Stefan FRÄNZLE

SOIL-BIOSPHERE INTERACTIONS

WZAJEMNE ODDZIAŁYWANIA GLEBA-BIOSFERA

Summary: Soil is more than a source of nutrients and water and a solid support for plants, animals, fungi, bacteria... which live in or on it. The organisms rather change the biogeochemical features of soils especially as far as mobility and thus bioavailability vs. retention of essential and other metal ions are concerned. The interactions among soil and soil-dwellers to change living conditions in contact to soil account for phenomena of succession as well as for competition or changes in (net) primary productivity of a given area over time; there is a general trend of chemical development counter-acted by earthworms and some fungi only: the most stable compounds in soil (polyphenols) retain iron and copper to impede fungal growth. By means of the relationship between metal complex stabilities, bioconcentration factors and the electrochemical ligand parameter developed by this author, corresponding data for biorelevant ligands and such concerning eg REE (rare earth elements) and Al partition (partition coefficients used as a kind of benchmark) between soil and organisms can be combined to identify both the present state of some soil and the possible or additional risks imposed by deliberate measures such as liming and by ongoing soil burdening (eg due to acid rain).

Keywords: soil differentiation, retention/extraction, metal ions, ligands, succession in ecosystems, bioinorganic chemistry

Introduction: “role” and functions of soil

Soil forms both a solid support and a chemical stockpile, buffer (for water, minerals, organics, heat) and „mirror“ for organisms – eg bacteria, fungi, green plants, earthworms - dwelling in and on it. As metabolism requires a rather constant exchange of materials between some organism and its environment, regardless of both complexity of the organism and its mode of metabolism (eg heterotrophic, photo- or chemolithoautotrophic), there will be some fairly steady exchange, with soil determining compositions of living beings and vice versa, although not “to scale”. These exchange processes include uptake of metal ions from soil effected by the biota when delivering organic ligands into soil to re-absorb the respective metal complexes afterwards. Certain metal ions (some 10 different ones in both plants and fungi) are required to accomplish
- biocatalytic functions (eg Mg, Fe, Zn, Cu, Ni, Mo) as central parts of enzymes,
- transport of principal reactants in metabolism such as CO₂ or O₂ (Zn and Mg [for CO₂ transport/fixation] and Fe or Cu),
- inter- and intracellular communication (Na, K, Ca) and
- other functions [1].

For these purposes, substantial amounts of some of the mentioned metals are necessary, whereas minute traces of others (Mo, V, Co) will do. Since ligands, both present in soil before and released from biota, control equilibria, transport and soil/organism partition of metals, coordination chemistry provides a link between the composition of soil

1 Internationales Hochschulinstitut (IHI; International Graduate School) Zittau, Markt 23, D-02763 Zittau, Germany; Chair of Environmental High Technology. email: fraenzle@ihi-zittau.de
2 Even most closely connected symbiotic arrays of autotrophic and heterotrophic beings such as lichens (composed of an alga and some fungus) cannot fully cross-supply each other but depend on external both C and metal ion sources (see below), hence produce solid phases and soluble complexes from support leaching and also respond negatively to changes in environmental conditions [2].
and that of an organism dwelling on soil. Since every organism - be it a soil bacterium, a plant or a fungus – produces and delivers but a very limited set of such ligands, the corresponding selectivities of any ligand with respect to metal binding (ie, unlike complex formation equilibria for different metal ions) cause shifts in composition (abundance ratios among the metals taken up in this manner) from soil towards the biomass. Accordingly, different living beings which (also) differ with respect to their above-mentioned metal requirements, say green plants and fungi the latter of which need larger amounts of Fe, Cu and also V (green plants can apparently do without the latter) for oxidative degradations of polymeric organic materials (cellulose, lignin), will employ unlike ligands for sequestering the corresponding metals in appropriate amounts. During this process of securating organic ligands (hydroxicarboxylic and amino acids, oxalic acid, hydroxamates, 1,2-diphenols, „crown“ polylactones and molecular combinations thereof - [Figs. 1, 2 and 4]) they will also take up unwanted, other metal ions by the same way of complexation, most of the latter being irrelevant to metabolism, but some being dangerously toxic (eg Cd, Be, Sb, Tl).

![Fig. 1. Complex stabilities of some essential (straight lines) and toxic (broken lines) metal ions depending on the electrochemical ligand parameter. The dots to the left (citrate) refer to citratocomplexes (tri- rather than bidentate binding to metals), from top to bottom: Cu, Zn, VO$^{2+}$, Mg; the respective - log $K_{	ext{diss}}$ values can be determined by following the name of the corresponding ligand perpendicularly up to the intersection with the line which in turn is a graphical representation of eq. (1) for the corresponding ion. Chromium, beryllium and, to a lesser extent, cadmium will be mobilized and accumulated by fungi rather than green plants due to their more “electropositive” sequestration ligands produced and delivered by fungi. Although the effect is smaller with cadmium, it still suffices for Amanita fungi to contribute significantly to Cd (and V) turnover in litter and topsoil layers [3, 4]
Hence - especially for cases of hyperaccumulation in plants or fungi - the factors in soil-biota interactions which give rise to such effects (both in biochemistry and geochemistry) must be thoroughly understood which requires a model which also accounts for extrema in this interaction.

**Chemical features of interactions among soil and organisms**

Soil contains quite a number of different kinds of organic compounds which act as ligands towards metal ions, besides some inorganic species such as fluoride, chloride, ammonia (in wet, reducing soils) or soluble polysilicates. Many of the former are products of soil-dwelling organisms, including species of widely varying complexities, such as oxalate, malate or simple amino acids at one end of the range and condensed species like polyphenols or bacteriosiderophores – renowned for their affinity towards Fe(III) - at the other (Fig. 2).

![Diagram](image)

Fig. 2. Different organisms (green vascular plants, fungi and mosses - the latter only when subjected to stress) deliver different ligands to soil or upper litter layers. The result was already shown in Figure 1: fractionation of metals takes place according to unlike demands.

Owing to metabolism, soil and organisms living in or on it are intimately linked; in addition, consumption of soil organics or mineral phases, with clay absorbing toxines from other foods, and excretion of biological wastes besides leaf or needle litter bring about a constant exchange of matter (C, N, P, metal ions, other elements [S, B, Si, Cl etc.]) between soil-dwellers and both ground-water- and solid phases. The colonization of soil by some organisms which are particularly active in this respect will change structure and chemistry of certain soil layers so much as to produce visible changes (Fig. 3 a and b).
Fig. 3. Soils from Central North America (close to the Great Lakes) after (a) and without (b) immigration of earthworms. Dark brown polyphenolic humic material is destroyed and converted into carboxylates, causing leaching (bleaching of soil) of both organicics and nutritive metal ions. The litter layer is consumed also by the worms, changing the extent of retention of essential ions and removing substrate required by e.g. sugar maple (*Acer saccharum*) seedlings and many kinds of fungi and soil arthropods.

In addition, efficient (effic. with respect to retention of ions like Fe(III), V(IV) or Cu(II)) ligands in soil are both produced and cleaved by soil biota, given the destruction of 1,2-diphenols including tannins by earthworms [5] and reduction of hydroxamates (from fungi including mycorrhizal ones) present in soils at 10÷100 nmol/dm$^3$ of soil water [6] – these low levels suggesting rapid degradation – into carboxamides. The latter transformation will not change the electrochemical ligand parameter (see tab. 1 below; data from [7]) and thus complex stabilities keep constant also, but the former oligophenol destruction efficiently reduces retention of the said metal ions. Hence, the “clock of soil aging” is “set back”, producing better conditions for organisms which depend on substantial supplies of Fe, Cu, V (ie, fungi, especially lignin-degrading ones) while others “preferring” metals with negative x-values (Ca, Mn) experience an disadvantage in supplies. Ca, Mg etc. may even get leached downward, out of the root zones (Fig. 3). Corresponding analyses strongly suggest that forest and similar ecosystems are actually shaped and and changed by the thermodynamics of metal ion retrieval and respective spatiotemporal dynamics.

**Ecological stoichiometry** [8] emphasizes that, as a rule, stoichiometric compositions of living beings are constant within a given species, regardless of nutritional status, except for algae which respond to trophic state of their home-waters by variable C/N and C/P ratios and for larvae which feed on something completely different than their adult counterparts and, moreover, live in another environment (eg tadpoles in Venezuela [9] for which C/N/P ≈ 200 : 23 : 1). One consequence of this fact already known for long is Liebig´s (1853) principle of minimum: that nutrient which is available in lowest amounts with respect to the demands of the corresponding species will limit growth, that is, it controls the production of biomass (especially in autotrophs). Now consider the above situation, being one where different organisms, partly autotrophs (green plants and chemolithoautotrophic bacteria) and partly heterotrophs (other bacteria, fungi, animals), compete for resources by sequestering them from soil periodically as well as steadily change its capacity to withhold or donate essential metal ions from/to the said organisms by altering the respective (average or sum) complex formation constants. Obviously, the soil ecosystem will then respond by changing its composition:
The length of trophic chains will vary, influencing the extent to which carbon is lost from soil as CO$_2$, thus changing the C/N ratio which eventually, yet, becomes constant (C/N ≈ 29 [5, 8]; presumably by dominance of long-term effects).

Net productivity will also change, depending on the extent of producer “grazing” by either animals or bacteria, with the remainder contributing to organic matter stockpile in the sediment during humification. The latter then tends to alter in a way (enrichment of the rather refractory polyphenoles) which tends to reduce Fe (and V, Cu) availabilities for the plants.

Accordingly, with its internal trends of development [shift of average $E_L(L)$ towards the positive with time for both N-containing and N-free soil ligands], soil is an “active player” in controlling both quantitative and qualitative bioproductivity.

Succession, concerning plant and animal societies in the most conspicuous way, is a result of this, starting with formation of a novel pedosphere-atmosphere interface$^3$, thereafter bringing about stratification of the novel soil (eventually producing all A to D horizons) and formation and ongoing changes in the organic contents of the developing and stratifying soil.

Now for “real” data: the ratio between the sum of metals thus obtained from soil and carbon (fixed by photosynthesis) is about 1 : 200 [10] in green plants [photosynthetic organs], with Ca, Mg, Zn and Fe (data eg in [11-13]) forming the lion’s share of this; most notably C/Mg does not decrease below C/Mg ≈ 1000 : 1 in green leaves regardless of the principal role of Mg in photosynthesis (chlorophyll and rubisco). Accordingly, it would take just a few % of the total net photosynthetic C gain to sequester these metals in green plants sufficiently even if it were not for C ligand recycling within the tricarboxylate cycle. Thus this state of metal biochemistry and – supply may be called the “low-metal pathway”: traces of metals are absorbed and passed through the organism when/while acting as biocatalysts only but accomplish substantial flows and fixation amounts of C and N. Matters are completely different with chemolithoautotrophs, which eg use Fe(II) as an electron source for reductions of CO$_2$, that is, Fe is then consumed as a stoichiometric reagent, hence it is required in far larger amounts. Then, the amount of “complexable” metal ions which must pass metabolism or at least get into contact with the cells must be considerably larger than the C gain: this is hence dubbed the “high-metal pathway”: C/Fe < 1$^4$ (in green plants, C/Fe about 20,000). This also takes place in soil, related to deposition of Fe and Mn oxides in B horizons (iron pan; spodic B).

However, iron bacteria use ligands to sequester Fe in very much the same manner like green plants or fungi, with these specialized ligands often containing 20 or more C atoms.

---

$^3$ For an abandoned open pit/quarry or formed by depositing “protosoil” materials like sand/gravel dug out somewhere else or sewage sludge on an area. When such a pit or quarry fills with water, however, the novel pedosphere-atmosphere interface turns into a hydrosphere-sediment interface, and long-term trends of development use to become different as water-covered sediments become reducing (with concomitant consumption of Fe(III) and sulfate) just a few centimeters beneath their surfaces. Metal availability from the sediment then depends on solubilities of sulfides, which, among the essential heavy metals, is very small for Cu, better for Mn, Fe or Zn, notwithstanding the alternative open to aquatic plants to obtain their metal ion demands directly from solution phase (water).

$^4$ For a strand of iron bacterium *Leptothrix ochracea*, isolated from a mildly reducing (20 $\mu$M/l Fe(II) but no H$_2$S in solute; pH = 7.65) mountain spring in Czech Republic (Lusatian Mountains) by this author, C/Fe = 0.68 (32.9 % Fe in dry mass), with levels of several other essential metals (Ca, V, Co, Ni but not Mg, Cu or Zn) and of S also substantially increased as compared to green plants, an enrichment which likewise holds for Al and REEs.
(Fig. 4), not 2-6 like with citrate, malate, oxalate, glycine or proline; they also make use of rubisco/ribulose phosphates for CO₂ fixation, exactly like green plants. Hence they can maintain chemolithoautotrophic metabolism only if ≥ 99% (!) of C gain which had been “invested” into these ligands (which must leave the cells also) can be recovered thereafter, notwithstanding the substantial metabolic effort it takes to synthesize ligands like bacillibactin (Fig. 4).

Fig. 4. Structure of a typical bacteriosiderophore, isolated from a thermophilic bacterium. It is a cyclic oligoester produced from the amino acid threonine with diphenol (2,3-dihydroxybenzamide) moieties attached to it by a glycine residue spacer each, *ie*, a kind of phenol-modified hexapeptide (isomer). Other bacterial or fungal siderophores contain hydroxamate moieties [14], with likewise extremely high affinities towards Fe(III) [log k = 30 – 52]

Inside soil, C/Fe may vary widely, too, with Fe(II) being the only mobile (soluble) form of iron in soils, limiting the contribution of Fe-oxidizing iron bacteria to primary production there. Fungi and animals, as heterotrophs, depend on C/Fe in soil also, but now with the focus on usable (metabolically accessible) carbon, sometimes with a limitation by soil ligand parameter electrochemical E(L) values.

**The electrochemical ligand parameter and its use for prediction of complex stabilities**

The strength of chemical, *ie* bond dissociation energies (gas phase) or the position of equilibria towards ligand replacement by some standard reactant such as the solvent (in a liquid [here: aqueous] phase) depends, *inter alia*, on the difference or similarity of energies among the orbitals involved in chemical binding. Upon interaction (here that occurring between some metal ion and vacant electron pairs of a ligand) these combine into a molecular orbital (MO), the energy level of which will be the lower the stronger the interaction (binding) becomes. When comparing several ligands, *ie* among several different complexes of the same metal ion, the MO energies will differ, as will the complex stabilities, *eg* towards hydrolysis. Now, with redox-active metal ions these changes in HOMO (highest occupied MO) energies can be probed directly by subjecting the complex to redox reactions, adding or removing one electron to/from this very orbital at a given expense of energy (the respective electrochemical potential of this complex). Thus
a relation between complex formation constants and the redox potential is obtained [15] which usually is given as the change of redox potential - a ligand-based electrochemical series - pertinent to some standard redox system, e.g., Ru(II/III) [7] or the [Mo\(^{0/II}\)](dppe)_2 fragment [18] (dppe = 1,2-bis-diphenylphosphino-ethane); corresponding scales for different metal centres do correlate in a linear manner. Accordingly, any of these scales (electrochemical ligand parameters; [7]) can be linked to complex stabilities; the one advanced by Lever was selected because it encompasses the largest number of ligands (> 500), all anionic and neutral, chelating and monodentate ones. From this reasoning, with the additional criterion of a log-linear relationship between chemical equilibrium (law of mass-action) and the free reaction energy of the corresponding chemical reaction, one empirically finds

\[- \log k_{\text{diss}} = x \cdot E_L(L) + c\]  

(1)

Table 1

<table>
<thead>
<tr>
<th>Ligand</th>
<th>(E_L(L)) [V]</th>
<th>denticity n</th>
<th>biologically relevant ligand (example)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)-aminocarboxylate</td>
<td>-0.05</td>
<td>2</td>
<td>glycinate</td>
</tr>
<tr>
<td>porphyrinate</td>
<td>0.00</td>
<td>4</td>
<td>haemin, chlorophyll</td>
</tr>
<tr>
<td>sugar</td>
<td>+0.11</td>
<td>2 (7)</td>
<td>anion of fructose (pKa = 12.3)</td>
</tr>
<tr>
<td>nucleic acids</td>
<td>(-0.30) V</td>
<td>2 or 3</td>
<td></td>
</tr>
<tr>
<td>pyridine</td>
<td>+0.24</td>
<td>1</td>
<td>vitamin (B_6)</td>
</tr>
<tr>
<td>hydroxamate</td>
<td>+0.02</td>
<td>2</td>
<td>rhodotorulic acid (in yeasts)</td>
</tr>
<tr>
<td>hydrogen carbonate</td>
<td>-0.37</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>carboxylate</td>
<td>(-0.21)</td>
<td>1</td>
<td>acetate, aspartate or glutamate</td>
</tr>
<tr>
<td>oxalate</td>
<td>-0.17</td>
<td>2</td>
<td>residues (deprotonated)</td>
</tr>
<tr>
<td>hydroxipolycarboxylate</td>
<td>-0.28</td>
<td>2 or 3</td>
<td>malate, citrate</td>
</tr>
<tr>
<td>phenoxyphenolate</td>
<td>[+ 0.23]</td>
<td>1</td>
<td>tyrosine residue, gallic and caffeic</td>
</tr>
<tr>
<td>2-acetylphenolates</td>
<td>about -0.07 V</td>
<td>2</td>
<td>salicylic acid anion,</td>
</tr>
<tr>
<td>2-acetylphenolate</td>
<td>([-0.33)</td>
<td>1</td>
<td>2-acetylphenolate</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>-0.11</td>
<td>1 or 2</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>-0.22</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>carboxamide</td>
<td>+ 0.03</td>
<td>1</td>
<td>peptide, asparagine residue, urea</td>
</tr>
<tr>
<td>carboxamidate</td>
<td>-0.38</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

**bold:** ligands which are involved in metal transport in plants

With the parameters \(c\) and \(x\) fitted by linear regression analysis (4÷7 different ligands, predominantly anions) for any single metal ion/oxidation state (data now covering the range \(Z = 4\)÷95) and mode of binding (denticity of ligand, mostly 1 or/and 2). Then, \(x\) is the slope of an equation which denotes the sensitivity of complex formation to the electrochemical ligand parameter \(E_L(L)\) and \(c\) is a constant hence called “intrinsic binding stability”; \(c\) refers to complex formation constants obtained with ligands for which the other term gets
essentially zero, like nitrate(III) (-NO$_2$), hydroxamates (O,O) or porphyrinate. For dipositive ions, $x$ is about $-10$ (Ca, Sr) up to $+22$ (Cu), $c$ ranges between $+0.5$ (heavy alkaline earths) and $+9$ (UO$_2^{2+}$, Cu$^{2+}$), for tripositive ions values of $x$ scatter between ca $-25$ (Nd, Dy) and $+40$ (Al, Ga), those of $c$ between $2.0$ (Nd) and about $12$ (Fe(III), Al, Ga). All essential metals other than Cu are located close to each other in a $c/x$ diagram: the “window of essentiality” [8]; [10]. The corresponding $E_L(L)$ values for biorelevant ligands are given in Table 1.

For water-borne fulvic acids (from small forest creeks), interactions with various metal ions translate into $E_L(L) \approx -0.15$ V, assuming bidentate behaviour (Fränzle; unpublished). Thus, they are not to be taken as simple oligophenolates or phenol-carboxylates but contain larger amounts of other donor moieties. The same will hold for small humic acids (the mobile fraction) in (forest) soils also from which the humic or fulvic acids obviously had been eluted by rain, presumably without any pertinent chemical changes, which thereafter will happen by oxidation, photochemistry and bacterial attack altogether.

Sequestering ligands produced by plants, fungi, lichens etc.
correspond to different demands

Plants, fungi and chemolithoautotrophs use metals in different ways, either as stoichiometric reagent or sometimes, though catalytic, for transformation which are hard to effect and thus take substantial amounts of catalytic or co-catalytic metal ions (Mn in exoperoxidases), without being capable to retain them efficiently over long periods of time. As a result, there will be a high-metal- and low-metal pathway, respectively. Relative bioconcentration of metal ions in some organism or parts of it follows similar trends like complex formation equilibria, eg the Irving-Williams series. Accordingly, after correlation of bioconcentration factors (BCFs) in (eg) leaves of some species fractionation behaviour and metal uptake efficiencies of this species can be described by means of an effective electrochemical ligand parameter which denotes the properties of a ligand which fractionates among metal ions in the same manner as this plant, animal, fungus... does: identical BCF values are taken to correspond to identical complex formation constants which allows for calculating effective $E_L(L)$ values from (1). For this purpose, eq. (1) is rearranged as follows:

$$E_L(L)_{\text{eff}} = (-\log k_{\text{diss}} - c)/x \quad (2)$$

Concerning the effective $E_L(L)$ values for different plants, there is an average value around which many plants - trees and understorey plants, grasses likewise - “gather”, namely about $-0.17$ V [3, 10-13, 15-17] while Ericaceae do differ in either direction and plants from a tropical savanna (grasses, trees and shrubs growing on mounds along a river downwards to a salinified river shore site in Ghana) generally have $E_L(L)_{\text{eff}} \leq -0.30$ V$^5$, while even lower values of $E_L(L)_{\text{eff}}$ hold for halophilic algae (Fränzle, unpubl.).

$^5$ However, Fe contents for these Ghanaan sites (up to 59% of soil DM) are in high excess even of those found in typical ferralsols, essentially corresponding to impure Fe$_3$O$_4$ rather than to an “usual” soil. $E_L(L)_{\text{eff}}$ values for photosynthetic organs of tropical plants from other sites are not yet known so it is an open issue whether this specific assembly of plants represents an adaptation to excessive exposition to iron, with the corresponding $E_L(L)_{\text{eff}}$ values hence being irrelevant for plants from other tropical sites, or whether this difference among $E_L(L)_{\text{eff}}$ values for moderate-climate and tropical plants is a more common bioclimatic feature. Similar arguments hold for halophilic algae ($E_L(L)_{\text{eff}} < -0.35$ V).
Retention of metal ions by soil and its modifications upon „aging“ of soil, extent/kind of litter supply and soil „digestion“ by earthworms, bacteria

Dependent on the functional groups which in turn determine their ligation properties, eg amino groups, primary alcohols, carboxylate or ester moieties, oligophenols and so on, these undergo oxidation sooner or later, accordingly differ with respect to persistence. Lifetimes of these ligands (biological half-lives in typical soils of moderate climates) range from a few days up to about ten years (polyphenols), with varying shares of the specific kinds of compounds [18, 19]. Only such components which will get fully (by some 99%) degraded within \( \leq 300 \) days - that is, before next year’s leaves will fall and replenish the litter layer with the corresponding compounds - which translates into a biological half-life \( \leq 45 \) days, will disappear from the mixture of ligands capable of retaining metal ions in soil in a periodic manner in deciduous forests at least. In coniferous forests, there is steady loss of some needles, containing substantial amounts of phenols, with a likewise continuous though probably small input of short-lived compounds which interact with metal ions, thus the input of needle litter permanently influences soil chemistry under such trees. As is well-known, biodiversity in understorey layers of conifers is lower than with mixed or deciduous forests. Considering the ground cover, grasses will grow (and deliver ligands like amino acids [20]) only during the warmer seasons while mosses, often covering most of forest soils, only give away amino acids and peptides to underneath soil if exposed to drought (Fig. 2).

Hence these efficiently complexing yet short-lived components will be introduced - by subsequent rain events - into the soil mainly during summer. For our endeavour to estimate:

1) the (local [3-D]) chemical potential of many essential ions (all but Na, K, Ca) in soils of a forest ecosystem, hence the difficulties to rise or maintain certain species on them, and

2) to understand how ecosystems are shaped by availabilities of essential heavy (and some light, like Mg) metals from the soil stockpile and the temporal trends induced by soil aging and periodic supplies like the above ones by mosses and deciduous trees, including phenomena of succession, these are principal pieces of information.

Except for an input by leaf or needle litters, providing eg oligophenols, the degradation of less-persistent ligands in soil or litter layers will steadily change their functional groups and thus, their electrochemical ligand parameters which are hardly sensitive towards substituent effects usually (eg, the \( E_L(L) \) values of benzylamine and ammonia are almost identical [7]). This change will accordingly alter the binding preferences towards positive-x (like Cu, Zn, Al, but also Cd) or negative-x (Mn, Ca, Sr, REEs except of Sm, Eu and Tb) metal ions of the soil and thus the pattern of (relative extent of metal ion) retention. As a quite simple rule, average \( E_L(L) \) will increase with time, converting sugars, glycolipids into polyphenols eventually, except for the activity of earthworms and few bacteria which convert the latter polyphenols into hydroxicarboxylates (Fig. 5).
Fig. 5. The average electrochemical ligand parameter increases with time ("aging" of soil), limited only by polyphenol degradation done by earthworms\textsuperscript{[5]} and by basidiomycete fungi\textsuperscript{[17]}. The positions of the contributors are not to scale in this diagram: root exudates and needle litter should be placed more to the right side of this diagram than. When uninfluenced by litter inputs, absorption of Cu, Al and to some smaller extent Zn will become increasingly difficult due to retention. On the other hand, Mn and Ce can be taken up more easily, providing better living conditions to Mn-accumulating plants, such as various kinds of nut-producers (cocoa nut-, Brazil nut-, almond trees, peanut plants)\textsuperscript{[13]} and also Ericaceae (\textit{Vaccinium} spp.)\textsuperscript{[12]}. If there is plenty of litter, Cu retention beneath the surface will be weak, improving growth conditions to many fungi.

Now, with C (in the backbone of the molecule as well as forming ligand groups\textsuperscript{6} without heteroatoms other than H or O as in carboxylates, phenolates), and N-based (often directly ligating like in carboxamides, porphyrines, nitriles, amino acids or nitrate(III) ion) ligands behave differently with regard to kinetics and products of this process of oxidative degradation. So N-free and N-containing ligands from litter will develop into different species upon soil aging, which, in addition, display unlike selectivities towards metal ions: $E_L(L)$ in C(O)-based ligands will change much more upon their geobiochemical alterations than with nitrogenous ones. Because the estimated complex formation constants from (1) change with 10 raised to x times (the difference of) the electrochemical ligand parameter, given as

$$-\log k_{\text{diss}} = x \cdot E_L(L) + c$$

translates into

\textsuperscript{6} Organometal species or corresponding ligands (directly binding via carbon atoms to metal ions) like alkenes, alkynes, CO, strong CH-acids are rather rare in soil, in addition, there are very few organometal species in biology whatsoever. CO ligands are almost restricted to enzymes (Ni/Fe hydrogenases) of organisms dwelling at very low ambient redox potentials whereas isocyanides R-NC as other "direct" C donors and their metal complexes mainly occur in marine sponges rather than in any soil-linked organism. However, some 3-ketoenolates or 3-carboxylenolates, present in humic acids, or malonate ions (which are but some of the above CH-acids) can coordinate to certain metal ions by both C and O sites rather than via O only\textsuperscript{[21, 22]}. \hfill \Box
\[ K_{\text{ass}} = 10^{k \cdot E_L(L)} \cdot 10^c \]  

A small change in the respective \( E_L(L) \) brought about by soil chemistry will thus produce a substantial (far more than proportional) change in \( k_{\text{ass}} \) for either type of ligands (ligands based on other atoms than C(O) or N, say, S [not S(O) in sulfate] or P(O), As, Se... can be neglected for their far smaller abundances). Thus, the sum of metal ion affinities of the soil components towards some metal ion will rapidly increase except if complex formation constants of N-free and N-containing ligands times the stoichiometric ratio of both ligand types become or are equal. From this reasoning, the nomogram in Figure 6 was constructed.

It gives the optima of bioavailability from soil depending on \( x \) as the single variable, with the list of \( c \) and \( x \) parameters (for bidentate binding) being used to „decipher“ the identities of corresponding elements. For very different soils over a larger range of climatic conditions (humidity, average annual temperature) and vegetation coverages, the above stoichiometric C/N ratio attends a stable final value of about C/N = 29 [8], with bacteria and fungi oxidizing an „overhead“ of carbon into \( \text{CO}_2 \) leaving the soil whereas „too much“ N will either be disconnected from C backbones as \( \text{NH}_3 \), oxidized up to nitrate and undergo washout to deeper (sub-root) layers or be tied up into insoluble „N-polymers“ (cp. [5]). This ratio of 29, modified by the average numbers of C atoms in the backbone which support a single (pair of) donor site(s), gives a correction for the above competition argument which is taken account of in the various lines of Figure 6.

![Fig. 6. Metal ions which undergo hyperaccumulation in certain plants, depending on the difference of electrochemical ligand parameters between N-free and N-containing (prevailing) soil ligands. The hyperbolic kind of function causes some discontinuity upon slight changes around \( \Delta E_L(L) \approx 0 \text{ \, V} \), causing a „switch“ from accumulation of Ba or REEs to that of Cd or Ni, with obvious toxicological implications for (human or animal) consumers of these plants.](image-url)
Conclusions, recommendations

In order to reestablish something which might be perceived as a “natural state of affairs”, an ecological/geochemical situation close to that of an unperturbed ecosystem, various measures might be taken (notwithstanding the issue what an unperturbed system means considering eg an economically strongly used forest or even some park etc. within a town or other settlement). The principal result, inspired by Liebig’s minimum principle will be that soil geochemistry controls metal availability by chemical thermodynamics mainly in a way which is effective enough as to favour growth/competition of certain - either autotrophic or heterotrophic - soil dwellers against most others given the geochemical state of soil. Indicator plant information then combines with theory and analytical data on soil/plant partition (BCF values) of various, especially non-essential metals to provide information on the present state and possible (geobio-)chemical labilities of some soil.

A necessary condition yet would be not to cause any additional damage when trying eg to stop soil acidification by liming or similar measures (nihil nocere). When it gets into selective uptake of certain elements, eg for phytoremediation, one must understand before which is the present state of the system. Making use of the above nomogram (Fig. 6), one can take the distributions of REEs as benchmarks which tell as much about the species retaining metals in the soil selectively as indicator plants will do. Only when metal distributions in vegetation leaves, fungus sporophores etc. are known, allowing to estimate what happens inside the soil, the risk of intervention can be taken in a responsible way.

References


**WZAJEMNE ODDZIAŁYWANIA GLEBA-BIOSFERA**

**Streszczenie:** Gleba jest czynnikiem więcej niż tylko źródłem substancji odżywczych oraz wody i miejscem życia dla roślin, zwierząt, grzybów i bakterii, które żyją w niej lub na niej. Organizmy mają wpływ na biogeochemiczną właściwość gleby, zwłaszcza na mobilność, a przez to na biologiczną dostępność oraz zatrzymanie substancji niezbytowych i innych jonów metali. Oddziaływanie pomiędzy glebą a organizmami glebowymi może prowadzić do zmian ich warunków życia i produktywności gleb oraz może prowadzić do rywalizacji; jest to ogólny trend przemian chemicznych, której przeciwdziałają dźdźownice oraz niektóre grzyby: najbardziej trwałe w glebie związki (polifenole) zatrzymują żelazo i miedź, co hamuje wzrost grzybów. Relacje między stabilnościami kompleksów metali, biokoncentracją metali i elektrochemicznymi parametrami ligandów np. REE (metali ziem rzadkich) i Al mogą być wykorzystane do opisu obecnego stanu gleby oraz jego zmiany i możliwego albo dodatkowego ryzyka związanego np. z wapnieniem i rosnącym obciążeniem gleby (np. z powodu kwaśnych deszczy).

**Słowa kluczowe:** bioindykator, jony metalu, chemia koordynacyjna, parametr elektrochemiczny ligandu, parametry jonu metalu, interakcje gleba-roślina, „ważne” dane biomonitoringowe