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RIO DE JANEIRO , BRAZIL

MEDICAL GEOLOGY IN BRAZIL

**ENVIROMENTAL AND HEALTH
EFFECTS OF TOXIC
ON MATERIALS
GEOLOGICAL FACTORS**



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GEOCHEMISTRY OF BRAZILIAN SOILS: PRESENT SITUATION

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ABSTRACT

Geochemical soil analysis is largely used to identify areas with high and low concentrations of trace-elements. It is also an excellent criterion to assess a given metal's accumulation in the soil, to guide studies on potential occurrences of nutritional (in plants and animals), human health and environmental problems.

The chemical composition data of Brazilian soils is scarce and concentrated in a few regions of the country, particularly São Paulo, and only for a couple of elements, usually micro-nutrients.

This study presents an up-to-date panorama of soil geochemistry research in Brazil and suggests improvement initiatives to establish reference trace-metal values important to human health.

INTRODUCTION

Pedology (the study of soil) evolved to the state of science in 1883 when the Russian scientist Dokuchaev realized the soil is, in fact, a natural and dynamic body, result of differentiated and organized entities and not merely a heap of mineral particles with organic matter on its surface (Moniz, et al., 1972). Hans Jenny in his book "Factors of Soil Formation" (1941), based on the ideas of soil genesis, until then diffusely presented, offered for the first time an equation to mathematically express the relationship between the properties and variables of soil:

$$S = f(Cl, O, R, M.O., T)$$

Thus, it is understood that any property of the soil (S) is a function of the climate (Cl), living organisms (O), relief (R), source material (M.O.) and time (T). It must be pointed out that McBratney et al. (2003) also included the question of spatialization as a key factor in digital mapping issues, as examined later.

In this sense, geology, through source material studies by petrology and geochemistry, had a strong influence on the research at that time, since the development of genesis studies and soil classification was largely dependent on the stage of the basic correlated sciences (Moniz, et al., 1972). Considering that the American School is one of the world's most influential in geology and soil studies, its development will receive a greater emphasis.

Shacklette & Boerngen (1984) reported the United States have used soil analysis in mineral prospecting since the 1940s. However, there were serious hindrances to trace-element analyses due to the lack of equipment with better detection limits. This situation changed in the 1960s with the introduction of the first commercial atomic spectroscopy equipment. Nevertheless, only in the 1970s a substantial improvement occurred in trace-element detection limits following a series of new instrumentation developments of atomic absorption/emission spectrophotometers (Cienfuegos & Vaitsman, 2000). Then also the first studies were produced to establish a relationship between human health problems and the geographical distribution of metals in the soil (Shacklette

& Boerngen, 1984). The development of new research confirmed that source material was the primary origin of trace-elements in the soil (Alloway, 1995; Kabata-Pendias & Pendias, 2001). In that view, one would expect basic rock originated soils to have higher contents of Zn, Cu, Ni, Mn and others, than those originated from granites, gneisses, limestones and sandstones. However, several works, especially Chen et al. (1993), have indicated that besides the source material, other pedogenetic factors exert a fundamental role in trace-element distribution in soil. In the last 20 years, the focus of geochemical soil analysis has been to establish reference values for toxic metals to introduce legislation that regulates the use of soil in relation to domestic/industrial waste and agriculture (USEPA 40 CFR Part 503 and Council Directive 86/278/EEC). It should be noted most European countries have established maximum permissible main toxic element (Cd, Zn, Cu, Cr, Hg, Ni and Pb) limits in soils (Table 1). Countries such as Spain, Portugal and the United Kingdom have even established variable values according to the soil pH. However, only a few countries followed the USA example to maintain a long established routine of soil analyses to form a data bank. This is able to indicate, more precisely, the mean trace-metal values in "natural" soils and man- changed soils (Shacklette & Boerngen, 1984; Holmgren et al., 1993; Burt et al., 2000; Burt et al., 2003). The limit values established, though, are still arbitrary, usually based on 95%.

In Brazil, like the United States, most geochemical soil studies initially followed the international tendency to give mineral prospection support and to understand soil genesis (Melfi & Pedro, 1977; Melfi & Pedro, 1978). With improved analytical techniques, new studies were directed towards correlating trace-element amounts with soil formation and classification (Araujo, 1994; Horbe, 1995; Ker, 1995; Oliveira, 1996; Castro, 1998; Lacerda, 1999). Following these initiatives, Ker (1995) and Lacerda (1998), for example, cite several authors who indicate certain iron oxides in the soil are important trace-element sources, particularly, Zn, Cu, Co and Ni. Specific Brazilian soil characterization studies of various metal concentrations (micronutrients, toxic or trace) have not been well

developed and most, initially, were concentrated in São Paulo State (Valadares, 1975; Valadares & Catani, 1975; Furlani et al., 1977; Valadares & Camargo, 1983). Based on that same international concern, some Brazilian groups began searching for background values of several elements in national soils. Pérez et al. (1997) analyzed 30 samples (A horizon and B diagnostic) of 15 Brazilian soil profiles for several elements (Co, Cr, Cu, Mo, Pb, Zn, Mn, Fe, Cd, Sr, Zr, Ba, Rb, U, Th, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). Besides developing a pedogenetic field thesis Marques (2000) also produced new data on a series of trace-elements in soils in Minas Gerais State. However, Cetesb (2001) defined soil quality reference values on the base of specific sampling, following Dutch methodology. From 13 different representative soil profiles of São Paulo, 84 composite samples were collected, representing the 0-20 and 80-100cm depth levels. The following elements were analyzed: aluminum, antimony, arsenic, barium, cadmium, lead, cobalt, copper, chromium, iron, manganese, mercury, molybdenum, nickel, silver, selenium, vanadium, zinc. Finally, Fadigas et al. (2002), analyzing a set of 256 Brazilian soil samples, separated in seven groups based on their soil properties similarities, determined reference values for Cd, Co, Cr, Cu, Ni, Pb and Zn.

OBTAINING REFERENCE OR BACKGROUND VALUES

If there is no knowledge of what can be considered the "natural" level of a given element in the soil, how can it be determined if it was anthropogenically contaminated, for instance, or if it had a considerable chemical deficiency that may affect the nutrition of living beings?

The national data base, as mentioned above, is concentrated on certain elements and limited to São Paulo State. Moreover, the soil sampling, preparation and extraction methodologies are usually different and not correlatable. However there are ways of planning the sampling to obtain mathematical functions that, through correlation with other soil properties (Pedotransfer), facilitate data prediction in unsampled regions. Fadigas *et al.* (2002), for example, suggested a model to estimate the

Table 1 – European limits of heavy metal concentration (mg/kg) in soils.

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
EU Directive 86/2781	1-3	----	50-140	1-1.5	30-75	50-300	150-300
France ²	2	150	100	1	50	100	300
Germany ²	1.5	100	60	1	50	100	200
Italy ²	1.5	----	100	1	75	100	300
Netherlands ²	0.8	100	36	0.3	35	85	140
Sweden ²	0.4	60	40	0.3	30	40	100-150

1. Long (2001); 2. Europe (2005)

“natural” contents of Cd, Co, Cr, Cu, Ni, Pb and Zn based on silt, clay, Mn, Fe contents and CEC. Data spatialization, as part of digital mapping procedures, contributes considerably to the pedotransfer validating process and reorientation of new sampling campaigns. According to (McBratney et al., 2003) few of the mentioned studies are considering these methodologies.

With respect to the analytical methods, extraction and analysis provided “Totals” produce little useful information since the chemical element’s ecotoxicological effects and environmental behavior (transport, reactivity, mobility, etc.) totally depend on its chemical form (Allen, 1993; Tack & Verloo, 1995; Hani, 1996; Quevauviller, 1998; Kot & Namiesnik, 2000; Abreu et al., 2001). Methods considered “Pseudo-Total” allow the anthropogenic influence to be determined and therefore can be used for environmental monitoring (Alloway, 1995; Walter & Cuevas, 1999; Scancar et al., 2000). However, if no standard analytical methodology is chosen, the data bank consolidation question returns, since most methodologies do not have the same extraction capability (Mattiazo et al., 2001). Likewise, there are methods that assess a given element’s transference potential to a plant (“available”). In that case, however, care must be taken not to use internationally recognized methods that have not been developed for our conditions and therefore do not allow proper interpretations. An example is shown in Figure 1, taken from Wasserman (1977), which presents Cs transfer factors from the soil to the plant (absorption similar to K) in some Brazilian soils and based on international data. The important difference found is a result of physical-chemical processes that typi-

cally occur in tropical soils and that have little influence in Northern Hemisphere soils. In Brazil, the most usual extraction methods for “available” micronutrients as well as “available” toxic metals, are DTPA and Mehlich 1 solutions (Cantarella et al., 2001; Mattiazo et al., 2001). Some research aimed at using this type of result to determine reference values for certain toxic elements in soils is being developed. Finally, there are other studies based on the complexity of possible soil reactions that use sequential extractions to identify where a given element is located (Ure, 1991; Das et al., 1995; Hayes & Traina, 1998). Most environmental studies that involve this technique generally consider the following stages (McLean & Bledsoe, 1992; Das et al., 1995; Morrow et al., 1996):

- soluble in water
- changeable
- linked to carbonates
- linked to Fe/Mn oxi-hydroxide
- linked to organic matter
- residual

There are several extraction technique problems (Ross, 1994; Hayes & Traina, 1998; Kot & Namiesnik, 2000): i) the lack of extractor selectivity; ii) element re-adsorption and redistribution during the extraction process; iii) the soil-extraction solution relationship influence on the analyzed element distribution; iv) the mineral and organic compounds solubility change during the extraction progress. Even though, as it allows the comparison of chemically similar fractions, sequential extraction is pre-

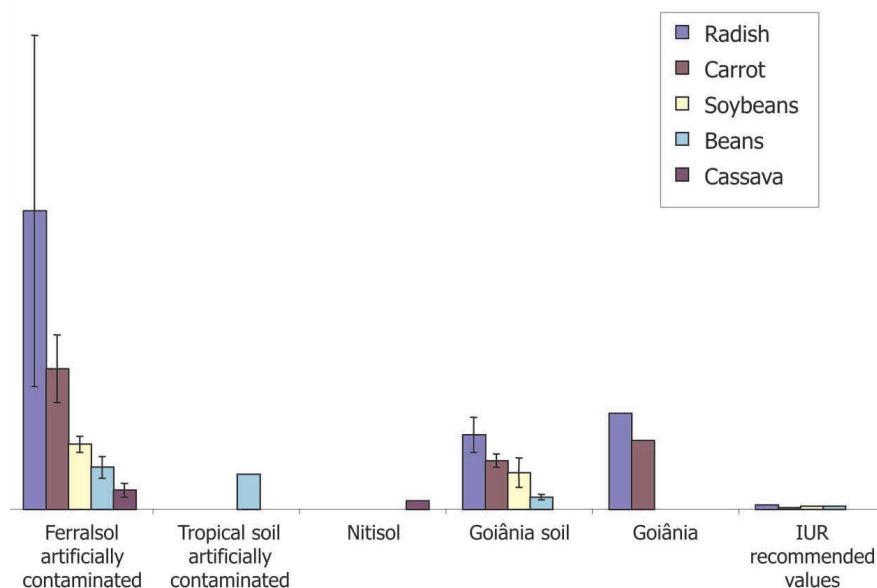


Figure 1 – Transference factors of Cs-137 to radish, carrot, soybeans, black bean and cassava crops in some Brazilian soils compared to international data generated in temperate climate (IUR).

ferred in soil solid phase speciation studies to determine the mobility potential and environmental bioavailability of several metals and radionuclides (Candelaria & Chang, 1997; Dean et al., 1998; Quevauviller, 1998; Wasserman et al., 2002). Figure 2, extracted from Mavropoulos et al. (2005), illustrates this case. Note, although the Pb total content remains unchanged in both soils (7.0g/kg), there was an element differential migration to distinct phases, representing a different mobility risk potential and bioavailability.

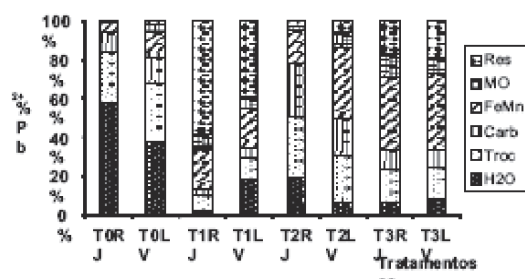


Figure 2 – Participation percentage of Pb obtained from two soils (RJ in a yellow-red Argisil, LV is a red Latosil) contaminated with 7.0g/kg and submitted to three remediation treatments (T1, T2, T3) in the six extractable phases in water (H₂O), changeable (Chang.), in carbonates (Carb), in Fe and Mn oxides (FeMn), in organic matter (MO) and residual (Res). TO is the control sample.

EXCESS X DEFICIENCY

The main purpose to establish soil reference values has always been linked to concerns regarding its contamination. However, due to the development of high-tech agriculture there is a strong tendency of certain micronutrients deficiencies because of the soil's low restoration ability, the low use of agrochemicals based on these elements and the low effectiveness of micronutrients in fertilizers (Yamada & Lopes, 1998; White & Zasoski, 1999; Welch & Graham, 2005). In Brazil, for instance, there is ample literature indicating the natural deficiency of Zn and Cu in our soils (Abreu *et al.*, 2001). Furthermore, the misuse of certain agricultural practices, especially soil liming (soil pH correction with limestone), can lead to the unavailability of otherwise naturally available micronutrients in soils, such as Fe and Mn (Figure 3). So, confirming previous observations, it is more important to know the conditions of the soil in which an element occurs than knowing its total content as a way of predicting its availability.

It is important to note, in cases of metal pollution of soil, plants have "defense" mechanisms that guarantee the low transference of these elements to the various vegetal organs, in particular those situated in the aerial parts (Shaw, 1989). However, if there is a given micronutrient deficit in the soil, the plant will hardly absorb it in

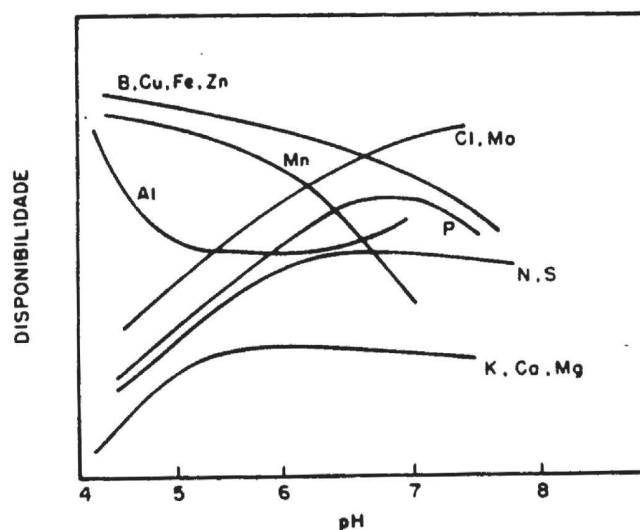


Figure 3 – Availability of several elements related to the soil pH (Nascimento, 1995).

sufficient amounts for its nutrition, although often no visual deficiency symptom is perceived ("hidden hunger"). However, this nutritional shortage may affect the animals and humans that depend on the plant for their nourishment (Welch & Graham, 2005)..

FINAL CONSIDERATIONS

Having recognized the need to establish trace-metal reference values, be they micronutrients or potentially toxic, it is fundamental to standardize the sampling, sample preparation and soil analysis methodologies based on a national work commission. However, because of the large area to be covered, it is evident that studies have to be carried out at a regional level, with a view to build a national geo-spatialized data bank. Efforts are being made in some states to research regional reference values but most of them collide with the lack of funds. Thus, it is extremely important to raise awareness among decision makers (the competent authorities), to enable state and federal Science & Technology development agencies to create specific research funds to subsidize this kind of study.

Finally, for those who intend to make a profound study of the implications of soil in human health, there are some international references that merit examination, namely: Oliver (1997); Dissanayake & Chandrajith (1999); Abrahams (2002); Deckers & Steinnes (2004).

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