MOBILITY OF CU AND CO IN METALLIFEROUS ECOSYSTEMS: RESULTS OF A LYSIMETER STUDY IN LUBUMBASHI (RDC)

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CONTEXT

Numerous soils in Katanga have been contaminated by the Cu-ore extraction and treatment activities. The copper-belt hosts ecosystems which have been able to adapt to metalliferous conditions. The knowledge of the interactions between plant and soil in these environments is crucial regarding the conservation of biodiversity as well as phytoremediation.

A view from a mining site in Katanga

OBJECTIVES

This study aimed at assessing the mobility of Cu and Co in the rock-soil system as can be found on slopes of the copper hills. We studied the impact of the addition of rocks taken from the upper part of the copper-hills to uncontaminated soils on the physico-chemical properties of soil and the composition of soil percolating solution.

MATERIAL & METHODS

Lysimeters

Small (1-L) lysimeters were built up and filled with mixtures of soil (800g) and rock (50g) samples. They were installed in open-air condition in the experimental garden of the University of Lubumbashi during one rainy season (October 2011 to march 2012). The percolating solution was collected and sent for analysis of Cu and Co content (Fig.1).

Soils and rocks

5 rock samples were used to contaminate two horizons of a typical forest soil. The characteristics of the surface A and subsurface B horizons are given in table 1, along with the geochemical content of the rocks. The mineralogical content of the rocks was evaluated by X-ray diffraction (Fig. 2).

Soil properties were measured at the end of the experiment. pH was measured in 1N KCl and in 0.01N CaCl$_2$. Methods for Total organic Carbon (TOC), granulometry and Cationic Exchange Capacity (CEC) were respectively Walkley-Black, Robinson pipette and Metson. Total content in elements were measured by atomic absorption after triacid-HF digestion; available elements after extraction with CH$_3$COONH$_4$+EDTA at pH 4.65 (Lakanen-Erviö) and soluble elements after extraction with 0.0N CaCl$_2$. Description of methods can be found in Van Ranst et al (1999).

Sorption isotherms of Cu and Co were performed on both horizons in order to characterize their retention potential. Solutions containing 1, 2, 5, 10, 20, 50, 100 and 200 mg.kg-1 of Cu or Co were equilibrated during 16h with soil. The element remaining in the solution were measured by atomic absorption.
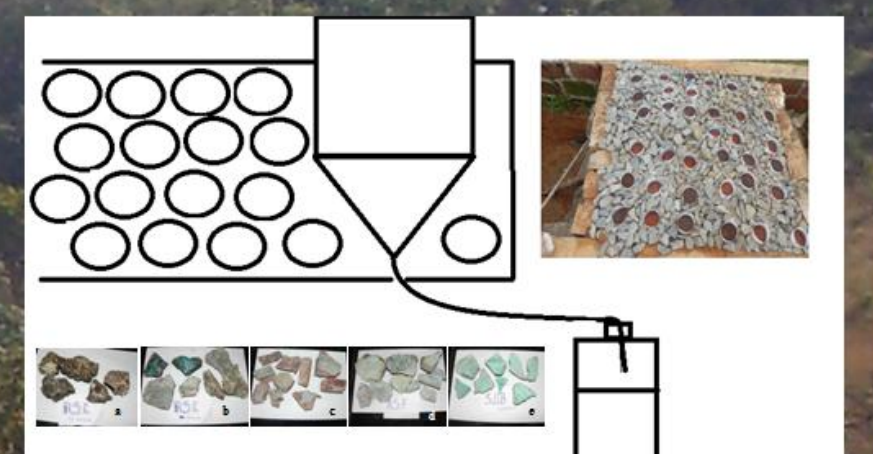
Figure 1: The experimental design
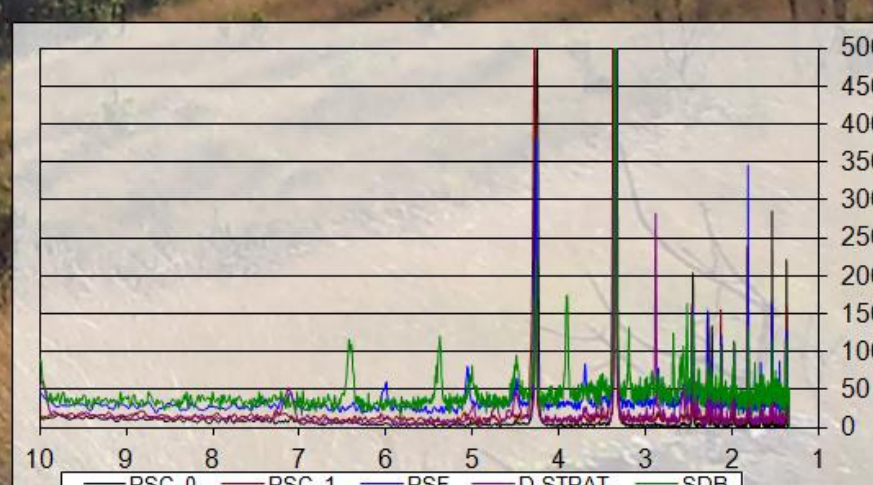
Figure 2: diffractograms of the rocks

Figure 3: Climatic data during experiment

Table1: Characteristics of soils and rocks used in the experiment

Sample	pH$_{H2O}$	pH$_{KCl}$	TOC	Clay	Silt	Sand	CEC	Al$_T$	Fe$_T$	Mn$_T$
Soil			g.100g^{-1}		%		cmolc.kg^{-1}		mg.kg-1	
Hor. A	4.42	3.89	2.70	31	34	36	25.4	2131	8971	261
Hor. B	4.27	4.27	0.27	34	25	40	17.6	3056	12714	234
Rock	pH$_{KCl2}$	Mineralogy after X-Ray Diffraction								
RSC	6.27	Quartz only					249	473	378
RSC min	6.51	Quartz + possible traces of malachite					332	253	57
RSF	6.68	Quartz + malachite					955	819	244
D-STRAT	7.86	Quartz + dolomite + kaolinite + traces of malachite / heterogenite					2525	3400	166
SDB	5.85	Quartz + illite + sepiolite?					2583	484	19
Sample	K$_{Al}$	Mg$_{Al}$	Ca$_{Al}$	Cu$_T$	Co$_T$	Cu$_{Al}$	Co$_{Al}$	Mn$_{Al}$	Cu$_{CaCl2}$	Co$_{CaCl2}$
Soil			g.100g^{-1}						mg.kg^{-1}	
Hor. A	14.7	9.9	1.4	158	44	20	2.4	53.2	0.26	1.03
Hor. B	4.5	0.5	0.1	90	48	2	0.7	9.4	0.19	0.12
Rock									mg.kg^{-1}	
RSC	ND	ND	ND	473	954	ND	ND	0.28	1.17
RSC min	ND	ND	ND	22569	1700	ND	ND	1.52	4.61
RSF	ND	ND	ND	95333	3897	ND	ND	5.4	14.0
D-STRAT	ND	ND	ND	14329	455	ND	ND	0.48	<1.0
SDB	ND	ND	ND	141551	5296	ND	ND	71.8	27.0

RESULTS

The properties of A and B horizons are slightly different with more organic matter, more nutrients but more acid reaction in the A horizon. The B horizon contains more clay and probably more Fe-oxides (Total Fe>>). Rocks present a great range of variation for chemical content with total Cu and Co ranging between 470 (RSC) and 140,000 (SDB) and between 450 (d-strat) and 5,300 (SDB) mg.kg^{-1}, respectively. Rock reaction is rather different according to nature of rock too (Table 1). Examples of lixiviation curves are given in figure 4. The adsorption curves are given in figure 5 and the soil properties at the end of experiment in table 2.
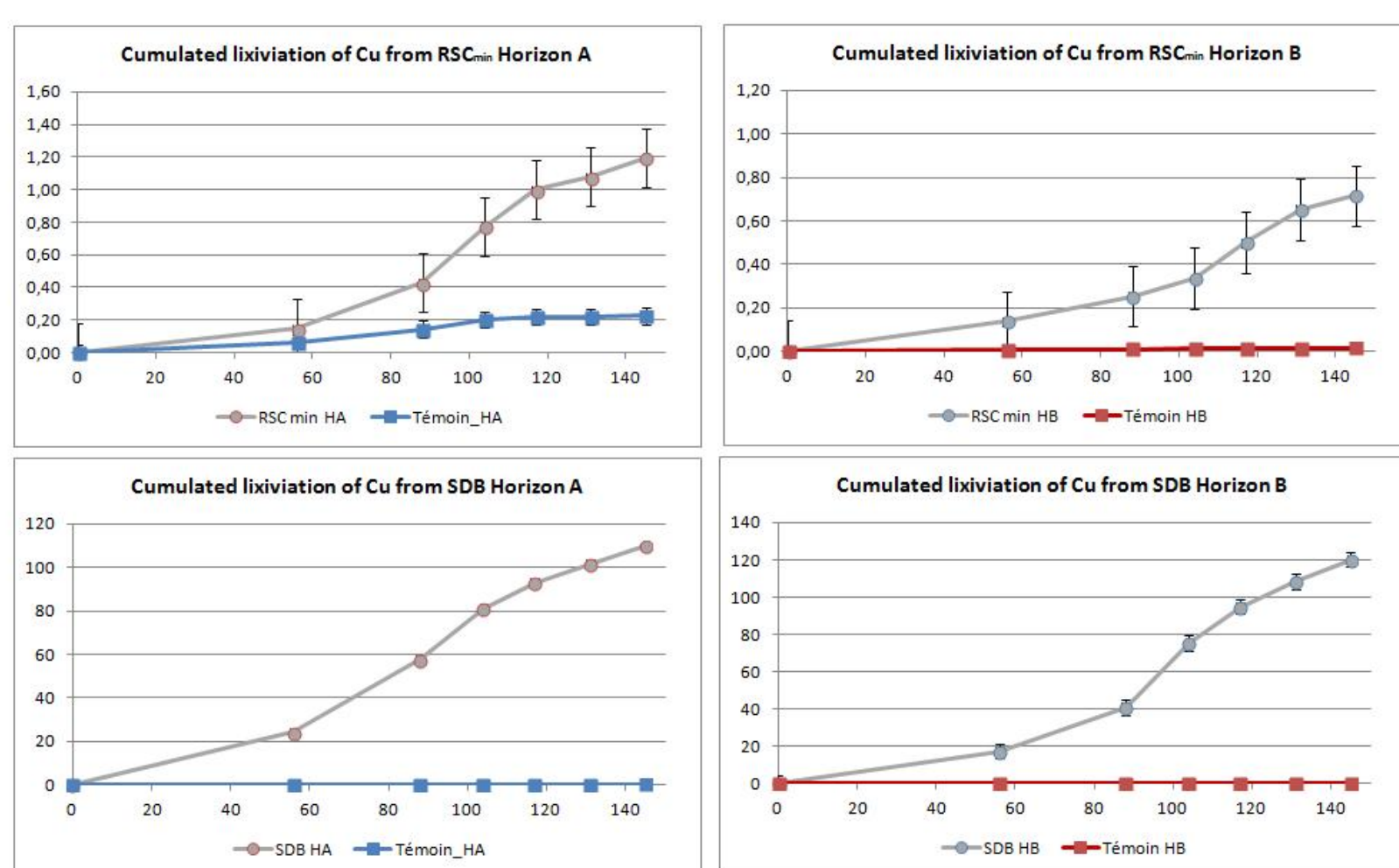
Figure 4: Cumulated lixiviation of Cu (mg) for RSCmin and SDB mixed to A and B horizons.

The adsorption experiment shows that the retention potential of A horizon is close to 10 times higher than for B horizon.
The ratio of retention potential of Cu to Co is close to 10, too.
This is due to specific sorption on organic matter.
Even if the quantities of Cu and Co that were lixiviated were small compared to soil total contaminations by rock addition, it can be seen that the mobile and mobilizable pools within the soil have been affected.
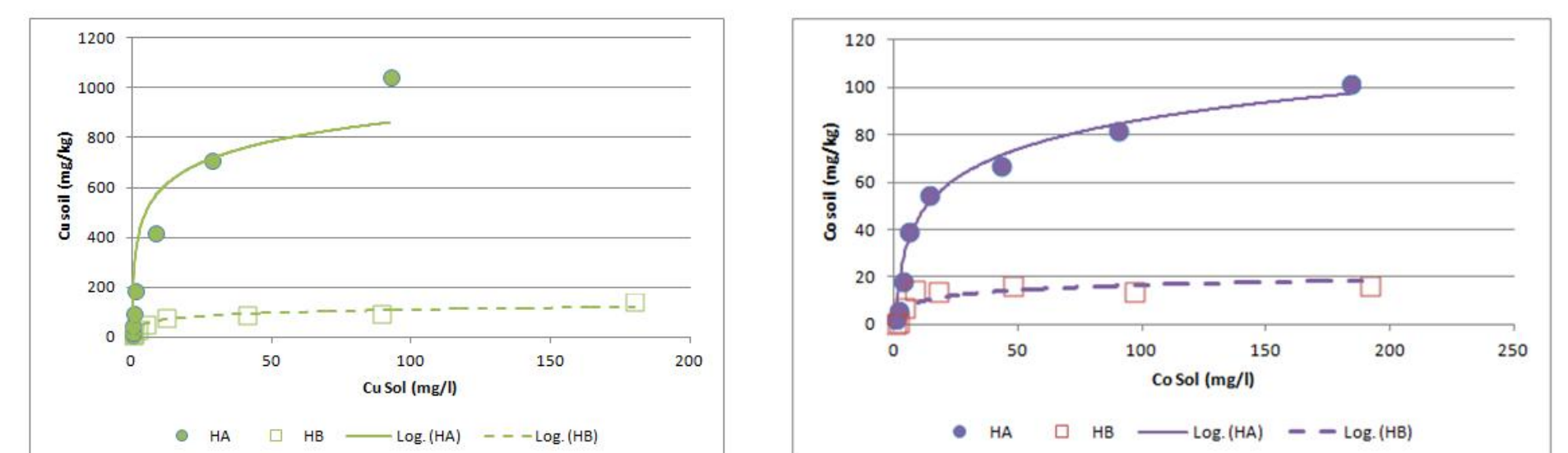
Figure 5: Adsorption curves of Cu (left) and Co (right) on the two horizons.

The quantities of lixiviated element follow :
(Cu) : SDB > > RSF > RSCmin > D-Strat > RSC
(Co) : SDB > RSF > RSCmin > RSC > D-Strat
The effect of pH appears as crucial as well as the solubility of the rock (SDB >>)

Table2: Soil characteristics at the end of the lysimeter study : pH, Total Organic Carbon, Mobilizable* and mobile** elements. Mean / Standard Deviation. N=3.

Horizon	Rock	pH$_{CaCl2}$	TOC	Ca*	Mg*	Mn*	Cu*	Co*	Cu**	Co**
			g.100g^{-1}		mg.100g^{-1}				mg.kg^{-1}	
A	No rock	4.11 / 0.07	2.87 / 0.23	2.20 / 1.65	8.17 / 1.80	53.1 / 1.6	21.5 / 1.1	2.6 / 0.0	0.42 / 0.22	1.39 / 0.04
	RSC	4.15 / 0.06	2.78 / 0.08	2.33 / 0.15	6.77 / 1.27	55.7 / 7.6	19.4 / 1.2	5.4 / 1.8	0.15 / 0.13	2.77 / 0.93
	RSCmin	4.22 / 0.03	2.96 / 0.09	3.57 / 1.02	9.37 / 1.40	63.9 / 4.4	297 / 24	14.8 / 1.0	14.6 / 1.6	9.70 / 1.88
	RSF	4.27 / 0.06	2.75 / 0.10	1.90 / 0.36	7.50 / 1.25	50.6 / 2.6	945 / 9	15.4 / 0.7	87.3 / 7.8	11.4 / 1.2
	D-Strat	5.65 / 0.05	2.78 / 0.17	121 / 3.9	70.3 / 2.6	38.2 / 11.4	286 / 30	3.0 / 0.6	0.60 / 0.03	0.30 / 0.06
	SDB	4.59 / 0.01	2.37 / 0.64	0.97 / 1.50	2.30 / 0.26	22.8 / 4.0	3083 / 57	2.7 / 0.2	180 / 14	2.13 / 0.14
B	No rock	4.53 / 0.01	0.26 / 0.01	< 0.20	0.67 / 0.46	9.0 / 0.4	3.2 / 0.6	0.6 / 0.0	0.50 / 0.47	0.24 / 0.03
	RSC	4.52 / 0.05	0.30 / 0.06	< 0.20	1.27 / 0.58	10.0 / 1.2	8.3 / 1.6	1.0 / 0.1	0.40 / 0.12	0.50 / 0.06
	RSCmin	4.66 / 0.04	0.23 / 0.02	< 0.20	1.10 / 0.10	14.5 / 1.4	314 / 17	11.7 / 0.3	108 / 6	8.45 / 0.89
	RSF	4.97 / 0.04	0.24 / 0.01	< 0.20	1.50 / 0.20	17.7 / 6.4	945 / 57	10.3 / 0.3	297 / 8	7.15 / 0.4
	D-Strat	6.68 / 0.01	0.23 / 0.02	55.4 / 1.87	29.1 / 0.5	12.9 / 0.4	205 / 9	1.9 / 0.1	0.14 / 0.13	0.06 / 0.07
	SDB	5.18 / 0.03	0.24 / 0.02	< 0.20	1.07 / 0.32	12.5 / 0.1	2128 / 50	2.0 / 0.1	365 / 15	1.30 / 0.07

Extraction solution : * CH3COONH4 + EDTA at pH 4.65 / ** 0,01N CaCl2

CONCLUSION

Our experiment clearly shows the importance of rock type on the dynamics of Cu and Co mobility in soils from the metalliferous sites of Katanga. The rock weathering in soils formed on outcrops as well as on colluvic materials can solubilize significant amounts of both elements within one rainy season. The soluble fractions of Cu and Co are prone to migrate through soil with percolating water. The retention of Cu and Co by adsorption on soil surfaces however are markedly different according to element and to horizon type. The retention of Cu in the surface layer is far bigger than in mineral layer, as a consequence of specific sorption on organic surfaces.

References : Van Ranst, E., Verloo, M., Demeyer, A., & Pauwels J, M. (1999). Manual for the Soil Chemistry and Fertility Laboratory-Analytical Methods for Soils and Plants, Equipment, and Management of Consumables. NUGI 835, Ghent, Belgium (ISBN 90-76603-01-4), 1999, 243 pp.

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