely iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), molybdenum (Mo), and nickel (Ni), are known to be essential micronutrients for living higher plants (Marschner 1995). The list of essential transition metals may grow as more and more protein structures are elucidated and analytical techniques as well as the purity of chemicals are being continuously improved. This may apply for cobalt (Co), which is currently considered a beneficial element (Marschner 1995), and cadmium (Cd), which acts as the cofactor of a carbonic anhydrase isoform produced under Zn-deficient conditions in the diatom *Thalassiosira weissflogii* (Lane and Morel 2000).

As an approximate, a search of the *Arabidopsis* Information Resource (TAIR) database protein descriptions retrieved 1230 proteins predicted to contain, bind, or transport Zn(II), including, among others, a large number of Zn-finger containing proteins and transcription factors, oxidoreductases, and hydrolytic enzymes such as metalloproteases. The same search retrieved 105 proteins for Cu and three proteins for Ni. To date, most information is derived from characterized metalloprotein homologues in other organisms, and plant-specific direct experimental evidence of the use of a specific metal ion in a given protein is scarce.

The chemical properties that made transition metal ions indispensable for life were their ability to undergo changes in redox state under biological conditions and to establish and maintain several stable coordinative bonds to electron pair donor atoms of organic ligands in a defined geometry. These properties of transition metal ions, however, pose a serious risk as soon as their interaction and binding partners are not fully controlled. Metal-induced uncontrolled redox reactions or the deactivation or modification of functional groups of organic molecules can endanger the survival and reproduction of an organism. It is, thus, not surprising that all organisms possess a tightly knit metal homeostasis network that serves to maintain concentrations of metal ions within physiological limits. Notably, different transition metal ions possess different chemical properties, i.e., different redox potential, coordination geometry, charge and thermodynamic and kinetic properties of ligand exchange. In a given metalloenzyme, a specific metal ion is thus used for a specific chemical function. However, according to the Irving-Williams series ($Zn^{2+} < Cu^{+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Mg^{2+} > Ca^{2+}$) metal ions bind to organic ligands, such as those in a metal-binding site of an apometalloprotein, with different affinities (Nieboer and Richardson 1980; Fraústo da Silva and Williams 2001). According to this, Cu ions can bind to metal binding sites of non-Cu metalloproteins, and so can each metal ion replace other metal ions down-

[1] In biology, only the oxidized forms of transition metals (and not the elemental forms) are relevant. In this chapter, the element names, e.g., zinc or Zn refer to the elements in their biologically relevant oxidation states, for example, the oxidation state +II for Zn [i.e. Zn is equivalent to Zn(II)]. However, biologically redox-active metals such as Cu occur in different oxidation states in biological systems. We specify the oxidation state, e.g. Cu(I), only to put a special emphasis on it, or when referring explicitly to one of several biologically relevant oxidation states, as for Cu(I) or Cu(II). The cationic form, e.g., Zn^{2+} is used to denote the free aqueous cation of a transition metal.