

Ni, Cr Cu & Zn speciation and biodisponibility in a grazed field from the Cantal volcanic mountains - France.

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Context and objectives

In the Cantal region, basaltic flows present particularly rich contents in Ni, Cr, Cu and Zn compared to other analysed types of rocks. These flows cover large cattle grazed areas. The MTE (Metal Trace Elements) deriving from the basaltic rock can therefore naturally be found in soil horizons and in the overgrowing grass. Objectives of our study are :

- 1) To determine the proportion and the type of the MTE naturally bearing phases present in the soil horizons (**speciation**)
- 2) To quantify the natural MTE distribution from the parental rock to the soil and to the overgrowing grazed plants (**biodisponibility**)

Studied area

The pastured field is located at the top of the occidental part of the Mauriac basaltic flow. A wet mountain climate is found locally (altitude = 700m / annual averages over the last 6 years : rainfall = 1300 mm, air temperature = 10,4°C). The rock is a massive basalt Ni and Cr contents encompass the values obtained in the 59 other basalts and basanites analysed over the Cantal volcanic mountains (bulk rock MTE contents : Cr = 371 ppm, Ni = 214 ppm; Zn = 118 ppm; Cu = 49 ppm). The soil is non allophanic andic ranker, 24 cm deep and fairly differentiated (A₁/A₂/R). The grass roots density is important in the A₁ horizon (0-8 cm). Roots still appear in great number at the profile bottom between the horizontal basaltic flagstones.

Methodology

Soil samples were taken along a pedological pit. Total MTE amounts were measured in bulk soil (with roots) and rock by ICP-MS after crushing and alkaline melting of dried samples (CRPG, Nancy). The MTE speciation was explored by optic and electronic microscopy (SEM & microprobe) and using selective extraction : water, cobalt hexamine chloride, sodium phosphate, ammonium oxalate. Grass samples were taken at the grass haymaking period (maturation stage) in tree 15 m-diameter circles located nearby the pedological pit. Composite topsoil samples (0-8 cm) were taken in each circle (5 sub-samples). The plant crushing and MTE contents measurements were determined by the LUPRAVE laboratory (INRA-Bordeaux). The soil bulk density and the plant dry matter yield were measured for calculating the MTE stocks (in g.m⁻²).

Results

- 1. Speciation in soil** : Referring to the fractions generally attributed to the extraction solution we have used, none of the studied MTE was found to be water soluble, except Zn (> 1%). Ni and Cu are the only exchangeable cations found in small proportion (< 6% of their total amount in soil). Organic matter and amorphous oxi-hydroxides bear up to 30 % of the total amount of Pb and Cu, and only 10% of the Ni and Cr contained in soil. The major parts of Ni and Cr are located in unweathered minerals (spinel, pyroxenes).
- 2. Biodisponibility (Table 1)** : Similar bulk soil MTE and major elements contents are obtained along the pit and in the 3 plant sampling circles allowing the comparison of the MTE amounts calculated in the rock, the soil horizons and the grass. An important dilution of the total MTE amounts is found from the rock to the plants, except for Pb. The A₂ horizon / rock ratios of **1/4** (Cu et Zn) to **1/5** (Cr et Ni) shall indicate a dilution by OM accumulation in soil. The plant / A₁ horizon ratios of **1/40** (Zn) to **1/80** (Cr) could be explain by effects of the root activity.

Table 1 : MTE stocks calculated from rock to plants

		Cr	Ni	Pb	Cu	Zn
		g.m ⁻²	g.m ⁻²	g.m ⁻²	g.m ⁻²	g.m ⁻²
Plants		0,1116	0,0903	0,0145	0,0313	0,1191
Horizon	Depth					
A ₁	0 - 4 cm	9,24	5,32	0,69	1,65	4,51
A ₁	4 - 8 cm	10,60	5,85	2,19	1,84	4,70
A ₂	8 - 24 cm	53,51	30,33	2,58	9,66	21,47
Rock	< 24 cm	252,7	145,9	2,79	33,26	80,40

Perspectives

Fraction accepted to be associated with the organic matter (Na pyrophosphate extracts) could plenty explain the low amounts of MTE found in the grass compared with the topsoil. Further analysis will aim at assessing the environmental risk (for water and grazed plants) of long-term weathering of minerals bearing up to 80 % of the total amount of Ni and Cr in soil (spinel and pyroxenes).