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Review

Alternatives for remediation and decontamination of soils from Brazil

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The aim of this work is to identify the main sources of contamination of soils, their effects on organisms also presenting alternatives for remediation and decontamination of these contaminated environments. The soils have in their composition organisms that are naturally present, as well as the presence of contaminants in increasing proportion when compared to the world industrialization and modernization of agriculture; therefore, increase in evolution brings with it a bigger totality of compounds, resulting in worrying rates in the soils of Brazil, such as trace elements (Cadmium, Lead, Arsenic, Mercury, Copper) and compounds organic (pesticides) and inorganic (waste fossil fuels). In many instances, this contamination can decimate forms of life in the soil. With that, remediation and decontamination of these soils becomes a fundamental need for the current economic models, making bioremediation and phytoremediation techniques consist in a feasible alternative for remediation and decontamination of soil, presenting performances satisfactory in removal and stabilization of contaminants.

Key words: Soil contamination, trace elements, pesticides, removal, stabilization

INTRODUCTION

Seeking to attend to the high demand of food, agricultural production has generated a shortage in the traditional sources of essential nutrients used in agriculture (phosphate rocks and minerals originating from extraction in the soil), resulting in the beginning of the search for alternative sources (industrial residue) Nacke et al. (2013); Gonçalves Jr. and Pessoa (2002), in some cases of dubious origins, bringing elements that have undesirable substances in its composition. Thus, there was an increase in the content of harmful substances and compounds in the soil (Coutinho and Barbosa, 2007). For the same authors (Coutinho and Barbosa, 2007), the

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search by the authorities on strategies and economically viable approaches to restoration of polluted areas and biodiversity conservation occurs in the same proportion as these contaminations.

The metal contamination usually occurs because of human activities, whether through waste from mining, steel, cosmetics industry, automobile scrap, agricultural activities, among others. Such factors generally expose the commercial crops to adverse situation of contamination (Tarley and Arruda, 2003). The contamination that affects the agricultural areas is now a major problem because many pollutants somehow exert essential roles in important economic activities, such as pesticides and fertilizers, and the most of those products there are characteristics of concern due to its composition and persistence in soil, water and food (Pires et al., 2003).

Heavy metals often accumulate in the surface soil layer (0 to 20 cm), also called arable layer, thus becoming present in the soil solution and available for plant absorption included in the food chain (Carvalho et al., 2008).

There is great interest in the study of heavy metals, having in mind that in relation to chemical action, these elements have no character of rapid biodegradation, remaining in the environment over time. Residuals of these global biogeochemical cycles are those with natural waters as their main means of conduction (Cotta et al., 2006).

In this scenario, Gonçalves Jr et al. (2014) presented several papers and case studies demonstrating the increasing number of cases of contamination in Brazilian soils. Also, one must take into account the toxic effects of these metals representing risks to living organisms, reducing plant growth, causing disturbing various metabolic processes that leads to yield losses, absorption and loss of commercial products quality (Silva et al., 2007; Gonçalves Jr. et al., 2014).

According to findings by Pandey et al. (2009), abiotic stresses in plants exposed to excessive levels of heavy metals produce oxidative stress and stimulate antioxidative responses in different efficiencies. Also, according to Pandey et al. (2009), the damage by oxidative action can be evaluated by external visual expression of toxicity of the elements in the order Ni> Co> Cd> Cu> Zn.

To regulate these events, the National Environmental Council (CONAMA) has drafted a resolution (Resolution 420) that briefly defines criteria and guiding values of soil quality. The explicit forms of prevention and control of soil quality provides guidelines for management of contaminated areas. It should be noted that, for the decontamination and remediation of contaminated soils there are several methods using variable principles (Gerhardt et al., 2009). Between them stands bioremediation and phytoremediation, which uses microorganisms and plants with the objective of removing, transferring, stabilize or destroy harmful elements. Having these high potential of removal or degradation of pollutants, its efficiency depends on the structure of the molecule, because the chemical formation of organic pollutants, have direct influence on the ability to break these substances (Mariano et al., 2007).

With that in mind, the use of phytoremediation appears promising as it is used in heavy metal contaminated soils, taking into consideration the dangers of this contamination for both soils like products from contaminated areas. Besides the soil-plant-water, taking into consideration the need to maintain soil fertility and ensure the health of food produced, the aim of this paper is to address the major sources of contamination of soils, their effects on organisms and presents alternatives for remediation and decontamination of these contaminated environments.

LITERATURE REVIEW

Contaminating sources

In the current production, both industrial and agricultural systems, generates by-products or waste, and when there are no practices of sustainable production, it can become contaminants to the soil. Five activities are known as sources of residues contaminants to soil, which are originated from industry, domestic, hospital, commercial and agricultural activity. Included in this are steelworks, leadworks, mining, leather, cosmetics industries and fertilizer industries, as well as cemeteries, cars cemeteries, agricultural activities and excessive use of pesticides (Tarley and Arruda, 2003).

The term heavy metal comprises chemical elements that have atomic number greater than 20 or specific mass greater than 5 g cm^{-3} and are potentially toxic to living beings (Malavolta, 1994). There are also essential elements that allow the development of metabolic pathways, which can represent risks and toxicity at high levels, such as Manganese, Zinc, Chromium and Cobalt (Gonçalves Jr. et al., 2009).

About this, Ribas (2007) made a research on the composition of fertilizers in 2006, where technicians of the Department of Supervision of the Secretary of Agriculture of the State of Paraná, obtained in their analysis of fertilizers positive results for 70% of the material analyzed, meaning that 30% of the analyzed fertilizers were below the rates specified on their labels. The author also gives a warning about the need of evaluation of the materials due to the possibility of contamination by heavy metals (Ribas 2007).

Causes and impacts of contamination

Heavy metals like, Copper (Cu), Zinc (Zn) and Cobalt (Co), play an important role in the nutrition of plants and animals (Silva et al., 2007). The metals occur naturally in the soil, however, elements such as Cadmium (Cd), Lead (Pb), Arsenic (As) and Selenium (Se) have unhealthy effects on various components of the biosphere (Kabata-Pendias and Pendias, 2001); among these effects, the bioaccumulation and biomagnification is worth mentioning due to the risks they present to living organisms, being ways to concentrate the contaminants over time and even the food chain. For example, organisms presented in a contaminated soil can be exposed to various contaminants absorbing them slowly, reaching levels up to 100,000 higher in their tissues, as in aquatic organisms, leading these levels along the food chain (Souza et al., 2014; Gonçalves Jr. et al., 2014).

For Arora et al. (2008) stemmed from ingesting contaminated with heavy metals is to be avoided, so that these can transfer these metals, and accumulate in the body areas food. In order to prevent excessive accumulation of heavy metals in the food chain, the use of wastewater in soil fertilization should be monitored.

In the case of soils, contamination comes from the high concentrations of heavy metals, often occurring where there is large concentration of industries that destines their waste to landfills, which suffers burials and sedimentation (Carvalho et al., 2008). The metals can be accumulated in these wastes and sediments that generate great concern, as they become potential sources of contamination and important indicators of environmental contamination. Positively, this capacity of sediment makes the environmental matrix one of the most important to evaluate levels of contamination. (Cotta et al., 2006).

The mobility of these elements in soils depends essentially on chemical reactions of adsorption and desorption occurring between the metal and the solid components of the mineral system. The reactions are influenced by several factors, with emphasis on the presence of organic and inorganic ligands and cation exchange capacity (CEC) of soils (Carvalho et al., 2008). Moreover, changes in environmental conditions, like acidification, changes in redox potential or increasing in the concentration of organic ligands, can affect the bioavailability of metals, favoring the contamination of plants that developed in the soil (Cotta et al., 2006).

Current legislation related to soil contamination

On the juridical context, the National Council on the Environment (CONAMA) N.420 treats the issue of contamination by heavy metals (Brasil, 2009). This legal letter, published on 28 December 2009, from the National Environmental Council, provides criteria and guiding values of soil quality on the presence of chemicals, and establishes guidelines for environmental management of areas contaminated by exogenous substances due to anthropogenic activities.

For the above-mentioned resolution, the Council exposes the need to prevent contamination of soil, aiming to maintain its functionality and protection of the quality of surface and underground water. It considers that the existence of contaminated areas can configure serious risk to public health and to the environment. It also states the need to establish criteria for setting guidance values for the prevention of soil contamination and to define guidelines for the management of contaminated areas.

The resolution determines that in the presence of chemical substances, the evaluation of the quality of the soil should be based on the Reference Values Guiding Quality (RVGQs), Prevention (VPs) and Investigation (VIs) described in Table 1, the RVGQs of the soil for chemical substance naturally present will be established by environmental agencies of the states and the Federal District. The VPs were based on tests of phytotoxicity or in evaluation of ecological risks, according to the resolution.

With regard to the VIs, the figures presented in the resolution are also adopted, which were derived based on evaluation of risk to human health according to exposure standardized scenarios for different uses and occupation of the soils. The soil classification is performed based on the concentration of chemical substances, as follows:

Class 1: Soils that have concentrations of chemical substances less than or equal to VRQ.
Class 2: Soils that have concentrations of at least one chemical substance greater than the chemical VRQ and less than or equal to VP.
Class 3: Soils where there is concentration of at least one chemical substance greater than VP and less than or equal to chemical VI.
Class 4: Soils which have concentrations of at least one chemical substance greater than the VI.

Highlight that the resolution lays down that the generation and availability of information, the joint, cooperation and integration of interagency between government agencies, owners, users and other beneficiaries or affected are basic principles (Di Giulio et al., 2010). The authors also emphasize that risk communication constitutes a key element for the environment's preservation. And in this case "should be created by the government, suited mechanisms to the different publics involved, providing easy understanding and access to information for the social group and environmentally vulnerable, targeting

Table 1. Values guiding of substances for soils and underground water.

Substance	Soil (mg kg^{-1} of dry weight)				Underground water (µg L^{-1})
	Prevention	Investigation			Investigation
		Agricultural area	Residential	Industrial	
Aluminum	-	-	-	-	3.500**
Arsenic	15	35	55	150	10*
Cadmium	1.3	3	8	20	5*
Lead	72	180	300	900	10*
Cobalt	25	35	65	90	70
Copper	60	200	400	600	2.000*
Mercury	0.5	12	36	70	1*
Zinc	300	450	1.000	2.000	1.050**
Lindane	0.001	0.02	0.07	1.5	2*
Aldrin	0.015	0.003	0.01	0.03	-

Source: Resolution 420/2009-CONAMA - Organized by the authors. * Standards portability of chemical substances that pose a health risk as defined in Ordinance N^o. 518/2004 of the Ministry of Health; ** Calculated based on risk to human health, according to the scope of this resolution. Differ from the standards for acceptance for human consumption defined in regulation 518/2004 of the Ministry of Health and the maximum value allowed for human consumption defined in CONAMA Resolution N^o. 396/2008.

the communication of risk to the population (Di Giulio et al., 2010).

A concern regarding the resolution is the fact that it allows the contamination of the soil until the concentrations of elements or substances of environmental interest are above a limit called intervention value. Understanding the resolution, according to Article 26, only at this time the area is declared Contaminated Area under Intervention (ACI), by the competent environmental agency. Thus ACI will be the one area in which is found the presence of chemicals in free phase or is proven, after detailed investigation and risk assessment, the existence of risk to human health.

It is understood that a soil in which the concentration of an element or substance of environmental interest is less than or equal to the naturally occurring, can be contaminated until the intervention values. The parameters of the values of prevention and investigation are variable between agricultural, residential and industrial area. This elasticity in the parameters demanding a detailed investigation can be crucial for the soil contamination with harmful consequences to the environment.

It is not about prohibition of the use or handling of heavy metals, it is about seeing the precautionary principle with the proper intensity, which in environmental law is invaluable for environmental preservation. The permittivity of Resolution 420/CONAMA comes against the environmental law, needing to be more careful with the matter of contamination, demanding an adequate monitoring and immediate intervention in areas that verify an increase in the concentration of heavy metals in soils already in their levels of prevention.

Alternative of remediation and decontamination

Out of the known methods of soil remediation, phytoremediation is distinguished by its applicability. Considering this, the use of phytoremediation was verified as an output decontamination for water bodies, since these resources are rarely reused due to the presence of contaminants. Concerned about the destination of this water, alternatives for treatment and recovery of waste and effluents, as the use of macrophyte plants for decontamination and reuse of these have been tested (Pires et al., 2003). In soils, the use of filamentous fungi and their metabolites in bioremediation processes has increased, due to the high potential for degradative and biossorption for metals and dyes and mechanisms of resistance to adverse environmental conditions (Conceição et al., 2005).

Phytoremediation, aside using processes that occur naturally by plants and their root systems, kidnapping and degrading organic pollutants and inorganics of the soil, appear as an excellent corrective strategy and its development is propagated for *in situ* remediation of contaminated environments (Pilon-Smits, 2005). Bioremediation is a viable and environmentally friendly alternative for the treatment of contaminated soils by organic compounds and metals that are potentially toxic. It is essentially the awakening of human consciousness to the need for development and application of these technologies in favor of the environment.

Also, as a decontamination method, adsorption is considered an effective procedure for removal of contaminants. It works through the binding of the interested compounds in the binding sites present on the adsorbent, making it unavailable to these plants or organisms (Dhankhar and Hooda, 2011).

PHYTOREMEDIATION

Phytoremediation is a viable technique for sustainable systems, characterized by the use of plants for remediation, mitigation and decontamination of resources that have the presence of contaminants. This technique presents a satisfactory cost-benefit, without spending the carbon credits, therefore is a practice energetically clean and sustainable (Dowling and Doty, 2009).

For the choosing of phytoremediator species, plants that show a set of specific characteristics must be considered for phytoremediation, as a potential to produce high amounts of biomass, fast growth rate, extensive root system, tolerance to the metal (contaminant) and accumulate in the aerial part high amounts of the elements in question. Considering all these characteristics, it is difficult to obtain ideal species, so the one with the greatest phytoremediation potential, or techniques that enable the associated cultivation of various species should be selected (Marques et al., 2009). In phytoremediation, processes of phytoextraction and phytostabilization are the most frequently performed in areas of contamination; however, the choice of the most appropriated method depends on the characteristics of the place, the concentration, the kinds of pollutants to be removed and the final use of the contaminated place (Xiang-Yan et al., 2005).

Phytoextraction is mainly applied to metals (Cd, Ni, Cu, Zn, Pb) and other inorganic and organic compounds. The process consists in the use of plants, especially hyperaccumulators and transgenic, through root uptake, transport and accumulation of contaminants in shoot, which will subsequently be sent to outside the place of contamination (Marques et al., 2009). The destination of the plant material obtained after extraction will depend on its constitution and the possibility of their use or not. Depending on the case, the plant tissue can be incinerated, deposited into landfill, co-processed in cement manufacture. In case of use, it can be used for the production of fibers and mobile (Eapen and D'Souza, 2005).

In turn, phytostabilization consists of the use of plants in order to immobilize the contaminants in the soil, preventing their dispersal to other locations and changing its bio-availability in the soil. The plants used must be able to tolerate high levels of metals and immobilize them in the soil by precipitation, complexation or reducing valencies (Schnoor, 1997).

For Alvarenga et al. (2011), the physical phytostabilization is due to the effect caused by vegetation in the processes of surface erosion and leaching of pollutants through the reduction of direct incidence of rain or by lignification of humification or contaminant in the soil. The chemical fraction of phytostabilization can occur by chemical modification of the contaminant due to the change in the soil's pH by the production and release of exudates and other substances through the roots, or by the production of CO_2.

Phytodegradation is the process in which plants are capable of degrading organic pollutants. It makes them undergo bioconversion, turning them into simple molecules which in some cases may be used for the growth and development of the plant (anabolism or catabolism) (Procópio et al., 2009).

Another possibility is phytostimulation, in which due to the release of root exudates metabolites, there is the stimulation of the microbial activity. Furthermore, plants may also secrete biodegradatives enzymes, in which both compounds act by degrading the contaminants in the soil (Santos et al., 2007). This mechanism of phytoremediation has as main target substances like non-chlorinated organic pesticides and herbicides (Pires et al., 2005).

In respect to phytovolatilization, it can be stated as the process in which plants perform the removal of pollutants by biodegradation in the rhizosphere or after the passage in the plant itself, performing the volatilization on the surface of the leaves. Thus, depending on the physiological state of the plant, the release of contaminants to the atmosphere can occur naturally or with energy expenditure (Procópio et al., 2009).

Rhizofiltration is defined as the use of terrestrial plants in order to absorb, filter and reduce the concentrations of undesirable elements in the soil solution, mainly heavy metals and pesticides, using basically the root system (Rai, 2009).

About the use of transgenic plants that carry out these processes, considering that those plants are accumulators of heavy metals, one should take into account that the use of transgenic plants for phytoremediation introduces an additional risk of horizontal transference of their modified genes to the next generation, and even its introduction into wild species. Yet an increasing number of studies have been performed to obtain plants that are tolerant to high concentrations of toxic metals and, in this way, can be used for phytoremediation of soils. There are already results showing a higher efficiency of removal of metal from the soils when compared to the wild plants (Kawahigashi et al., 2006).

Several species of phytoremediator plants are known, highlighting the gender *Brassicaceae* as the most

Table 2. Main phytoremediator species and compounds removed from soil.

Species	Compounds removed from soil	Reference
Thlaspi caerulescens	Cd, Ni, Pb, Zn	Cosio et al. (2004)
Rye grass	Cu, Cd, As	O'Connor et al. (2003)
Thlaspi ochroleucum	Ni , Zn	Prasad and Freitas (2003)
Thlaspi rotundifolium	Ni, Pb , Zn.	Prasad and Freitas (2003)
Brassica juncea	Cd, Cr, Cu, Ni, Pb, Zn	Schmidt (2003)
Arabidopsis halleri	Zn , Cd	Cosio et al. (2004)
Solanum tuberosum	Herbicides	Doty et al. (2000)
Nicotiana tabacum	H. halogenate	Yamada et al. (2002)
Euphorbia cheiradenia	Pb	Chehregani and Malayeri (2007)
S. photeinocarpum	Cd	Zhang et al. (2011)
A. rusticana P.	Phenols	Kotyza et al. (2010)

important hyperaccumulators of heavy metals and organic compounds, presenting several species that are able to accumulate more than one element (Prasad and Freitas, 2003). As for phytoremediation and removal of Copper using various cultures, among the main results, we can highlight the performance with the cultivation of perennial peanut, where it was observed that the concentration of Cu in the aerial part of the plants were between 50 to 60 mg kg^{-1} (Andreazza et al., 2010). A high tolerance of the species *Elsholtzia haichowensis Sun* was observed in soils with Copper in excess and its presence in plant tissues was also verified (Xia and Chen, 2007). The *Canavalia ensiformis* also showed high levels of copper in their root system and aerial part (Zancheta et al., 2011).

Between those species, the *Gentiana pennelliana* (Wire grass) is considered promising for phytoextraction of contaminated areas by Cd, Cr and Pb in tropical and sub tropical locations (Yoon et al., 2006). Indian mustard (*Brassica juncea*) is one of the most studied species and the one that presents great success in phytoextraction of contaminated areas with more than one metal, as well as the sunflower (*Helianthus annuus*) that accumulate high amount of Pb in its tissues, reaching up to 5 g kg^{-1} of Pb in dry matter (Prassad and Freitas, 2003).

A species with several phytoremediator characteristics, the *Crotalaria spectabilis*, has great capacity to store Lead (Lindino et al., 2012), as well as the Vetiver Grass (*Vetiveria zizanioides* L.) which showed high tolerance and efficiency of absorption and translocation of Pb in its roots tissues and aerial parts, attributing to these species phytoextraction potential and providing great importance in the programs for phytoremediation of contaminated areas with this metal (Alves et al., 2008).

Working with leguminous crops in soils contaminated with herbicides, revealed that *Crotalaria juncea* showed high phytoremediation capacity of the contaminated soils at levels up to 400 g ha^{-1} of active ingredient (Madalão et al., 2012), in a general aspect related to the removal of heavy metals, some plant species have high efficiency, as mustard (*Brassica hirta*), peanuts (*Arachis hypogaea*), broccoli (*Brassica oleracea*), buckwheat (*Fagopyrum esculentum* Moench), vetiver grass or smell (*Chrysopogon zizanioides* L.), among others (Accioly and Siqueira, 2000). These data are presented in Table 2.

The phytoremediation has as main advantages the low cost, landscape improvement, little environmental impact, public acceptance, economical recovery of the plant from the recycling of metals after harvesting, easier control process with plants than using microorganisms, plants production of their own energy (through photosynthesis) and ready availability of technologies to harvest these plants (Lamego and Vidal, 2007).

BIOREMEDIATION

Bioremediation is a technique that involves the use of natural occurrence or cultivated microorganisms that, through metabolic routes, promote physical-chemical reactions, transforming compounds of hard degradation into simple compounds, making degradation an easy process, being used in the removal of contaminants in surface water, groundwater and soils (Andrade et al., 2010). Some studies report that most microorganisms used in this technique are bacteria and fungi, in reason of the ability to degrade a wide range of organic substances (Pereira and Freitas, 2012).

There are two methods of bioremediation when referring to the place of work: *in situ* bioremediation, also known as natural remediation. In this technique, the contaminant remains in place and decontamination occurs through physical, chemical and biological processes. In general, it occurs slowly, requiring monitoring of the site in long term, aiming to restore the environmental equilibrium (Foght, 2008). And *ex situ* bioremediation, that requires the removal of the contaminated soil from the place so that it can be treated in another location. Removal may be required when there is possible contamination of people and of the environment near the soil to be bioremediated, or the presence of high concentrations of contaminants requires the use of techniques such as: composting, bioreactor, among others (Jacques et al., 2007).

Microorganisms are considered efficient biodegradation promoters, because of its abundance, diversity of species and catabolic and anabolic versatilities, as well as its capacity of adaptation to adverse environmental conditions (Moraes and Tornisielo, 2009). Several metabolic pathways of degradation of PHA's have been identified in various microorganisms. The possibility of the use of some biochemical pathways allows the bacteria to grow using PHA's as the only source of Carbon and energy for growth, degrading these compounds and eliminating them from the environment. The same author said that bacteria of the genus *Pseudomonas*, degraded on average 51% of the anthracene present in middle mineral culture. In the case of lignolyticus fungi, they oxidize lignin extracellularly by the action of lignin peroxidases, manganese and laccases dependent peroxidases (Jacques, 2007).

In studies conducted with *Fusarium moliniforme,* it was concluded that it is a good indicator for consumption of contaminants, acting in the elimination of glyphosate molecules, lixiated and diesel oil. It can also be used in the treatment of contaminated soils (Silva and Rondon, 2013). Satisfactory results were found in the substitution of a chemical surfactant for the biosurfactant produced by *Corynebacterium aquaticum*, aimed at bioremediation of benzene, toluene and xylene (BTX) in sandy soil (Zilio et al., 2012).

The information obtained in this work makes it possible to understand the importance of using microorganisms in biotechnology for remediation of contaminated soils, considering that they use toxic substances as a Carbon source, resulting in an effective and safe method to human and environmental health.

CONCLUSIONS

Activities of agriculture and industry are one of the mains sources of soil contamination, depositing contaminants like toxic metals and pesticides, affecting the development of plants and humans that depend on it.

Both bioremediation and phytoremediation consist of viable alternatives techniques for soil decontamination and remediation with satisfactory performance on stabilization and removal of contaminants.

Conflict of Interest

The authors have not declared any conflict of interest.

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