

AGEING OF METALS IN SOILS CHANGES BIOAVAILABILITY

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Why is ageing important?

Many of the metals that are essential elements are purposefully added to soil to increase plant and animal production. This addition increases the concentration of metal in the soil pool most available to organisms — the bioavailable pool. Once the concentration is sufficient for plant or animal growth, any reductions in the bioavailable pool (e.g., through ageing) can lead to deficiencies that require further metal addition to satisfy the organism's nutritional requirements. In the case where toxic concentrations are reached because too much metal is added inadvertently, reductions in metal bioavailability result in the amelioration of the toxicity response.

Time of contact between soil and metal is a critical factor in determining bioavailability

For both essential and non-essential metals, it has been found that time of contact between soil and metal is a critical factor in determining bioavailability. Various technical and non-technical terms have been given to this process — attenuation, ageing, fixation, reversion, irreversible binding, adsorption/desorption hysteresis, etc. To clarify nomenclature and also to understand the processes involved, discussion of the various reactions of metals with soils is useful.

Processes involved in ageing

When a soluble metal salt is added to soil it enters the soil pore water and initially increases concentration of the soluble metal ion. In solution, the

metal is usually initially present either as a cation (Cd^{2+} , Co^{2+} , Cu^{2+} , Cr^{3+} , Fe^{n+} , Hg^{2+} , Mn^{n+} , Ni^{2+} , Pb^{2+} , Zn^{2+}) or as an anion (AsO_x^{n-} , CrO_4^{2-} , MoO_4^{2-}). Several reactions can take place immediately after addition of the metal to soil. The metal may complex with other inorganic or organic ions in soil pore water, thus reducing the concentration of the most available form in solution. Simultaneously, solution metal concentrations may decrease through adsorption or precipitation processes. Adsorption processes are due to an electrostatic bond between the metal and the charged surfaces in soil. Soil surface charge is highly dependent on pH, with greater negative charge at higher pH. Thus, cationic metals are sorbed most strongly at high pH and anionic metals sorbed most strongly at low pH (Figure 1).

DEFINITIONS

CATION

Positively charged ion

ANION

Negatively charged ion

ADSORPTION

The surface binding of metal to soil solid phases, e.g. clay, organic matter

PRECIPITATION

The combination of metal with an associated ion in soil pore water to form a new solid phase compound in soil, e.g. lead phosphate (chloropyromorphite)



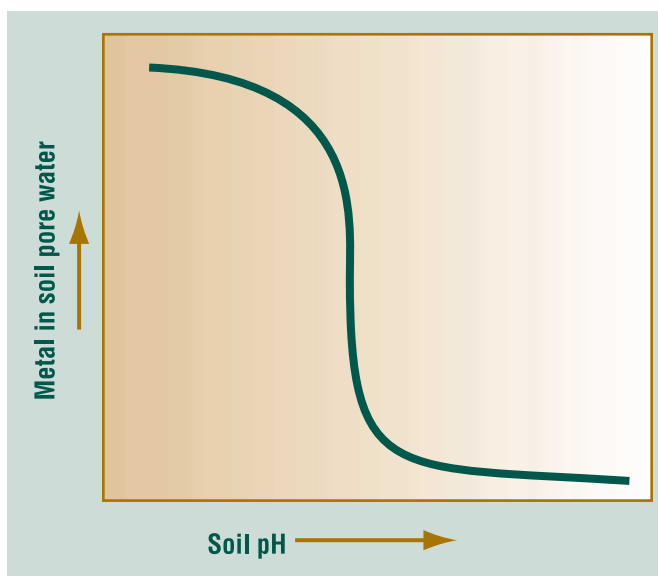


Figure 1

Example of the relationship between pH and cationic metal concentration in soil pore water.

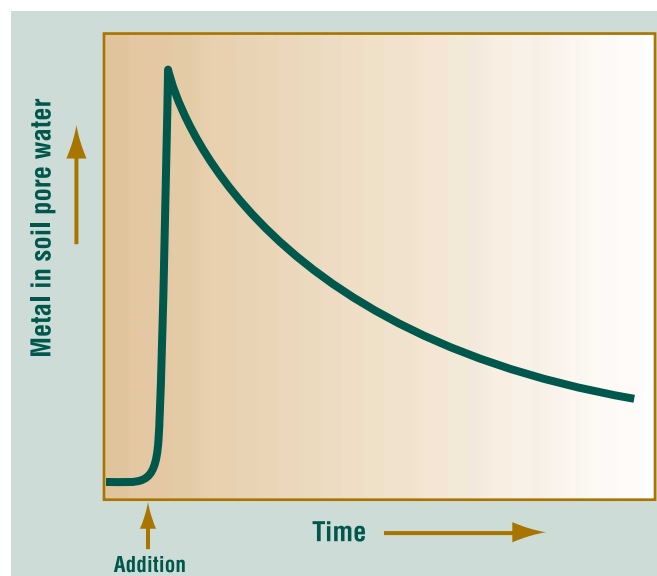


Figure 2

Generalised example of effect of time on concentration of added metal in soil pore water.

Precipitation reactions remove metal from soil solution through the formation of new solid phases, usually in association with a corresponding anion or cation already present in the soil solution.

Both adsorption and precipitation reactions exhibit time-dependent reaction rates. It is evident that the longer the metal is in contact with the soil, the greater the strength of bond formed or the more stable the solid phase formed (Figure 2).

For metal that has been adsorbed, this increasing strength of bond may be due to a rearrangement of the metal on the surface of the solid phase, e.g. diffusion of metal into micropores on the surface of the soil mineral or organic material (Figure 3a). An additional hypothesis is that the adsorbed metal slowly diffuses away from the surface into the crystalline structure of soil minerals (Barrow 1987) (Figure 3b). Numerous laboratory studies have demonstrated this phenomenon, and there are suggestions that the rate of the reaction is

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metal-specific, with the rates of ageing as measured by adsorption-desorption hysteresis differing as follows: Cd<Mo<Zn<Ni (Barrow 1986; Barrow et al. 1989).

Precipitation processes are most important where metal loadings are high, or where counter ion concentrations are high, e.g. phosphate, carbonate. The metal will combine with other ions in solution to form new solid phases in soil (Figure 3c). For example, for Pb the presence of phosphate in solution leads to rapid precipitation of Pb as hydroxy- or chloropyromorphite as follows:



where L = OH (for hydroxypyromorphite) or Cl (chloropyromorphite). These compounds are highly insoluble, so that a large portion of added metal is effectively “fixed” in the soil.

A second precipitation process that may lead to reduced bioavailability of metals is where new solid phases form in soil and occlude available metal, thereby removing it from the bioavailable pool. For

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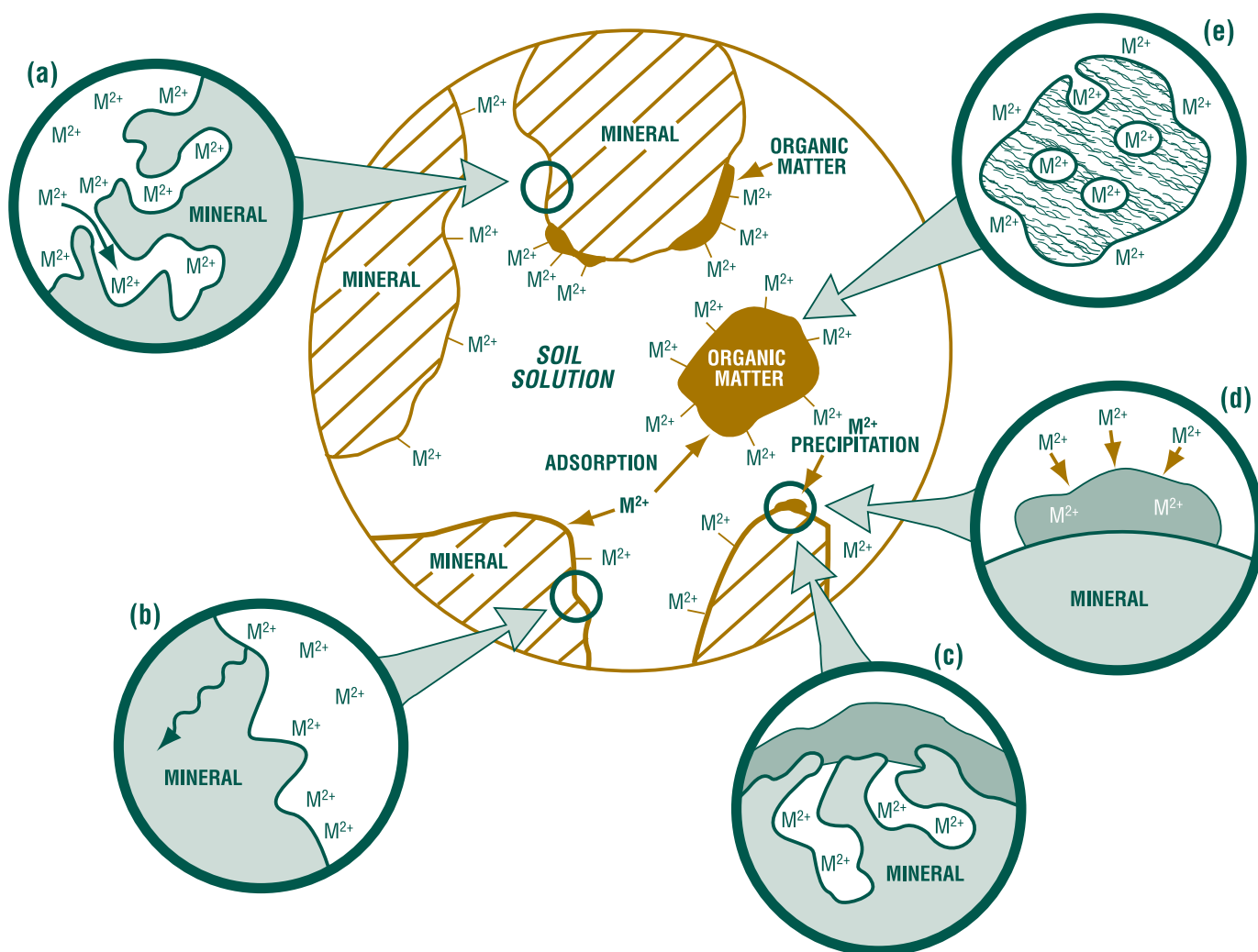


Figure 3

Adsorption and ageing processes in soils. Adsorption moves metals from solution to soil surfaces. Ageing moves metal from soil surfaces to deeper in the solid phase through (a) surface pore diffusion, (b) solid state diffusion, (c) occlusion of metals through precipitation of other phases, (d) precipitation of new metal solid phases, and (e) occlusion in organic matter.

example, in a seasonally water-logged soil, reduction and oxidation processes cause iron and manganese oxides to be solubilized and re-precipitated several times, thus “burying” available metal within solid forms and reducing bioavailability (Figure 3d). A similar process may also occur as organic matter forms in soil, with metal being occluded in the structure of the organic molecule.

Finally, there is the possibility that metals become more tightly bound in organic materials, either through diffusion into organic molecules or through occlusion in the organic molecule (Figure 3e).

The availability of the metal ion decreases with time of contact with soil

Irrespective of the mechanisms, the end result is that the availability of the metal ion decreases with time of contact with soil. This has important implications both for the beneficial use of trace metal nutrients in agriculture, and for the assessment of risk posed by high concentrations of metals in contaminated soils.

Implications of ageing reactions for micronutrient fertilizers

Early evidence for ageing reactions in soil comes from reductions in effectiveness of metal micronutrient fertilizers in agricultural systems (Figure 4). For example,

work with Cu and Zn fertilizers has clearly shown a decline in the extractability and effectiveness of these fertilizers related to the time of incubation with micronutrient-deficient soil (e.g. Boawn 1974, Brennan et al. 1980; 1990). This means that in nutrient-deficient soils, repeated applications of micronutrient fertilizers are needed to ensure continued production of healthy crops.

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toxicity is related to soil pore water concentrations of metal, toxicity end-points using short soil-metal contact times will tend to overestimate toxicity compared to field conditions where metals are in contact with the soil for longer periods.

However, evidence for ageing affecting toxicity responses is scarce or equivocal, mostly due to the lack of studies in this area. Smit and van Gestel (1998) examined the toxicity of Zn to springtails (*Folsomia candida*) in “fresh,” “leached,” and “aged” soils, finding significant increases in no-effect concentrations due to ageing, but their data are confounded due to differences in soil pH between fresh and aged soils. Bruus Pedersen et al. (2000) found little effect of short-term ageing (12 weeks) on Cu toxicity in soil.

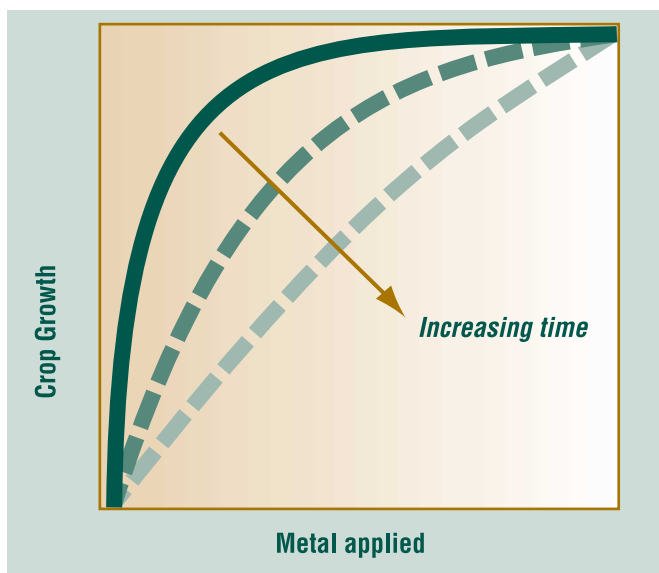


Figure 4

Effect of incubation time on response of crop plants to added essential metal in micronutrient-deficient soil.

Is ageing important for toxicity of metals?

The outcome of ageing reactions in soils where metal loadings are higher will be similar to those in metal-deficient soils, although processes may differ due to the higher metal concentrations involved. For example, precipitation reactions may become more important at high metal loadings. Certainly, for short contact times of metal with soil, e.g., minutes to hours, adsorption processes will have a significant effect in reducing soil solution metal concentrations. However, for longer contact times, it is expected that the same processes of diffusion, precipitation and occlusion will reduce metal availability, and hence toxicity, over time (Figure 5). Consequently, where

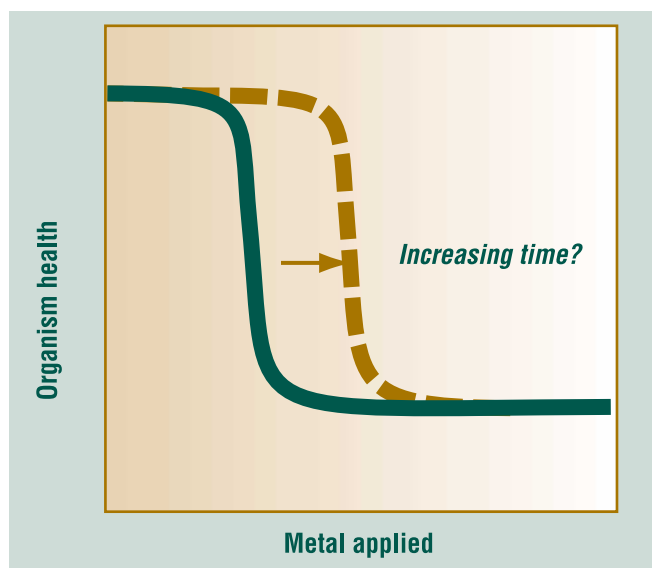


Figure 5

Hypothetical change in toxicity response to added metal as a function of time of soil-metal contact.

Due to the few studies in this area, firm conclusions cannot be drawn regarding ageing reaction rates and toxicity for the various metals.

Is ageing reversible?

A key question for both supply of micronutrient metals and toxicity of metals is whether ageing reactions are reversible. Due to the incomplete knowledge of the actual mechanisms responsible, it is difficult to

firmly state that ageing reactions are either irreversible or totally reversible.

Certainly, where changes in pH are responsible for ageing through precipitation of metal compounds in soil, these reactions will be reversible if the soil subsequently acidifies. Similarly, where reduction reactions form insoluble metal sulphides, oxidation will subsequently release metal from these solid phases. Metals bound in organic matter may also be released upon oxidation of the organic molecules.

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Where ageing reactions are postulated to be due to diffusion of metals into micropores and/or crystal lattices, reversibility depends on the situation. Diffusion is a process driven by concentration gradients (and temperature), so that where metals are continually being added to soils, the direction of movement of metal would be predominantly from available to non-available forms. Therefore, if metals continue to accumulate in the soil, ageing can be regarded as an irreversible reaction. However, in metal-deficient soils, where metal concentrations in soil pore water are extremely low, the concentration gradient will be such that metals slowly migrate from non-available forms to the bioavailable pool. In this situation of metal mobilisation deficiency, ageing is reversible, albeit at a slower rate than the initial ageing reaction.

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References

- Barrow NJ (1986a) Testing a mechanistic model. 1. The effects of time and temperature on the reaction of fluoride and molybdate with a soil. *Soil Science* **37**, 267-275.
- Barrow NJ (1987) 'Reactions with variable charge soils.' (Martinus Nijhoff: Dordrecht, The Netherlands).
- Barrow NJ, Gerth J, Brummer GW (1989) Reaction kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite. II. Modelling the extent and rate of reaction. *Journal of Soil Science* **40**, 437-450.
- Boawn LC (1974) Residual availability of fertilizer zinc. *Soil Science Society of America Proceedings* **38**, 800-803.
- Brennan RF, Gartrell JW, Robson AD (1980) Reactions of copper with soil affecting its availability to plants. I. Effect of soil type and time. *Australian Journal of Soil Research* **18**, 447-459.
- Brennan RF 1990. Reaction of zinc with soil affecting its availability to subterranean clover. II. Effect of soil properties on the relative effectiveness of applied zinc. *Australian Journal of Soil Research* **28**, 303-310.
- Bruus Pedersen M, Kjaer C, Elmegaard N (2000) Toxicity and bioaccumulation of copper to black bindweed (*Fallopia convolvulus*) in relation to bioavailability and the age of soil contamination. *Archives of Environmental Contamination and Toxicology* **39**, 431-439.
- Smit CE and Van Gestel CAM (1998) Effects of soil type, pre-percolation, and ageing on bioaccumulation and toxicity of zinc for the springtail *Folsomia candida*. *Environmental Toxicology and Chemistry* **17**, 1132-1141.

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Fact Sheet on Environmental Risk Assessment

This is the fourth in an occasional series of *Fact Sheets* to be produced by ICME on metal-specific issues in environmental risk assessment. Authorship selection and editorial review are coordinated by Dr. Anne Fairbrother of Parametrix, Inc. Each *Fact Sheet* is reviewed for technical merit by Dr. Erik Smolders of Katholieke Universiteit (Catholic University) Leuven, Belgium, and by a panel of experts on metal-related regulatory issues. While the *Fact Sheets* reflect the views of the authors, they are intended to provide an objective review of each topic. ICME hopes these publications provide insights into complex issues in regulatory science, and welcomes questions and comments.

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