

Concentrations of trace elements in soils: The three keys

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Abstract

Taxonomic categories of the highest level (e.g. the RSG of the World Reference Base for soil resources) are not adequate when dealing with trace element concentrations in soils. This does not however mean that pedology, its basic concepts and knowledge accumulated over more than a century, are of no use in this domain. Examples of the role of soil forming processes on trace element contents in soils will be provided.

Key Words

Trace elements, soil classification, geochemical background, pedogeochemical concentration, pedology

There is no question here of denying the importance of soil classifications or reference bases as languages of communication between scientists, as well as tools for soil cartographers wishing to class and compare soils. However, the highest categories of national or international systems are often used in an inappropriate way, for example as stratification units in the study of trace element contents in soils. Trace elements (TE) are the 80 stable elements, each with a mean concentration of less than 0.1 % of the upper continental crust. Together, they represent only 0.6 %, while the 12 major elements constitute 99.4 %.

Inadequacy of taxonomies

Categories at the highest taxonomic level, such as the reference soil groups (RSG) of the WRB (IUSS, 2006) are not relevant to the study of TE concentrations in soils. There are two main reasons: 1°) the attribution of a particular solum to a high level taxon is a hazardous and subjective practice. Sometimes the analytical determinations needed for an irrefutable diagnosis are unavailable. The result of all this is that, even using the same system of classification or reference base, different specialists do not give the same name to a given solum. 2°) Names such as Leptosols, Fluvisols, Cambisols, Anthrosols, Regosols, Gleysols, etc. give no information either as to the particle-size distribution or about the mineralogical composition, hence on the geochemical inheritance! Any stratification of a given data-set of soil chemical analyses according to this criterion is doomed to failure!

RSGs are few and far between which, because they are closely linked to a specific particle-size distribution or parent rock, can give us any useful indication in this domain. Podzols like Arenosols, are developed in sandy materials which are very poor in weatherable minerals and hence display very low TE contents. In contrast, by their very definition, Vertisols always show heavy clay textures, although the information given does not go beyond a mere granulometric description. In the same way, it is well known that most Andosols are developed in volcanic rocks, but these can present widely variable chemical compositions.

The initial inheritance: the geochemical background

Under any climate, the **number one key** which from the outset determines the concentrations in TE found in soils today is the chemical composition **inherited** from the parent material, usually called "geochemical background". This corresponds to the mineralogical composition of the rock whether originally-formed (in the case of extrusive and igneous rocks) or initially deposited (in the case of marine sediments, moraines, loess and alluvium), which have sometimes been modified by subsequent mineralization (Figure 1).

A first example is given by still weakly differentiated soils, which are abnormally rich in nickel and chromium, because they developed from rocks containing large amounts of olivine, pyroxenes, chromite, spinels, etc., which are all minerals bearing Ni and Cr. This is the case, for example, of the basalts and basanites of the French Massif Central (Soubrand *et al.*, 2007) or of the Réunion Island (Doelsch *et al.*, 2006) and the serpentinites in the Swiss Alps (Gasser *et al.*, 1995).

Another example is that of certain soils developed in alluvium showing abnormally high contents of some TEs. As a general rule, alluvium display extremely variable particle-size (from heavy clays to large boulders), but above all, their composition is totally dependent on the lithology of materials abraded upstream. So, some alluvial soils of little streams flowing down the Vosges or the Cévennes (France), exhibit

high concentrations of Pb, Zn, and Cu, simply because these alluvium are located downstream of strongly mineralized rocks.

The case of moraines is different, being deposited by Alpine glaciers (Switzerland – the canton of Geneva and France – the Savoy region). The glacial tills deposited by the ancient Rhone glacier contain numerous little fragments of "green stones". That is the reason why the still weakly differentiated soils developed in them are heavily loaded in nickel (40 to 220 mg/kg) and chromium (78 to 226 mg/kg), whereas they are poor in iron and of medium texture. Nothing similar is observed in the case of the Jura glaciers.

The second key: soil processes leading to natural pedogeochemical concentration (NPGC)

In regions with temperate climates and in those with cold climates, the **soil forming processes which can markedly change this inheritance** in upper soil horizons are few. These are:

- Partial or total dissolution of carbonates results in the relative accumulation of non-lixivated TE; the total dissolution of limestone causes huge changes since the calcite constitutes between 90 and 99 % of the rock dissolved (Prudente *et al.*, 2002). Thus, those constituents which have not been evacuated in the deep karst network (clay minerals, iron oxides, cadmium, and zinc) reach very high concentrations in residual soils.
- Dilution by very abundant organic matter (in the case of Umbrisols with humose topsoils);
- Translocation of clay particles (vertical or lateral illuviation – e.g. case of Luvisols and Planosols) leading, over the long-term, to the formation of upper soil horizons which have markedly lower TE content than deeper soil horizons;
- Direct and total weathering of clay minerals by acidolysis, ferrolysis, etc. giving rise to upper soil horizons which are very poor in trace and major elements;
- Podzolisation, where iron, aluminium and most trace metals form organo-metallic complexes, which are able to move down from the upper A and E layers and accumulate at depth in spodic B horizons;
- Absolute accumulation of iron, manganese and a suite of associated trace metals, in particular soil horizons with a dominantly blackish hue.

A good instance of this is provided by soils formed in the clayey residue resulting from the total carbonate dissolution of Jurassic limestone with a unusually high cadmium content (i.e. with 0.40 to 8 mg/kg rock - France, Swiss Jura). A large part of the freed cadmium remaining *in situ*, adsorbed onto iron and manganese oxy-hydroxides, gives rise to soil horizons whose natural concentrations exceed 2 mg/kg, and can even reach 22 mg/kg (Baize and Sterckeman, 2001; Prudente *et al.*, 2002; Rambeau, 2006).

Another illustrative case is that of soils of the Sinemurian "back slope" in Auxois (Burgundy). The marine limestone of Sinemurian age was locally mineralized by a suite of trace elements (As, Cd, Cu, Co, Ni, Pb, Zn, Tl). These TE come from hydrothermal venting along a network of faults delimiting an old Hercynian horst. The soils which can be observed today developed in the residual clay resulting from the limestone dissolution, which provoked a further TE concentration process in soils, which consequently have much higher TE contents than the underlying rock (Baize and Chrétien, 1994).

In the case of very old strongly and deeply weathered soils of the inter-tropical areas with a perhumid climate, many elements are lixiviated (e.g. Mg, Ca, Si), but others accumulate *in situ* (e.g. Cr, Ni, Cu, Mn, Ti, V) and combine with the diverse iron oxide forms (e.g. Nalovic et Quantin, 1972; Anand and Gilkes 1987; Becquer *et al.*, 1995; Trolard *et al.*, 1995).

The third key: contamination induced by man

Diverse anthropogenic additions have much more recently been added to the pre-existing natural stocks: i) atmospheric fallout from origins both far or near; ii) trace elements brought unwittingly by fertilizer, sewage sludge or waste spreading. The extent of this contamination and its chemical nature clearly have no relationship with the taxonomic category of the receiving soil.

Distinguishing the natural from the anthropogenic – Why is this necessary?

“For environmental risk assessment the question of reactivity is of even greater relevance than the question of total concentration because it determines the mobility, human exposure and ecotoxicological importance of the elements. For proper environmental soil management it is of vital importance to be able to distinguish between natural pedogeochemical concentrations and anthropogenically elevated levels of TEs” (Mol *et al.*,

2009). Thanks to this distinction, it is possible to obtain an initial assessment of possible dangers to human health, especially through phyto-availability to cultivated plants. Trace metals of anthropogenic origin are actually, much more reactive species than those of natural origin, even when in abnormal abundance. In fact, the latter have been strongly adsorbed for millennia onto various solid phases or are co-precipitated with Fe or/and Mn oxy-hydroxides. The determination of local natural pedogeochemical concentrations (NPGC) and subsequently of the local level of contamination allows us not to declare as being "polluted" (with the serious socioeconomic or financial consequences which may ensue) a plot of ground in a context of strong natural anomalies. If necessary, it allows us to fix realistic and relevant target de-pollution values, suited to the geological and pedological context.

Distinguishing the natural from the anthropogenic – How?

Stratification by "soil series" or by parent material are two ways of simply and appropriately determining the local NPGC. The latter (Figure 2) requires sufficient geological knowledge and can only be done where these parent materials are sufficiently geochemically homogeneous.

The determination of the natural pedogeochemical background of a given soil series requires the ability to recognize it in the field and to characterise it. Between 25 and 50 soil samples must be analyzed for each soil series and these samples must be as little contaminated as possible. Therefore, the sampling must be organized by giving priority to i) soils which have remained under forest which, indeed, have also received atmospheric deposition but are free of agriculturally induced contamination; ii) deep horizons of cultivated soils, assumed to be uncontaminated. Some obstacles may sometimes occur: i) in some circumstances, contaminants did not remain in the surface horizon and went down to deeper ones (Sterckeman *et al.*, 2000); ii) most mining or industrial areas are strongly contaminated over their entire surface. Fortunately, for each "soil series" strong natural relationships exist for most of the trace elements (e. g: zinc vs clay content or lead vs iron (Figure 2) or chromium vs nickel) which are useful as a base for reasoning. It must be noted that these approaches and reasoning require the use of analytical methods giving access to the really "total" contents, which requires the dissolution of silicates using hydrofluoric acid or by alkaline fusion.

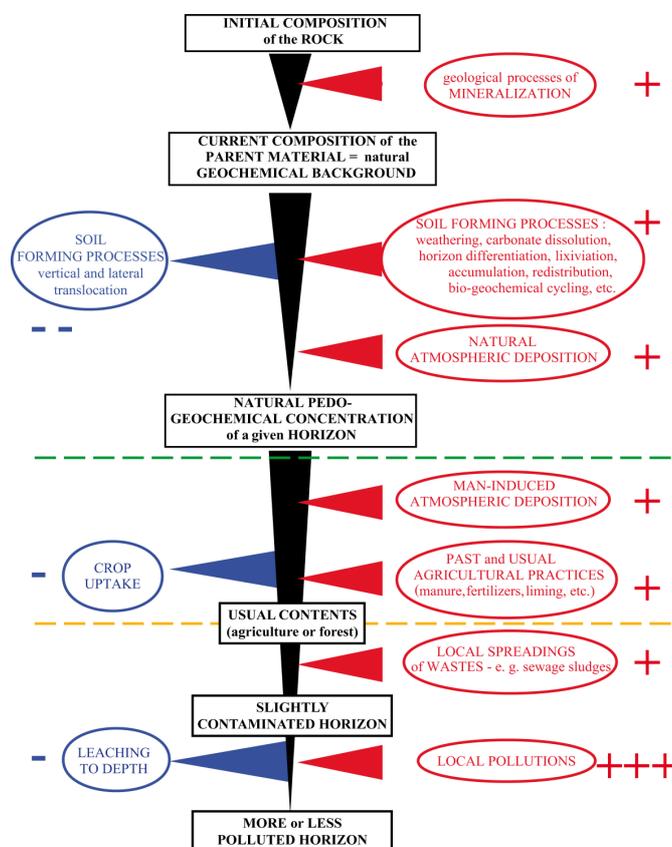


Figure 1. Progressive acquisition of trace element composition of a soil horizon: from the initially-formed rock to the ploughed surface horizon. On the right, in red: factors increasing the trace element contents. On the left, in blue: factors decreasing the trace element contents.

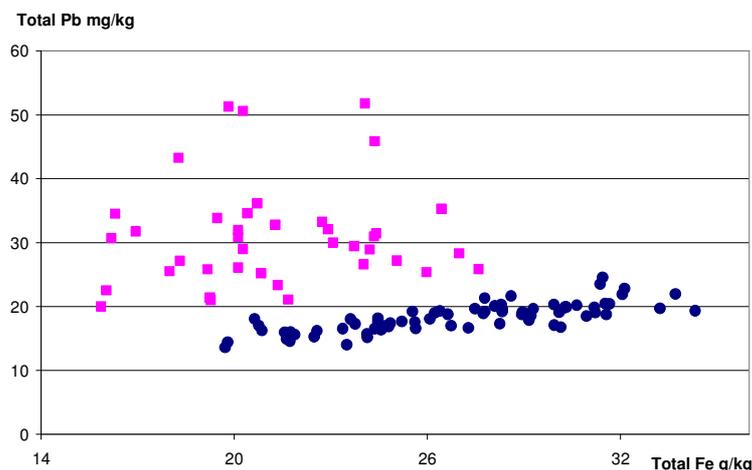


Figure 2. Cultivated soils developed from loess in the Northern France: relationship between total lead and total iron (Sterckeman *et al.*, 2006). Pink squares represent the ploughed surface horizons, blue circles all types of deep horizons. The natural geochemical relationship between Pb and Fe is strong for all deep horizons because it is not modified by anthropogenic additions. The same does not apply to surface horizons, more or less contaminated by lead.

Conclusion

It would not be sensible to deal with trace element contents in soils (pedogenetical modifications brought about the geochemical inheritance, speciation, soil-plant transfers) without taking into account the basic concepts and knowledge acquired by pedology over more than a century. We have just seen that it is essential to take into account pedological information to optimize sampling strategy and interpretation of results. Moreover, when a contamination by trace elements is recognized, all information about soils contributes to a correct assessment of the dangers induced. Finally, we are, however, led to the conclusion that the highest taxonomic categories do not give us the right key.

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