International Journal of GEOMATE, July, 2016, Vol. 11, Issue 23, pp. 2216-2221
Geotec., Const. Mat. & Env., ISSN: 2186-2982(Print), 2186-2990(Online), Japan

USE OF SI-PHYTOLITHS IN DEPOLLUTION OF MINING AREAS IN THE CERRADO-CAATINGA REGION, MG, BRAZIL.

Heloiza Márcia Fernandes-Horn[1], Regynaldo Arruda Sampaio[2], Adolf Heinrich Horn[3], Ely Sandra Alves de Oliveira[4], Igo Fernando Lepsch[5] & Essaid Bilal[6]

[1,2,4,5] Federal University of Minas Gerais, ICA, 31630-900 Montes Claros - MG, A. Universitária, 1000, Brazil;
[3] Federal University of Minas Gerais, IGC, 31.270-901 Belo Horizonte - MG, Av. Antônio Carlos, 6627, Brazil;
[5] Ecole des Mines de St. Etienne, 42023 St. Etienne, Cedex 2 158, cours Fauriel, France

ABSTRACT: Treating of metal contaminated areas became a very important problem with increasing industrial and agricultural activities. Many of the used methods are very expensive, need intensive human interaction or have a very negative influence on the cleaned regions. The use of Si-Phytoliths is a simple, low cost and a very effective way to obtain good results in low contaminated or as the final process in highly contaminated places. The method is based on the fact that plants produce Si-Phytoliths and trap significant quantities of heavy metals in these amorphous to microcrystalline structures. The solubility of the Si-Phytoliths under tropical soil conditions is lower than that of the heavy elements brought directly in the soil by wash-fall out, or by degrading of organic parts of the plants on the surface. In this way, it is possible to retain liberation to the environment from short to long periods and attend environmental laws and norms. Initial tests with different plants like *Ricinus comunis* L., *Andropogon arundinaceus* Willd., *Zea Mays* L., *Brachiaria sp.* L. and *Saccharum officinarum* L. planted on substrates with metal concentrations (Al, Fe, Mn, Ti, Zn, Cu, Pb, Cd, Ba, Hg, S) have shown that the plants absorbed elements and quantities in the different parts like leaves, roots, stems, flowers and fruits. This allows a selective use due to contamination varieties and a possible economic use of parts of the plants and an effective planning of the decontamination conditions.

Keywords: Si-Phytoliths, Soil contamination, Heavy metals, Decontamination, Mitigation,

1. INTRODUCTION

1.1 Contamination process

With the increasing population, the necessity for more raw materials and manufacturing products increases significantly. With this increasing activities also the intensity and the amount of introduction of polluents increases. During the history a lot of environment disasters were described and also an increase of health problems due to the changes of environmental quality. Mining, metallurgy or industrial process produces waste material, which is able to contaminate surface areas and need to be disposed. The areas around these sites often suffer with high metal contents.

1.2 Decontamination processes

A lot of decontamination methods are known. A lot of them are very expensive, other are very aggressive or need a longtime accompaniment (table 1). The conservative methods are very aggressive, very expensive or need a big amount of human intervention and monitoring. The effects are changes in soil structure and composition, the introduction of strange compounds or plants. Often it is necessary to take of the biological material and deposit it on special places.

The use of Si-Phytoliths seems to be one of the less aggressive, low-cost and independent methods (table 2).

Different to the classic methods, the use of Si-Phytoliths does not interfere in soils and it is possible to use local plants.

Table 1: Used decontamination methods and their properties

Method	Impact	time	Contam. type
Removing of soil	Very strong	short	Inorg./org., high
Use of biomass	low	intermediate	Inorg./org.
Using of additives	Strong to very strong	Short to long	Inorg./org.
Use of phytoliths	Very low	Intermediate to long	Inorg./org. Medium to low

After seeding no more intervention is necessary, only the heavy metal content of the soil needs to be verified time in time.

Table 2: Medium quantities of phytoliths in the used plants

Part of plant	Localization	Quantity
Leaves	Surface, inside /between cells	500 ppm
Stem/trunk	Inside/ between cells	300 ppm
Fruits	Inside/ between cells	200 ppm
Roots	Inside and between cells	250 ppm
External	surface of roots, leaves and trunk	800 m

1.3 Phytoliths

Phytoliths are inorganic material like SiO_2, $CaCO_3$, $(CaMg)CO_3$ or other which are formed in some plants by precipitation of these materials in amorphous ore microcrystalline structures. These organelles are formed in and between plant cells that give them their peculiar form. This form can be used for plant determination.

These particles are formed for different purposes like to enhance structure, to create sharp and hard tissue alimentation and probably also to trap dangerous compounds. Figure 1 show there different forms and where they are localized.

The relative high heavy metal content in the Si-Phytoliths and their low solubility is the basic concept of the use in long-term decontamination of polluted areas like deposits, well regions, mining and industrial sites.

Figure 2 show the possibilities of metal trapping in the organic amorphous SiO_2-structures.

1.4 Biomass and Phytolith production

All plants produce biomass and distribute them to the different parts. The production of biomass depends on soil, eather and other physical-chemical factor and therefore differs very between authors [5] and [17]. The biomass for millet (Pennisetum sp. Schum.) is informed between 9000 and 15.000 kgha-1y-1 [13], [15], for Amaranthus spp. L. 2500 to 3000 kgha-1y-1 [2] and for some grasses from 4000 to 6000 kgha-1y-1 [8]. All plants contain significant quantities of some heavy elements. The problem is that after decomposition these quantities return to the soil.

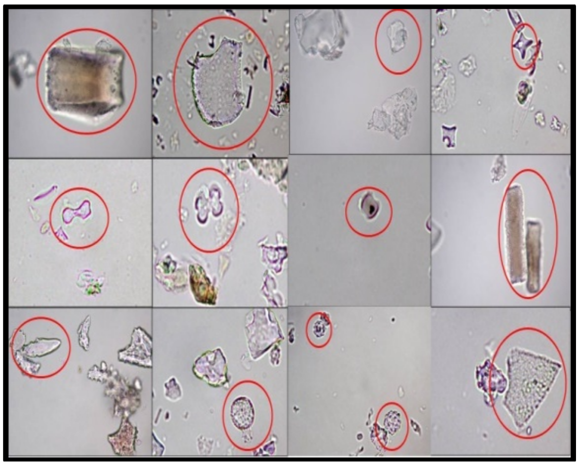

Figure 1: Phytolith forms of plants from Cerrado-Caatinga [14], [11] Left up to right down:
1st row: bulliform; parallelepipedal; cuneiform; blocky; rondell;
2nd row: bilobate; cross; saddle; elongate;
3rd row: acicular; globular granulate; globular echinate; cone shape;

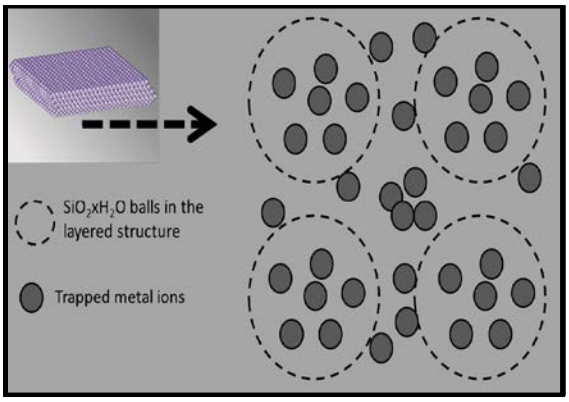

Figure 2: SiO_2-Structure and possible sites of metal ions [1], [7];

The phytolith concentration varies from plant to plant. The grass used herehave around 9-30 $kgha^{-1}y^{-1}$ and the other plants around 35-65 $kgha^{-1}y^{-1}$.

This phytoliths can trap from 1 ppm (Hg) up to 0,05 % (Fe). This is an important amount for yearly plants. Due to the solubility of SiO_2 (figure 3) this amount returns very slowly to the soil, reducing in this way its heavy metal concentration [4], [6], [9].

The next table 3 shows the heavy metal maximum trapping in SiO_2-modifications. The biological opal due to its structural features, his high content of water and OH^- and it open organization can capture up to 200 g kg^{-1} of metal ions like Al, Ca, Fe, K, Na, Cu, Zn, Ti, Zn and Hg.

These elements are fixed in the structure and closed between the SiO_2 structures.

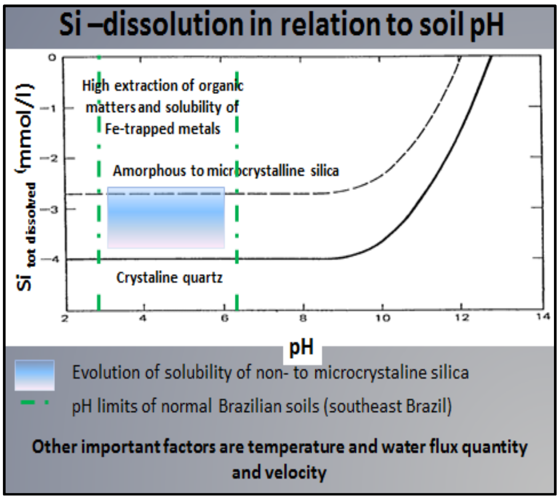

Figure 3: Solubility of the different SiO_2-modifications in relation to the pH.

Table 3: Principal properties and trapping capacities of crystalline quartz, geological- and biological opal [11], [10].* for Cerrado plants; ** analyses of fifty opal specimen.

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	$\leq$ 200**	2-10

1.5 Biomass and Phytolith cycles

During growing all plant produce biomass distributed between its part and also different amounts of phytoliths. During the decomposition this material returns to soil were the biological part is reintegrated by decomposition, liberating the extracted metals. The phytoliths stay without alteration for some thousand years and therefore liberate metals very slowly (figure 4). The next table 3 shows the heavy metal maximum trapping in SiO_2-modifications. The biological opal due to its structural features, his high content of water and OH^- and it open organization can capture up to 200 g kg^{-1} of metal ions like Al, Ca, Fe, K, Na, Cu, Zn, Ti, Zn and Hg.

These elements are fixed in the structure and closed between the SiO_2 structures.

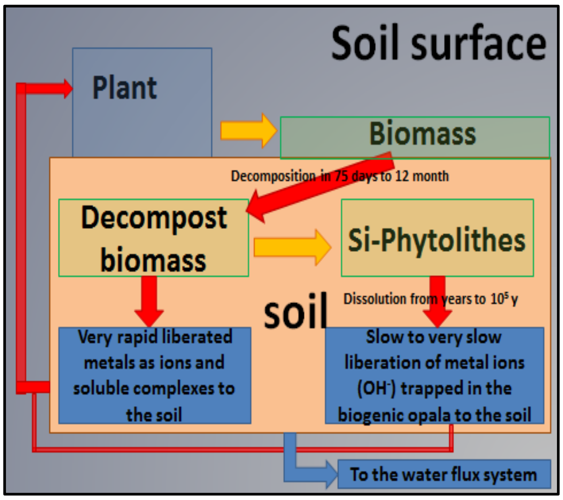

Figure 4: Scheme of principle remediation circulation of phytoliths, biomass and elements in the biogenic and geological cycle.

2. MATERIALS AND METHODS

2.1 Soil

We used collected soil from northern part of Minas Gerais. This soil was mixtured with different concentrations of heavy metals and put in 10l bags (table 4).

Table 4: Physical-chemical properties of the used soil. (Laboratory of ICA-UFMG after EMPRAPA methodology)

N	**P**	**K**	**Na**	**Ca**
%	%	%	%	%
3,24	0,75	3,36	0,02	2,21
Mg	**S**	**Fe**	**Mn**	**Al**
%	S	ppm	ppm	Cmolc/dm^3
0,26	1,93	44,8	195	0,2
Cu	**Cd**	**Pb**	**Cr**	**Ni**
ppm	ppm	ppm	ppm	ppm
147,5	1,27	36,53	50	24,7

2.2 Used plants

For this initial tests to obtain information of heavy metal uptakes several one year plants like ***Ricinus comunis* L., *Andropogon arundinaceus* Willd., *Zea Mays* L., *Brachiaria sp.* L.** and ***Saccharum officinarum* L.** were used (figure 5).

Figure 5: Example of planted corn like used in the remediation tests.

2.3 Field tests

Table 5: Element concentration used in the experiments with the different plants

Compound	$g_{element}$/pot	$g_{element}/kg_{soil}$
$BaCl_2$	**1**	**0,2**
HgO	**0,11**	**0,022**
$Pb(CH_2COO)_2$	**0,2**	**0,04**
$Zn(CH_2COO)_2$	**3,5**	**0,7**
MnO_2	**0,4**	**0,08**
$Cu(CH_2COO)_2$	**1,0**	**0,2**
$FeCl_3$	**0,7**	**0,14**

2.4 Preparation of the samples

The plant samples were separated in its, leaves, roots, fruits and stems and then send to laboratory for drying.

2.5 Laboratory

In the laboratory the phytolith preparation and separation were done using process described by [16]. The separated phytoliths were opened by dissolving with mixtures of HNO_3/HF/HCl and the metal concentrations in the filtered solutions determined by analyses with ICP-OES and ICP-MS. Semiquantitave determinations in single phytolith were carried out by using a microprobe with ed-analyzer. The analyses were done in comparison with national and international metal standards.

3. RESULTS AND DISCUSSION

All analyses indicate the presence of significant quantities of Al, Fe, Mn, Cu up to 10^3 ppm, S, K, Ca, Cr, Zn and Pb (>10 ppm) and a lot of other trace elements near the detection limits of the employed methodologies.

Concentration of elements in phytoliths from ***Brachiaria decumbens*** and ***Andropogon arundinaceus*** (falso massanbará) grown on substrate with or without sewage sludge addition. The analyses were done with ICP-OES and ICP-MS equipment. The results show significant enrichment of some interest trace elements like Cu and Zn.

Andropogon arundinaceus (*Poacea*) shows a significant presence of Si, de S, K, Ca, Cr e Fe (>10mgkg^{-1}). Zn e Cu was found in concentration near detection limits.

Ricinus communis show high Al, Fe, Ti and K (<500 mgkg^{-1}). Only slightly differences in element concentrations between the plants from pots with and without sewage sludge were observed.

Table 6: Analytical results of *Brachiaria decumbens* from substrates with element addition. (Analyses done by ICC-OES at NGqA-UFMG)

Treatment	Fe	Mn	Cu	Zn	Ba
	%	ppm	ppm	ppm	ppm
Soil/Fe	0,05	9	35	11	13
Soil/Mn	0,04	**12**	33	12	14
Soil/Zn	0,03	8	29	**3**	12
Soil/Cu	0,02	10	**453**	13	12
Soil/Ba	0,03	10	28	12	**26**
Soil/Hg	0,03	10	28	11	11
Soil/sludge	0,03	8	**119**	**3**	17
Pure soil	0,03	11	29	12	12

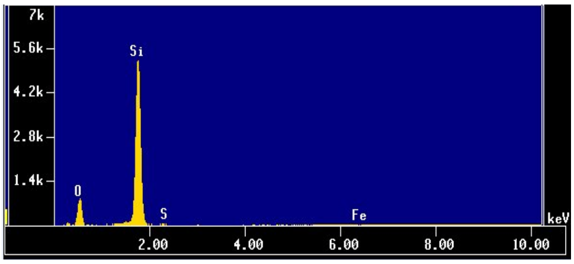

Figure 7: Element trapping of Al in Andropogon arundinaceus.

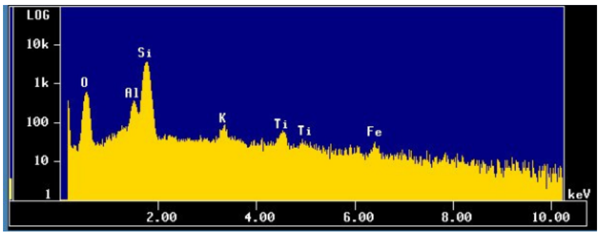

Figure 8 Element trapping shown for Phytoliths of *Ricinus comunis.*

4. CONCLUSIONS

The obtained results show that a significant amount of metal ions can be trapped in Si-Phytoliths of a variety of specific plants.

This concentration related to the biomass production show that it is possible to clean areas with considerable soluble metal contamination by using this method of planting selected species of local plants.

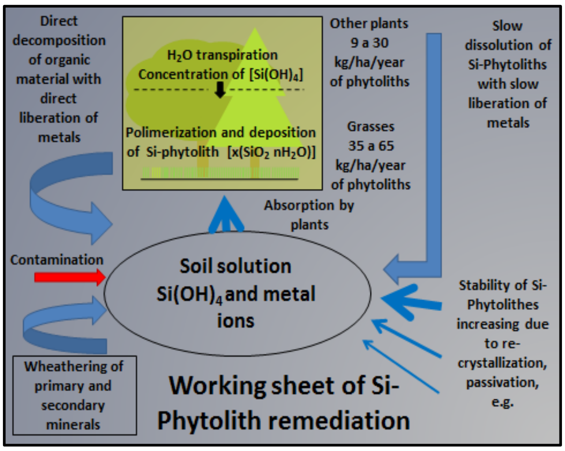

Figure 9: Suggested remediation process using phytolith rich local plants.

The relative simplicity of application and use, the employment of local plants and the long time process predestinate this method for cleaning of sensitive biotopes in endangered environments.

5. ACKNOWLEDGEMENTS

We thank CNPq, CAPES, IGC-UFMG and ICA-UFMG for financial and logistic support.

6. REFERENCES

[1] Alexandre, A.; Meunier J.D.; Colin, F. & Koud, J.M. Plant impact on the biogeochemical cycle of silicon and related weathering processes. Geochim. et Cosmochim. Acta, 1997, Vol. 61. No. 3: 677-682.

[2] Azevedo, D.M.P. & Nascimento H.T.S. Potencial forrageiro de espécies para cultivo no período de safrinha em solos de tabuleiros costeiros. Teresina, Embrapa, 2002. 4p. (Com. Téc. 148).

[3] Costa, L. M. Da; Santos, R. F. Dos; Schaefer, E. G. R.; Moreau, A. M. S. Dos S. & Moreau, M. S. Ocorrência de corpos siliciosos em horizontes superficiais de solos de diferentes ecossistemas. Rev. Bras. Ciênc. Solo. 2010, Vol. 34(3): 3-7.

[4] Dandurand, J.L. & Schott, J. New data on the Solubility of Amorphous Silica in Organic Compound-Water Solutions and a New Model for the thermodynamic Behavior of Aqueous Silica in Aqueous Complex Solutions . J. of Sol. Chem., 1987, Vol. 16, No. 3: 237-256.

[5] Boer, C.A.; Assis, R.L.De; Silva, G.P.; Braz, A.J.B.P.; Barroso, A.L.De, L.; Filho, A.C. & PIRES, F.R. Biomassa, decomposição e cobertura do solo ocasionado por resíduos culturais de três espécies vegetais na região Centro-Oeste do Brasil. Ver. Bras. Ci. Solo, 2008, 32: 843-851.

[6] Dove, P.; Han, N.; Wallace, A.F. & Yoreo, J. J. DE Kinetics of amorphous silica dissolution and the paradox of silica polymorphs. Proceed. of the Nat. Acad. Sci. 2008, Vol. 105, No. 29: 9903-9908. www.pnas.org

[7] Felipe, P.L.L.; Cecchet, F.A.; Brustoline, L.; Calegari, M.R. & Pessenda, L.C.R. Coleção de referência de fitólitos da floresta ombrófila densa (Linhares; ES): Subsídios para reconstrução palaeoambiental. Reference collection of phytoliths from Ombrophilous Dense Forrest (Linhares, ES): Support for palaeo-environmental reconstruction. CENA-USP: 1971, 33p.

[8] Franscisco, E.A.B.; Câmara, G.M.S. & Segatelli, C.R. Estado nutricional e produção do capim-pé-de-galinha e da soja cultivada em sucessão em sistema antecipado de adubação. Bragantia, 2007, 66:259-266.

[9] Gunnarson, I. & Arnórsson, S. Amorphous sílica solubility and the thermodynamic properties of H_4SiO_4 in the range of 0º to 340ºC at P_{sat}. Geochim. et Cosmochim. Acta, 2000, Vol. 64, Issue 13: 2295-2307.

[10] Horn, A.H.; Lepsch, I.F.; Sampaio, R.A.; Rodrigues, M.N.; Alvarenga, A.C. & Oliveira, E.S.A. Heavy metals and aluminum content inside silica phytoliths from *Ricinus comunis*, *Andropogon arundinaceus* Willd, *Ricinus communis* and *Brachiaria decumbens* grown on soils added with sewage sludge and heavy metal salts. 2014, 2p.

[11] Lepsch, I.F.; Ribeiro, J.M.; Horn, A.H.; Cavalcanti, T.F.M.; Rodrigues, M.N. & COE, H.H.G. Morfologia, quantidade e análise elementar de sílico-fitólitos em tecidos de *Andropogon arundinaceus* Willd crescida em solo com e sem adição de lodo de esgoto· XXXIV. Cong. Bras. Solo. Florianopolis, SC. 2013, 2p.

[12] Element - Issue 3 - The new CT 200h speaker is crafted from bamboo. http://www.lexus-int.com/magazine/issue3/element/; Accessed at 25.3.2015

[13] Moraes, R.M. de. Decomposição das palhadas de sorgo e milheto, mineralização de nutrientes e seus efeitos no solo e na cultura do milho em plantio direto. Lavras, UFL, Master Thesis, 2001, 90p.

[14] Mulholland, S.C. & Rapp G.Jr. A Morphological Classification of Grass Silica-Bodies In: Rapp Gré. & Mulholland, S.C. (eds.) 1992. Phytolith Systematics; Emerging Studies. Advances in Archaeol and Mus. Sci., 1992, Vol. 1, p 65-89.
[15] Oliveira, T.K.; Carvalho, G.J. & Moraes, R.N.S. Plantas de cobertura e seus efeitos sobre o feijoeiro em plantio direto. Pesq. Agropec. Bras., 2002, 37:1079-1087.
[16] Parr, J.F.; Lentfer, C.J. & Boyd, W.E. A Comparative analyses of wet and dry ashing techniques for the extractions of phytoliths from plant material. J. of Archaeol. Sci., 2001, 28: 875-886.
[17] Usp-Lcn Dinâmica de Ecossistemas-Cerrado. http://www.ib.usp.br/~delitti/mestres.html; Accessed at 15.3.2015

International Journal of GEOMATE, July, 2016, Vol. 11, Issue 23, pp. 2216-2221
MS No. 1169 received on July 15, 2015 and reviewed under GEOMATE publication policies.
 Pertinent discussion including authors' closure, if any, will be published in March 2017 if the discussion is received by Sept. 2016.
Corresponding Author: H. M. Fernandes-Horn