DECONTAMINATION OF MIDDLE TO LOW-GRADE CONTAMINATED AREAS, USING A LOWCOST METHOD

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Abstract: Protected areas and wetlands often suffer contamination due to outcrops or by passage of contaminated fluids as rain, subsurface water or river infiltration. Due to legislation, in these areas activities which alter the natural environment are not permitted. Here we suggest and describe a methodology that can be used in all low to middle-grade contaminated areas without the necessity of structure changes, intense human interference and/or supervision.

Keywords: contaminated regions; plants; Si-Phytoliths; heavy metals; soils; native plants.

1. Introduction

With the increase of industrial and mining activities, larger areas are affected by contamination, often passing the limits established by local authorities or causing hazardous effects for living-, especially human beings.

Many different decontamination techniques, like mechanical, chemical or biological/biochemical intervention were developed and suggested (e.g.: Cunningham et al., 1996; Accioly and Siqueira, 2000; Meurer, 2004; Melo et al., 2006), but nearly all are based on a strong interaction with the contaminated soil, destroying natural structures and biotopes, or need a permanent supervision during their execution.

The method here suggested is simple to apply, cheap, very adaptable and does not imply great monitoring efforts during its execution and is qualified to be applied under a wide spectrum of climate situations and different types of contaminations. Here in this text an example from the Savanna system in Brazil is shown (Fernandes-Horn, 2016).

The methodology is based on two concepts:

a. Plants absorb metals in their parts and trap them especially in Si-Phytoliths (Figure 1).

b. Organic opal is nearly insoluble and has a long resistance to attack under normal soil conditions (Fig. 2; Table 1).

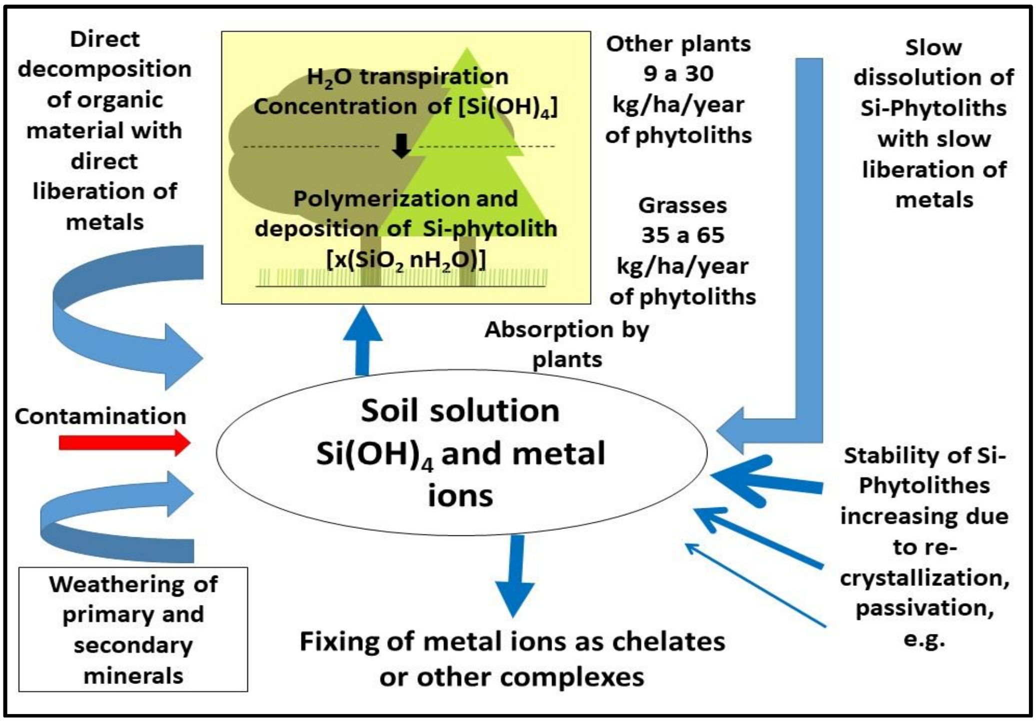

Fig. 1: Schematic diagram of heavy metal behavior in the soil-plant system. Other important factors are temperature, water flux quantity and velocity. Metal trapping per ha is estimated.

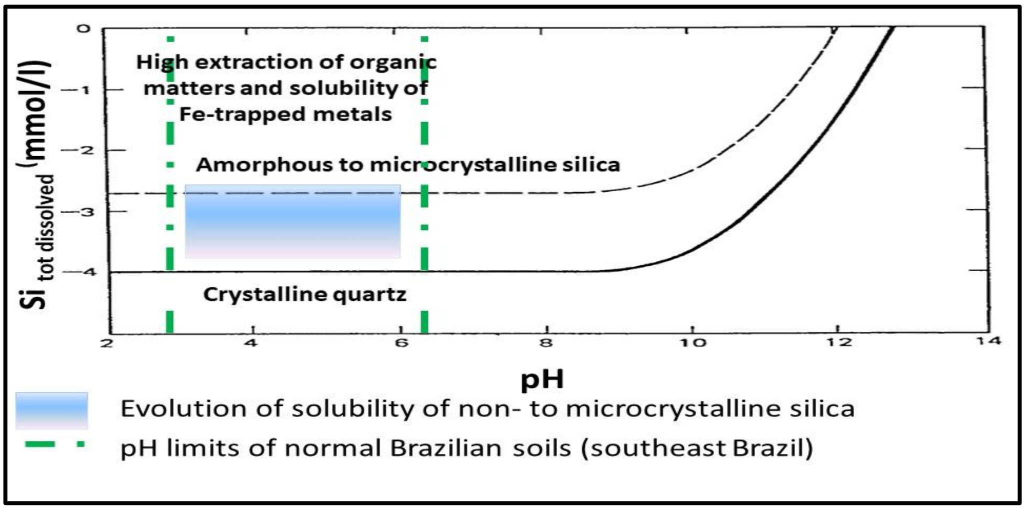

Fig. 2: Opal conditions in the natural environment (Sources: Ondo and Sase, 1986; Iller, 1979).

Table 1: Opal properties and element trapping compared to other SiO_2- compounds.

Mineral	Density	Hardness	Impurities g kg^{-1}	H_2O g kg^{-1}
Quartz	2,65	7,0	traces	0
Plant opal	1,5 – 2,3	5,5 – 6,5	50-150*	40-90
Geol. opal	1,2 -2,9	5,5 – 6,5	up to 200**	2 - 10

*Al_2O_3, C, Fe, K, Na, Cu, Ti and others;
**not only in the structure.

2. Regional setting

The target area of about 500 m^2 is localized at the northern border of the Minas Gerais State (UTM 702600E – 702300E and 8230750N – 8230350N), near the town of Riacho dos Machados in the transition zone between semiarid to arid conditions (Fig. 3). It belongs to a region were the mineralized rocks, explored by the Carpathian Gold Inc. crop out and caused anomalies of Zn, Pb and Cu.
Typical plant associations (Campos and Labouriau, 1969; Buján, 2013) form the vegetation in these hot and dry conditions.

3. Geology of the study area

The study area consists mainly of Precambrian rocks, migmatites and schists with intrusive granites, which suffered tectonism and hydrothermalism during the Brasiliano Event, causing impregnation with metals, especially Zn, Pb, Cu and Au by ascending liquids. Heavy metal concentration is limited on fractures and surrounding contacts. All is covered by soils, predominantly quartzitic sand, not well developed (~10–40cm) Ultisols and Inceptisols, disposed over an undulated landscape.

4. Materials and methods

The existent natural species, occurring in the working areas, were sampled. Three species of them adequate to the conditions and with favorable biological properties, were selected (Table 1). In this case *Rollinia leptoptella*, *Piptadenia gonoacantha* and *Sida sp*.
To compare metal concentration from plants with that from soil-Phytoliths, soil samples were collected over the investigated area.

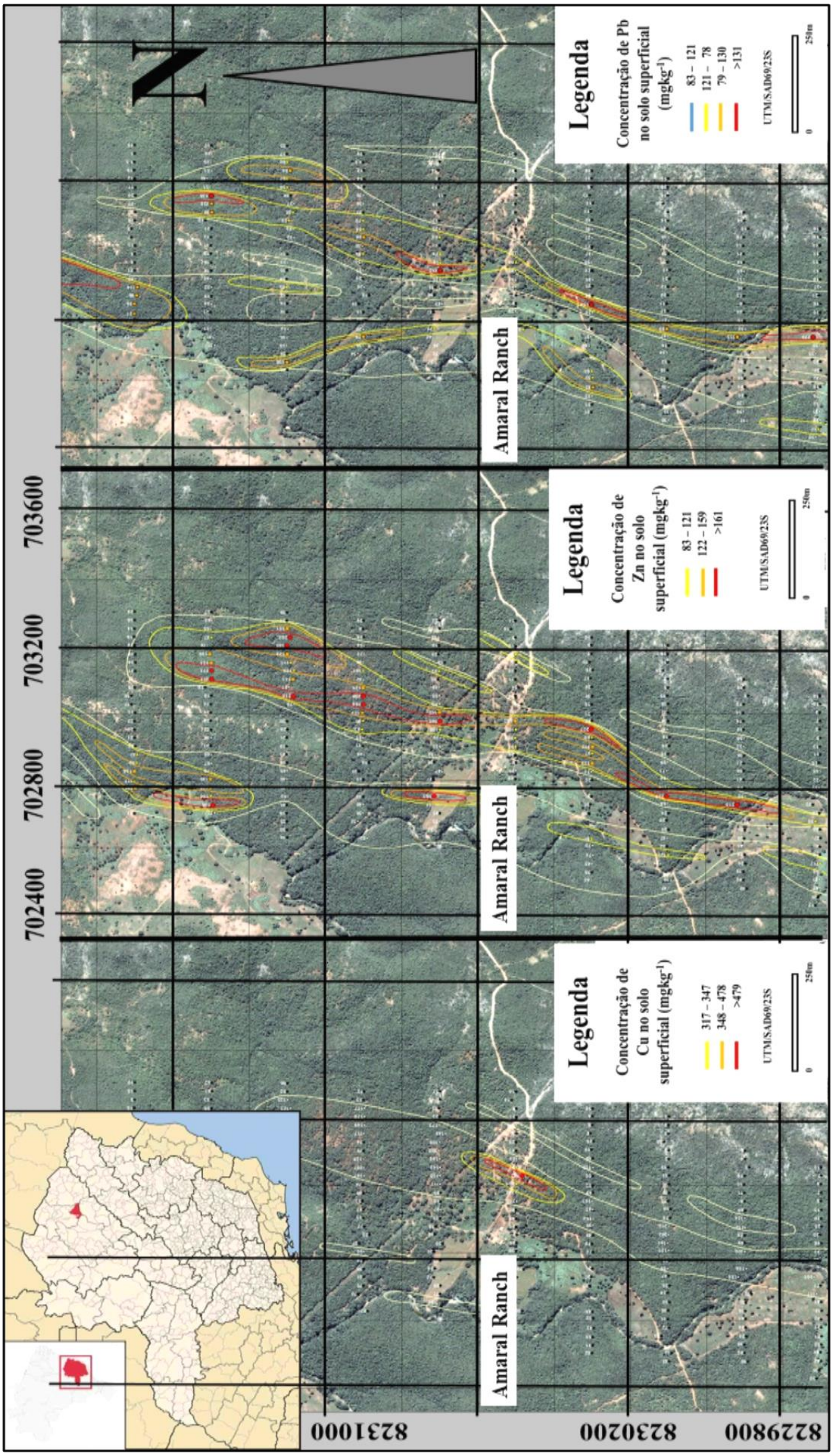

Fig. 3: Location and element-distribution at the experimental area (Source: Crocco et. al., 2006).

The separation of the Si-Phytoliths was executed using the extraction methodologies of Coe (2009) for soil samples and of Parr et al. (2001) for plants.
The separated Si-Phytoliths were dissolved using hot HF/HNO_3 mixtures to separate metal concentrations. The soil samples were treated with different solutions (H_2O; HNO_3 10%; HNO_3 conc.) to obtain information about total and available concentration of metals.
The analyses for total metal concentrations in soil were performed using a Shimatzu X-ray fluorescence (XRF) equipment at the multiuse laboratory at UFVJM, Diamantina. The Si-Phytolith extracts were analyzed by ICP-OES, model M 4165, Spectroflame-*Spectro*, at the laboratory of NGqA of the UFMG in Belo Horizonte. All applied methods were according to international and national standards.

5. Results

5.1. Element behavior in the plants

All three plants formed nearly the same totalized Si-Phytolith quantities. The highest concentration was found in the leaves, which also showed the highest dry mass, followed by roots and stems.
The element showed a peculiar distribution in plants and their organs. It seems that there are groups with homogeneous correlated behavior while other ones have no correlated behavior. In addition, variations in the deposited elements concentrations can be observed in the leaves, stems and roots of the investigated plants (Table 2). This may be a result of element inherent chemical properties or related to the accessible soil concentrations (Fig. 3).

Table 2: Phytolith mass of the selected plants, metal content per plant and the calculation per kg dry mass. ps = wet mass (100g); pc = dry mass; pf = Mass of Si-Phytoliths.

Species		Pc (g)	Pf(g)	ps/pc (%)	ps/pf (%)
Rollinia leptopetala	Leaves	109,76	15,18	11	1,5
	Stems	88,86	13,12	8,9	1,3
	Roots	76,84	15,48	7,7	1,6
Piptadenia gonoacantha	Leaves	70,38	13,67	7	1,4
	Stems	74,98	8,62	7,5	0,9
	Roots	35,98	8,20	3,6	0,8
Sida sp	Leaves	90,97	22,71	9,1	2,2
	Stems	98,86	16,39	9,9	1,7
	Roots	85,75	7,71	8,6	0,8

Each one of the three investigated plant species enriches metals differently in leaves, roots and stems. For *Rollinia leptopetala* and *Piptadenia gonoacantha* the leaves, followed by roots and stems concentrate more metals. *Sida sp.* shows a different behavior with a sequence from root and stems to leaves.
The highest metal concentrations are that of Mn, Ba, Zn, Pb, Ni, Cu, Co, Cd and Cr. This order correlates with the element's concentration in the substrate.
Table 3 shows the trapped element concentrations in the selected plants, which are similar to those observed in other plants and biotopes (Campos and Labouriau, 1969).

Table 3: Metal trapping per selected plants and parts of the plants.

Species		Ba	Cr	Co	Cu	Cd	Ni	Pb	Ti	Mn	Zn
Rollinia leptopetala	Leaves	61021	49	293	6329	216	5434	1603	21886	112016	17171
	Stems	27375	73	270	7550	200	1505	1627	16969	31358	34821
	Roots	57943	2689	824	20911	357	9643	11244	312192	80589	16172
Piptadenia gonoacantha	Leaves	37252	3291	726	8862	210	4044	2971	60569	148271	32811
	Stems	90686	717	461	8785	182	2892	2061	26316	75980	32314
	Roots	8526	3352	580	3489	642	2563	3580	74659	37813	32670
Sida sp	Leaves	19788	193	157	5290	127	874	1825	8068	92732	22714
	Stems	25721	116	618	8121	572	7499	3503	6040	118652	32214
	Roots	32369	749	303	4192	108	1328	30546	53467	31172	14562

5.2. Soil (substrate) evolution

The observations made over a period of four years (2015-2018) permit to suggest that there is a real reduction in available metals in the treated soils.

In Table 2 it can be seen the respective concentration of Phytoliths in the selected plants related with dry mass. Combined with the data from Table 3 it is possible to evaluate the transfer factor from available metal ions to fixed metal compounds in soil after plant activity.

Table 2 shows the relation between plant mass, dry plant mass and Phytolith content. We may calculate 10 to 80 kg/ha/year of Si-Phytolith production (Fig. 1) with a trapping between 150 to 150000 ppm of Metal-ions/kg of Phytoliths (Table 3) to the total element immobilization of about 100-300 g/ha/year.

In Fig. 4 a schematic element balance is shown.

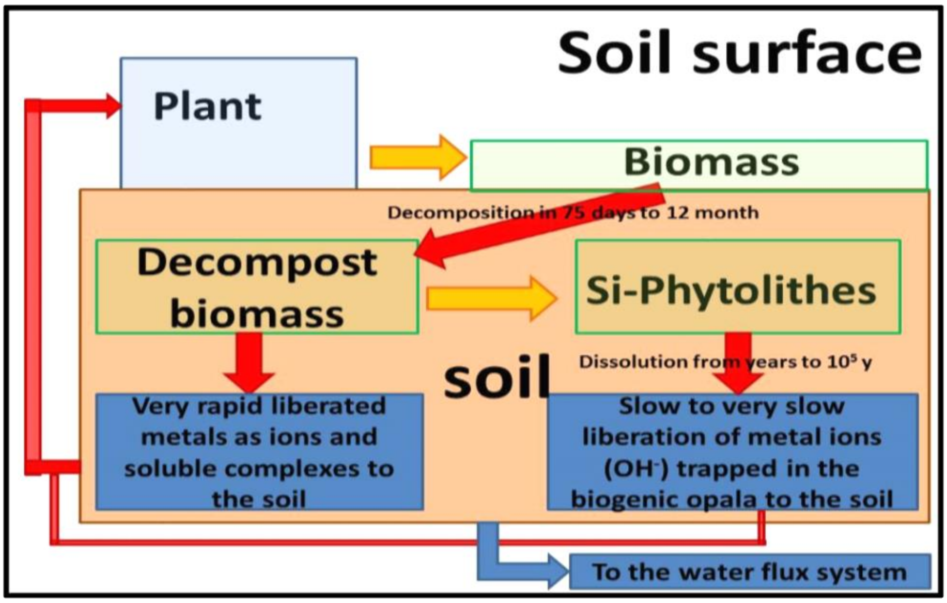

Fig. 4: Schematic decontamination process, using plants with Si-Phytoliths.

6. Conclusions

This paper presents a methodology to reduce metal concentrations in soils affected by natural enrichment or by industrial and mining site contributions, if the concentrations are not too high. The overall reduction of available metal is higher than the annual production by natural processes like weathering (Fig. 4).

The results show that is it possible to use invaders, or better, natural species to transform available element concentration from a contaminated soil or substrate in compounds of low solubility, and to reduce in this way the contamination of the soil making the area available for agricultural activities like cattle breeding or plantations after a certain period.

Before the use of this method, it is necessary to select adequate plant species and to obtain information about the soil properties to estimate the time between fixing and slow liberation to the aquatic system.

7. Acknowledgements

We thank CNPq, FAPEMIG and CAPES for financial and local Farmers and the Carpathian Gold Ltda. for logistic support.

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