

Cadmium toxicity and phytoremediation in trees - A review

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Abstract

Over time, the anthropic activity has contributed to alter biogeochemical cycle of heavy metals by releasing contaminants into water, soil and air. Due to contamination of environments with heavy metals, plants and animals consumed by population have presented some level of contamination, which has caused worries and also attempts to minimize these problem. Among heavy metals, cadmium is one of the most toxic to living creatures, occupying seventh position in toxic substances ranking, even with very low concentrations. One of measures adopted to reduce negative impact of soil contamination by heavy metals is phytoremediation. It consists of use of plants that tolerate presence of heavy metals in soil, absorbing, translocating and compartmentalizing them in aerial part, with little or no negative impact on plant growth. Among plants, trees are the most suitable for phytoremediation due to their considerable production of air biomass, which is associated with higher accumulation and consequently higher extraction of heavy metals. In this review, we address main nutritional, biochemical, physiological and molecular aspects of cadmium toxicity in plants, emphasizing role of trees in phytoremediation studies, especially recent studies on *Khaya ivorensis* or african mahogany and its cadmium phytoremediation potential.

Keywords: Heavy metal; phytoremediation; chelation; metal compartmentalization; oxidative stress.

Introduction

Heavy metals (HM) are important pollutants for environmental, ecological, nutritional and evolutionary reasons. It has origin of anthropogenic and/or lithogenic processes in the soils (Nagajyoti et al., 2010). These contaminants are introduced into soil by natural process. It includes minerals weathering, volcanic eruptions and erosion when not accelerated or induced by humans (Frohne et al., 2015; Antoniadis et al., 2017).

Rock formations are vast site for heavy metals, mainly in their dispersed form. However, industrialization and urbanization contribute on larger scale to increase concentration of chemicals in biosphere (Rehman et al., 2015).

HMs are widely available in soils and aquatic ecosystems. Also, small amount of HMs are available in atmosphere as particles or vapors, such as lead (Pb), cadmium (Cd), nickel (Ni), arsenic (As), silver (Ag), chrome (Cr), cobalt (Co) and iron (Fe) (Nagajyoti et al., 2010, Gautam et al., 2016; Luo et al., 2016).

These chemical elements constitute a group of metals or metalloids with an atomic density greater than 4 g cm⁻³ or five times or more density of water. However, it should be noted that chemical properties of PM such as bioaccumulation and highly reaction are factors that best determine their classification rather than their density as main characteristics (Hawkes, 1997; Nagajyoti et al., 2010; Kabata-Pendias and Szteke, 2015; Rizwan et al., 2016)

HM toxicity varies depends on plant species, HM type and concentration, chemical form, pH and soil composition (Sharma and Agrawal, 2005; He et al., 2015). Some of HMs act as cofactor and enzymatic activator such as Zn and Fe. Others assume functions related to catalytic properties in prosthetic groups in metalloproteins (Ivanov et al., 2016; Mathur et al., 2016).

HMs including Cd, Pb, and have no known biological functions are are toxic to most living organisms and even low concentrations are highly harmful to MP-sensitive enzymes resulting in reduced growth and death of organism (He et al., 2013; Luo et al., 2016).

Among HM cadmium (Cd) appears as seventh most toxic, according to United States Agency for Toxic Substances and Disease Registry (ATSDR, 1999) ranking and is among the most widely distributed environmental pollutants from natural or industrial sources (Sabeen et al., 2013; Mead, 2010).

Cd was discovered in 1817, zinc oxide samples obtained by roasting zinc carbonate in Salzgitter, Germany, by researchers Friedrich Stromeyer and Karl Hermann (Borsari, 2011). Cd is an element of group 2B of periodic table, with an atomic number of 48 and a density of 8.6 g cm^{-3} (Hasan et al., 2009). It is a relatively rare element and is not found in its pure state in nature.

In air, Cd is rapidly oxidized to cadmium oxide. This nonessential microelement easily reacts with carbon dioxide, water vapor, sulfur trioxide or hydrochloric acid producing carbonate, hydroxide, sulfide or cadmium chloride. Furthermore, it may poorly bond with carbon and other more electronegative atoms (Tran and Popova, 2013). Toxicity to plants has been recorded through reduced growth of shoot and root (Bonet et al., 2016; Akhtar et al., 2017; Anjum et al., 2017).

Decreased photosynthetic activity (Chaffei et al., 2004; Cao et al., 2015; Kaur and Jhanji, 2016) anatomical changes (Castro et al., 2015; Ibrahim et al., 2015; Pereira et al., 2016) and nutritional (Castro et al., 2015; Ibrahim et al., 2015) have been observed in plants.

Leaf concentration above $100 \mu\text{g Cd g}^{-1}$ of dry mass is considered exceptional, the values above which in plant is considered hyper-accumulating. The HM hyperaccumulation feature in plants is uncommon and less than 0.2% of all angiosperms have been classified as hyperaccumulative (Baker et al., 2000).

All plants extract metals from soil, but some plant groups have different ability to extract, accumulate and tolerate high levels of HM that are toxic to organisms (Cunningham and Ow, 1996).

These plants are known as hyperaccumulators and are used as phytoextractors in HM contaminated environments. Success in HM phytoextraction presupposes use of plants with high HM absorption capacity and high biomass production (Lasat, 2002).

In this review we will address main aspects related to cadmium phytoremediation performed by trees, emphasizing physiological, biochemical and nutritional mechanisms involved, as well as addressing the most recent findings regarding use tree of Meliaceae family, potentially cadmium phytoremediation.

Growth

The efficient decontamination of areas affected by HM by phytoremediation requires fast growing species, high dry mass production, high tolerance and ability to accumulate Cd in shoots.

Trees are among the best species due to their large size and ability of root system to grow into a greater depths. Considering that a considerable part of phytoremediation studies are based on herbaceous plants, some studies conducted with trees have shown promising results, indicating phytoremediation potential of Cd.

In a study, two trees of Lythraceae family, species *Lagerstroemia indica* (*L. indica*) showed high growth compared to *Lagerstroemia fauriei* (*L. fauriei*), when grown in a pot condition containing 20, 40 and 80 mg kg^{-1} Cd. The phytoremediation character of species *L. indica* was

evidenced by high translocation factor, which was always high at all concentrations of Cd compared to species *L. fauriei* (Wang et al., 2016). The high growth and translocation factor of Cd presented by species *L. indica*, suggests this species as potentially phytoremediation plant, as it presented considerable levels of Cd in shoots in parallel with low growth reduction and increase of Cd concentrations in shoots.

In another study involving four species subjected to five concentrations of Cd under greenhouse conditions, leucena legume (*Leucaena leucocephala*) showed great phytoremediation potential due to growth gains and large accumulation of Cd in shoot as a function of Cd concentrations applied to vessel. In addition, chemical analysis of soil where leucena plants were cultivated after harvesting showed a reduction in Cd levels, compared to analysis of soil prior to planting. This has evidenced phytoremediation potential of leucena in extracting Cd and maintaining satisfactory growth (Kaur et al., 2018).

The evaluation of two clones belonging to Salicaceae family showed that species *Populus deltoides* (clone B-81) has phytoremediation potential with differential tolerance to concentration of 8.14 mg kg^{-1} Cd applied to soil under greenhouse conditions. This clone presented high total biomass, root mass, leaf mass and leaf area. In addition, clone presented high Cd concentration in stem, as well as high biological concentration and translocation factor of stem when cultivated in presence of Cd (Nikolić et al., 2017). The accumulation of Cd in stem is positive factor because it avoids secondary soil contamination if accumulation of Cd was in leaves.

Salix dasyclados showed a potential phytoremediation when grown in a pot containing soil moderately contaminated with Cd (5.46 mg kg^{-1}). This species showed pronounced growth, besides accumulating high levels of Cd in leaves and branches (57.5 and 28.7 mg kg^{-1} , respectively) without showing symptoms of Cd toxicity (Fuksová et al., 2009).

Another species with phytoremediation potential is *Populus trichocarpa*. This species showed high tolerance to Cd toxicity as it did not show significant differences in total biomass production between Cd treatments, except for the highest Cd dose of 243 mg kg^{-1} . However, up to limit concentration of 27 mg kg^{-1} , *Populus trichocarpa* was highly tolerant to Cd toxicity (de Oliveira and Tibbett, 2018).

Dendropanax cuneatum (*D. cuneatum*) showed considerable total accumulation of $697 \mu\text{g kg}^{-1}$ Cd with 63% of total accumulated in stem of plants in Cd (135 mg kg^{-1}) contaminated dark red (LE) Oxisol mixed with LE but uncontaminated, in proportion of 40 and 60% (contaminated/uncontaminated soil, respectively). The high accumulation of Cd in stem of *Dendropanax cuneatum* showed potential of this specie in phytoremediation of Cd contaminated soil and reduction of Cd secondary soil contamination from leaf accumulation (Soares et al., 2001).

Antioxidant mechanisms

Reactive oxygen species (ROS) or reactive oxygen intermediates (ROI) are partially reduced forms of atmospheric oxygen (O_2). They typically result from electronic excitation of O_2 to form singlet oxygen (O_2^1) or transfer one, two or three electrons to O_2 to form respectively superoxide radical (O_2^-), hydrogen peroxide (H_2O_2) or hydroxyl radical (OH^\cdot) (Mittler, 2002).

ROS promote oxidation of various cellular components and leads to oxidative destruction of cells in phenomenon called

oxidative stress. They are capable to induce cellular damage through protein degradation, enzyme inactivation, alterations in genes what interferes in metabolic pathways (Dat et al., 2000; Choudhury et al., 2013).

Oxidative stress comes from an imbalance between synthesis of oxidant and antioxidant compounds, in which former is considerably increased (Vaidyanathan et al., 2003; Gill and Tuteja, 2010). Despite harmful effect on cells, ROS are usually produced due to photosynthetic and respiratory cell metabolism (Mittler, 2002).

In addition, plants use ROS as molecules to regulate development and various physiological responses such as growth, cell cycle and programmed cell death (Kovtun et al., 2000; Pitzschke et al., 2006; Veal et al., 2007). However, under stressful conditions (*i.e.*, salt stress, water deficiency or excess, heavy metal toxicity or elevated temperatures) plants increase their yield.

Cd is not directly involved in redox reactions and; therefore, cannot change its oxidation state in plant cells as it does not participate in Fenton and Haber-Weiss reactions (Cuypers et al., 2011; Liu et al., 2015; Khan et al., 2013).

It appears that Cd can indirectly activate membrane NADPH oxidases, inducing higher production of ROS such as O_2 and H_2O_2 , eventually lead to an oxidative explosion (He et al., 2013; Choppala et al., 2014). The mechanism of Cd triggered ROS production involving activation of protein, NADPH - oxidase, which is regulated by free Ca and ethylene.

To increase Ca levels plants require phospholipase C activity as well as involvement of 3-phosphate inositol in activation of calcium channels and ADP ribose (adenosine triphosphate ribose). In addition, Cd and Ca induced ROS production is triggered by reaction cascade involving calmodulin, protein kinases, phospholipase C and D.

Phospholipase also initiates signalization by increasing levels of phosphatidylinositol triphosphate (IP3) or phosphatidic acid. These molecules act by activating secondary messengers such as lipids and protein kinase, including 3-phosphatidylinositol kinase, mitosis activates protein kinases and calcium dependent protein kinases.

Activation of Cd induced mitosis activating protein kinases requiring not only ROS, but also calcium-dependent protein kinases and 3-phosphatidylinositol kinase. It also may be triggered by closure of mitochondrial permeability transition pore. ROS induced secondary messengers can modify transcription factors, affecting expression of plant signalization and gene-promoted defense. ROS are associated with signal transduction in conjunction with nitric oxide, leading to necrosis and programmed cell death (Chmielowska-Bak et al., 2014).

Prolonged exposure to Cd causes high ROS production, causing oxidative damage. H_2O_2 is formed in the same cell sites as O_2 . In high concentration in cell, it inhibits carbon fixation activity such as many Calvin cycle enzymes which are extremely sensitive to H_2O_2 . Also, it breaks cell membranes and cause damage to DNA (Scandalios et al., 2000).

Autors He et al. (2013) showed that exposure to Cd increased levels of 1O_2 and H_2O_2 in root tissues of two varieties of *Populus* (*Populus cathayana* e *Populus deltoides*), when compared to control.

In pine tree (*Pinus sylvestris*), Tran and Popova (2013) demonstrated that treatment with 50 μ M Cd increased levels of O_2^- and H_2O_2 in roots in just 6 h after initiation of treatment with metal.

Cuypers et al. (2011) reported ability of Cd to induce highest production of ROS as a result of oxidative damage, which

causes redox homeostasis impairment and leading to emergence of secondary stress, oxidative stress (Chen et al., 2014; Tauqeer et al., 2016).

Sequestration, compartmentalization and cadmium partition in trees

In MP exclusive plants, roots impose restriction on absorption of HM by retention, which avoids dispersion of contamination in aerial organs, preventing appearance of toxic effects, especially in photosynthetic apparatus of plants (Li et al., 2015; Liu et al., 2015; Lysenko et al., 2014).

The root cell wall (PC) positively contributes to Cd retention and constitutes first barrier protecting protoplast from Cd toxicity (Chen et al., 2014; Mahar et al., 2016). The negative charges resulting from dissociation of carboxylic groups (COO^-) from galacturonic and glucuronic acids of root cell wall, mainly rhizoderm and cortex makes sequestration of Cd possible. In addition, barriers imposed by Casparian strips and plasmalema of endoderm cells represent mechanisms that restrict Cd's access to xylem, reducing translocation to plant shoots. Similarly, pectin and cellulose functional groups of root tissue cell wall can complex metalloids (Chen et al., 2014; Pereira et al., 2017; Pietrini et al., 2015).

In studies of woody plants, sequestration of Cd by constituents of root cell wall were found, which evidences sequestration of Cd as primary tolerance mechanism of these species to phytotoxic effect of Cd (Chen et al., 2014; He et al., 2013).

In research on *Eucalyptus camaldulensis*, Souza et al. (2013) showed that under high concentrations of Cd metal was sequestered by cell walls of root cortex of plants. According to authors, this fact may be related to chelation of Cd by organic acids present in root exudates, which contributed to low translocation of Cd to organs of aerial part of plants.

An increase in root PC thickness has also been observed in response to Cd contamination. In this case, plant maximize filtering capacity by increasing negative charge and protecting inner tissues that comes from damage effects of heavy metals (Souza et al., 2013; Shi et al., 2015).

In fact, radial rise of Cd in plants is limited by root system and development of endoderm, exodermis and other extracellular barriers that may restrict Cd translocation to xylem (Lux et al., 2011; Fontanili et al., 2016).

Metal ions are probably adsorbed to cellular matrices or apoplast components that is unavailable to transport. In addition, movement of Cd through simplasto is reduced by production of non-protein thiol compounds (Cao et al., 2018; Xu et al., 2017).

Some studies have show negative correlation between thiol group content and variation of Cd concentration inside plants, indicating that thiol metabolism may limit flow of Cd (Nocito et al., 2011; Mahar et al., 2016; Xu et al., 2017).

In this sense, chelation of Cd by thiol-peptide compounds in roots regulates systemic ion homeostasis and ensures great retention of Cd in roots (Xu et al., 2017; Cao et al., 2018). The movement of metal ions is only possible as non-cationic metal chelates because cell walls have comparatively high cation exchange capacity (Thakur et al., 2016; Cao, et al., 2018). Under limiting concentrations of Cd in plant tissue there is increased synthesis of high (HMW) and low (LMW) molecular weight chelators such as glutathione (GSH) and phytochelatins (PCs), which facilitate transport of Cd to vacuoles (Fontanili et al., 2016; Mahar et al., 2016; Thakur et al., 2016; Xu et al., 2017).

Studies by Souza et al. (2013) suggest that synthesis of phytoalequitins is influenced to great or less extent according to affinity for stressor metal. In this sense, Cd appears as MP that determines highest synthesis of peptide, followed in sequence by Pb^{2+} , Zn^{2+} , Sb^{3+} , Ag^+ , Hg^{2+} . The phytocellatin of Cd complex has about 1,000 times lower phytotoxicity than free Cd ions (Stolt et al., 2003; Olguín et al., 2007). Different root mechanisms contribute positively to high Cd retention, leading to apoplastic barriers, synthesis of chelating molecules such as phytalekithins and vacuolar sequestration. These factors are main processes that mediate Cd retention in roots (Gomes et al., 2011; Sghayar et al., 2015; Cui et al., 2016).

The results of metal chelating complex is actively transported from cytosol by ATP dependent transporters present in vacuole tonoplast. Binding of phytoalequitins to Cd decreases cytosol activity and toxicity (Cobbett, 2000; Stolt et al., 2003). For example, Vögeli-Lange and Wagner (1990) studied protoplasts isolated from mesophyll of tobacco plants (*Nicotiana rustica* var. pavonii) exposed to Cd and reported that metal was chelated by phytoalequitins (PCs) and Cd PC complex was actively transported to vacuole through tonoplast.

Cell wall and vacuoles are primary subcellular fractions for Cd storage (Li et al., 2017; Cao et al., 2018). Vacuolar seizure is one of main events that clarify differences in variation of Cd retention in plant roots. Vacuum sequestration mainly depends on activity of transporters located in tonoplast (Mendoza-Cózatl et al., 2010; Sharma et al., 2016) and number of Cd ions (free and retained Cd^{2+} in thiol-peptide complexes) in cytosol.

Previous studies have shown an increase in root meristematic cell vacuolation in Cd treated plants, which has been attributed to chelation of metal to low molecular weight compound and transport and sequestration in vacuoles (Verbruggen et al., 2009; Fan et al., 2011; Batista et al., 2014). In vacuole, Cd dissociation with HMW compounds occurs due to vacuolar pH. In free form, ions bind, even with cell compartment or organic acids and amino acids (Zoghalmi et al., 2011; Li et al., 2017).

After crossing walls of root cells, Cd reaches plasma membrane (MP). H^+ ATPases control MP polarization through formation of an electrochemical gradient as driving force, which is fundamental for transport of ions such as Mg^{2+} , Ca^{2+} , Fe^{2+} , Cu^{2+} , Mn^{2+} and Zn^{2+} across membrane and otherwise suppress input of toxic ions in cell compartments (Gallego et al., 2012; Clemens et al., 2013; Song et al., 2014; Shi et al., 2015; Stoláriková-Vaculíková et al., 2015; Pereira et al., 2017).

Some species show ability to tolerate and accumulate heavy metals (Liu et al., 2013). Depending on MP, plants can accumulate them in different organs. Accumulation of Cd varies in plant structures (*i.e.*, root, stem, branches and leaves) in different trees and may be high in root compared to leaves. Table 1 shows different species that can accumulate Cd in shoot (stem, branches or leaves) or root.

Mechanisms cadmium absorption

Cd is a nonessential and toxic element to plants. Even under low concentration, plants manifest symptoms of toxicity evidenced by reduced photosynthetic rate, nutritional imbalance and decreased growth.

Although Cd may be in atmosphere in form of particles and vapor, absorption by plants occurs mainly from root with translocation to aerial part. This absorption mechanism is

more important in agricultural environments because rate of deposition of Cd in air is typically less than $2 \text{ g ha}^{-1} \text{ year}^{-1}$ (Smolders, 2001).

Cd uptake by plants is modulated by set of factors such as pH, temperature, aeration, total soil Cd concentration and presence of macro and micronutrientes (McLaughlin et al., 1999).

In plants, primary xylem transport, phloem retranslocation and xylem transfer to phloem are important processes of translocation of an element within plant (Marschner, 2012). The transport in xylem is directed to aerial part through transpiratory current, while in phloem transport occurs from source to drain, being more selective (Marschner, 2012).

Root cell absorption of Cd from rhizosphere is mediated by *OsIRT1* and *OsNRAMP5* membrane transporters, according to proposed model for *Oriza sativa* (Gao et al., 2016).

These transporters are located in plasma membrane of root cells which allows passage of Cd located in rhizosphere into cells. After entering root cell, part of Cd is chelated, forming Cd - phytocellatin complex, which is sequestered in vacuoles. After entering root cell, part of Cd is chelated, forming Cd - phytocellatin complex, which is sequestered in vacuoles.

In root, the other part is translocated to aerial part via xylem and passes to phloem through *OshMA2* transporter (Li et al., 2017).

The *OsLCT1* and *OshMA2* transporters are located in node region and base of shoot. The *OsIRT1* transporter is located in root epidermis and exodermis cells and in stele (vascular cylinder) cells. In turn, *OsNRAMP5* transporter is located in root epidermis, exodermis and endoderm cells.

In phloem, Cd binds to specific proteins and weakly to thiol groups called glutathione - GSH (Figure 1) (Yoneyama et al., 2015).

In tonoplast, there is *OshMA3* transporter, which allows passage of Cd - phytocellatin and sequestration in vacuoles (White and Broadley, 2011). This mechanism of Cd sequestration in root cell vacuoles is strategy of stress tolerance for Cd, as it prevents translocation to shoot and appearance of Cd toxicity symptoms.

On the other hand, there is another mechanism called avoidance, in which plant presents physical mechanism such as Casparian strips (Figure 2) or exudes a set of compounds (sugars, proteins and organic acids) that prevent entry of Cd inside xylem cell, a strategy adopted by plant to avoid Cd toxicity.

Plants have ability to absorb and translocate Cd differently. Plants considered as accumulators have a considerably high Cd content in aerial part (leaves, branches or stem) compared to non-accumulators.

The value of threshold concentration separating accumulative and nonaccumulative plants is 100 mg kg^{-1} dry mass of shoot (Baker and Brooks, 1989). Cd levels in shoot above this value indicate that species is phytoremediator (Barker et al., 2000).

However, few species have capacity to accumulate Cd contents above 100 mg kg^{-1} . Only species *Populus trichocarpa* × *P. deltoides* (Robinson et al., 2000), *Salix caprea* (Lepp and Madejón, 2007; Unterbrunner et al., 2007) and *Salix* × *smithiana* (Wieshammer et al., 2007) accumulated more Cd, above 100 mg kg^{-1} . Due to large biomass production of leaves, branches and trunks, trees have potential for MP phytoextraction.

As one of main products of silvicultural exploitation is wood from trunk, phytoextraction and immobilization of MP in these structures allows almost total removal of MP from contaminated area.

Table 1. Preferred accumulation of Cd in different organs of tree species.

Species	Organs	Authors
<i>Melia azirach</i>	Root > Stem > Leaf	Khamis et al. (2014)
<i>Populus alba</i>	Root > Leaf > Stem	Khamis et al. (2014)
<i>Populus alba</i>	Root > Green leaf > Stem=Fallen leaf	Rafati et al. (2011)
<i>Ulmus laevis</i>	Root > Leaf > Stem	Mleczec et al. (2017)
<i>Quercus robur</i>	Root > Stem > Leaf	Mleczec et al. (2017)
<i>Acer platanoides</i>	Root > Stem > Leaf	Mleczec et al. (2017)
<i>Acer pseudoplatanus</i>	Root > Stem > Leaf	Mleczec et al. (2017)
<i>Betula pendula</i>	Root > Stem > Leaf	Mleczec et al. (2017)
<i>Quercus robur</i>	Root > Stem > Leaf	Mleczec et al. (2017)
<i>Tilia cordata</i>	Root > Stem > Leaf	Mleczec et al. (2017)
<i>Acacia mangium</i>	Stem > Leaf = Root	Majid et al. (2012)
<i>Prosopis juliflora</i>	Leaf > Root	Varun et al. (2011)
<i>Populus×euramericana</i> cv. 'Neva'	Root > B > YL > S > ML > W*	Ge et al. (2012)
<i>Populus nigra×Populus ussuriensis</i>	Root > YL > B > S > ML > W*	Ge et al. (2012)
<i>Gamblea innovans</i>	Root > Stem > Leaf	Hayakawa et al. (2011)
<i>Salix discolor</i>	Root > Wood > Stem	Kuzovkina et. (2004)
<i>Salix eriocephala</i>	Root > Stem > Wood	Kuzovkina et. (2004)
<i>Salix exigua</i>	Root > Wood > Stem	Kuzovkina et. (2004)
<i>Salix lucida</i>	Root > Wood > Stem	Kuzovkina et. (2004)
<i>Salix nigra</i>	Root > Wood > Stem	Kuzovkina et. (2004)

*B: barks; YL: young leaf; ML:mature leaf; W:wood; S: stem.

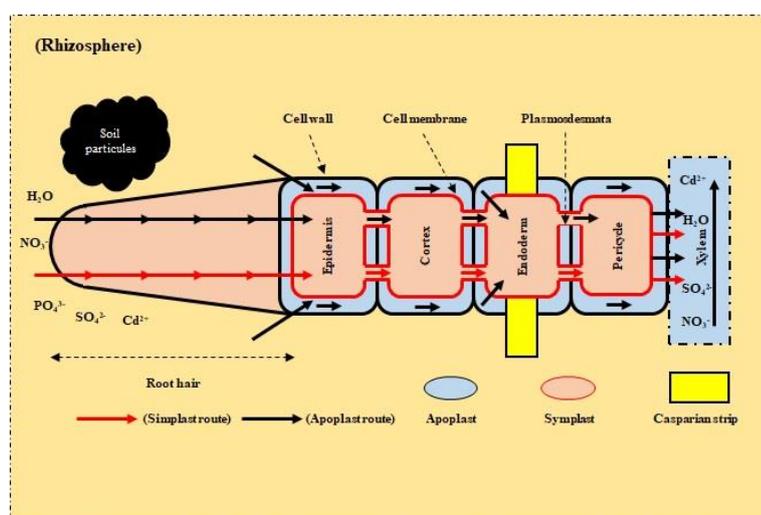


Fig 1. Cadmium absorption and sequestration mechanism in plants. Proposed model for rice. Adapted from Gao et al. (2016).

Table 2. Phytoextractor potential of tree species in soils with different cadmium contents.

Species	Cd content in growth substrate	Author
<i>Dendropanax cuneatum</i>	74 mg dm ⁻³	Soares et al. (2001)
<i>Salix dasyclados</i>	5.46 - 60 mg kg ⁻¹	Fuksová et al. (2009)
<i>Salix spp</i>	0.42 - 30,5 mg kg ⁻¹	Vysloužilová et al. (2003)
<i>Lagerstroemia indica</i>	0 a 80 mg kg ⁻¹	Wang et al. (2016)
<i>Averrhoa carambola</i>	0.51 mg kg ⁻¹ (Extractable)	Dai et al. (2011)
<i>Averrhoa carambola</i>	12 mg kg ⁻¹	Li et al. (2010)
<i>Populus trichocarpa</i>	27 mg kg ⁻¹	Oliveira e Tibbett (2018)
<i>Swietenia macrophylla</i>	15 mg L ⁻¹	Fan et al. (2011)
<i>Populus deltoids × Populus nigra</i>	4.28 mg kg ⁻¹	Wu et al. (2010)
<i>Leucaena leucocephala</i>	40 mg kg ⁻¹	Kaur et al. (2018)

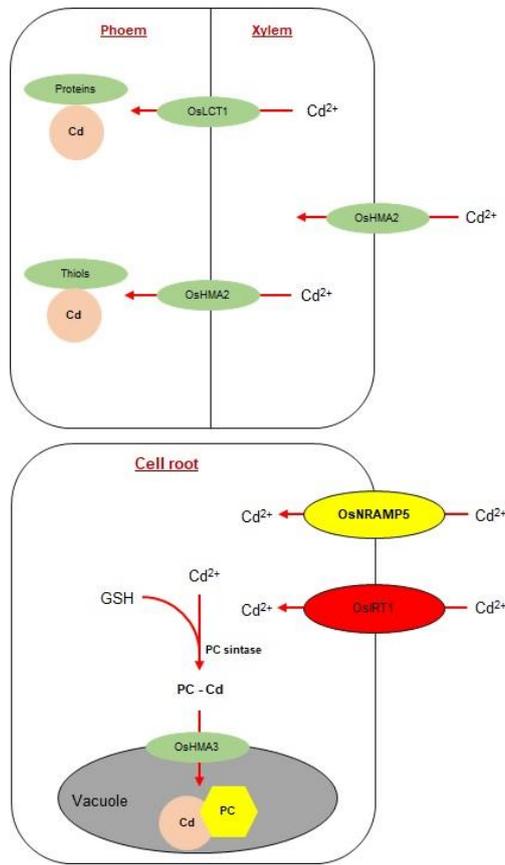


Fig 2. Symplastic and apoplastic flow of water and mineral nutrients. The presence of Casparian strips limits the passage of heavy metals into the xylem. Casparian strips are important physical barriers to xylem absorption and translocation of Cd to the shoot in a mechanism called avoidance. The exoderm-coupled endoderm also acts as a barrier to the passage of Cd. Simplast and apoplast are involved in Cd absorption. Cd absorption is modulated by OsIRT1 and OsNRAMP5 transporters located on the plasma membrane.



Fig 3. Young plant, adult plant and reproductive structure of mahogany (*Khaya ivorenses*) a potential tree phytoremediator.

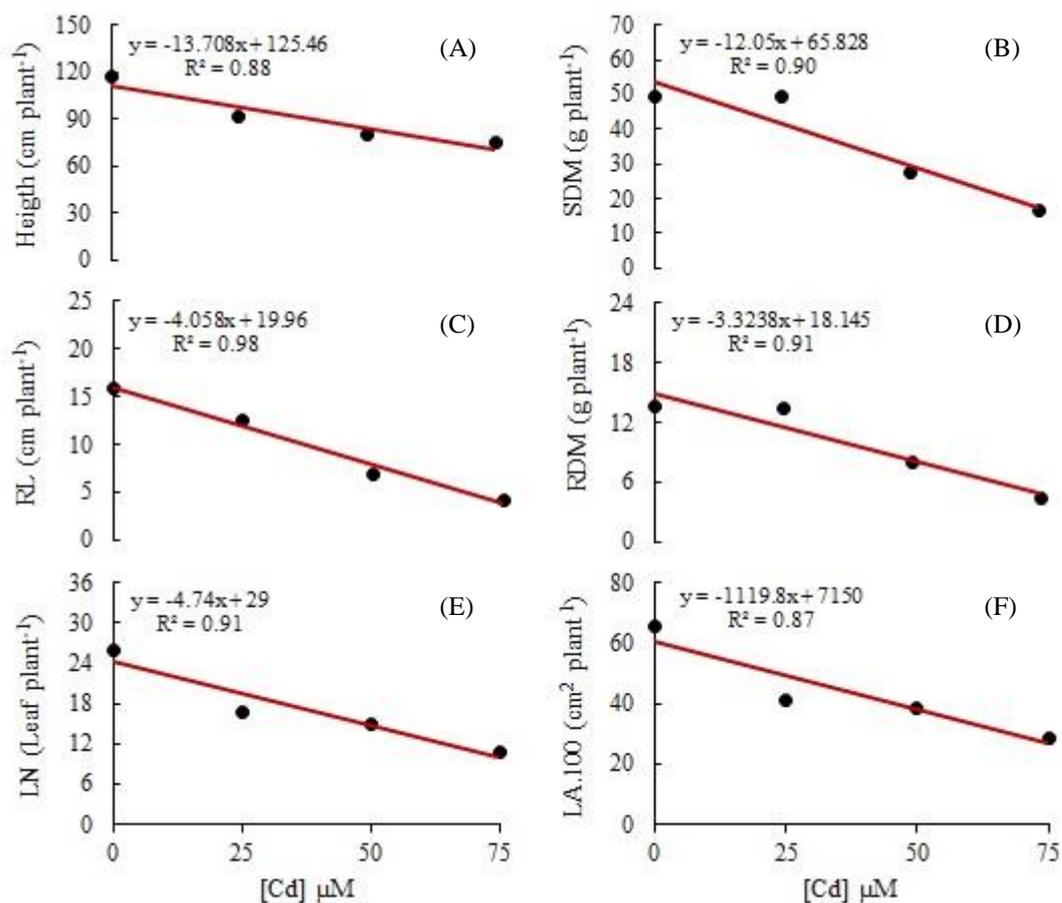


Fig 4. Height (A), shoot dry matter (B), root length (C), root dry matter (D), leaf number (E) and leaf area (F) of young plants of *Khaya ivorenses* (three hundred day old plants) submitted to Cd concentration.

However, leaves and branches must be properly disposed so that secondary PM contamination does not occur. Therefore, phytoextracting capacity of a species is determined by two factors: metal concentration in aerial part and biomass production in aerial part. Plants suitable for phytoextraction should have good shoot biomass production and ability to accumulate and transport Cd to shoot.

Plant nutritional disorder and Cd toxicity

HMs conflict with essential nutrients, a relationship that can be antagonistic or synergistic with accumulation of species - organ dependent HM. The relationship between Cd and essential nutrients may imply emergence of nutritional disorders that accompany reduction of plant growth.

For example, Cd competes with Ca^{+2} for same membrane transporter during root absorption process and may decrease Ca^{+2} . Influx may be replaced with membrane phospholipid bonds.

In poplar clone I-214, application of 150 μM Cd reduced leaf Ca content by 23% and plant dry mass (Di Baccio et al., 2014). False - open presence of 0.5 μM reduces root Ca content by 17.5% (Österås and Greger, 2006).

On the other hand in Cedar, application of 0, 22, 44, 88 and 132 μM of Cd did not alter root Ca levels, but promoted a significant linear and quadratic increase in Ca and stem contents, respectively (Paiva et al., 2001).

Despite conflicts in some results, Ca reduces Cd toxicity by decreasing absorption and competing Cd transport site. In addition, liming or alkaline media reduces Cd absorption, which is facilitated by low pH (Naeem et al., 2019).

In *Pinus pinea*, concentration of 5 μM Cd considerably reduced leaf and root Ca contents, while Mg levels were reduced only in leaves. On the other hand, in *Pinus pinaster* Ca and Mg contents increased in leaves and roots, showing differential genotypic response to Cd toxicity (Arduini et al., 1998). This same differential genotypic pattern of Cd response was observed in *Populus tremula* × *Populus alba*. The cultivation in presence of 360 mg kg⁻¹ of Cd increased contents of Mg, K in leaf and Zn, and Fe in roots. K contents were reduced in roots (Durand et al., 2010). Macro and micronutrient deficiency in plants may be due to indirect effect of Cd on mineral nutrients through role in inhibiting H⁺ ATPases. It is assumed that Cd can bind to electron bombs by changing conformation and causing inactivation. H⁺ ATPases use an electrochemical gradient as driving force, thereby controlling transport of ions across membrane, which is supposed to depend on lipid composition of organelle (Tran and Popova, 2013; Rivelli et al., 2014; Matraszek et al., 2016).

Thus, decrease in H⁺ATPase activity due to toxic effect of Cd may inhibit absorption of some essential mineral nutrients, which causes imbalances in cellular homeostasis, loss of MP permeability and lipid peroxidation (Astolfi et al., 2005).

Hernandez and Cooke (1977) reported modifications in plasma membrane lipid composition in *Pisum sativum* roots treated with Cd. This effect may have caused variation in membrane selectivity. Biochemical events results of decreased membrane fluidity include: interference with protein functions, reduced energy supply, loss of compartmentalization, and electrolyte leakage.

Therefore, it is plausible that changes in MP (loss of selective permeability) due to toxicity by Cd cause a decrease in absorption or translocation of potassium ions (K) from roots to aerial parts. The role of these nutrient in stomatal regulation determines gas exchange processes in plants with negative implications for plant growth and development (Nocito et al., 2011; Saifullah et al., 2014; Pereira et al., 2017).

In addition, Cd competes with iron (Fe) for same absorption site or membrane carriers, which implies reduction of absorption of micronutrient by plant and emergence of Fe deficiency as reported for a large number of plants (Konlechner et al., 2013; Solti et al., 2011; Kabata-Pendias, 2011; Chmielowska-Bak et al., 2014; Gong et al., 2015; Rahman et al., 2017).

The visible symptoms of Fe deficiency due to Cd poisoning can appear as brown spots on leaves and roots, atrophy of latter organ and chlorosis (John et al., 2008; Kabata-Pendias, 2011). Pereira et al. (2017) observed decreases in Fe⁺² concentration in leaves of *Calophyllum brasiliense* Cambess, which reflected in decrease of photosynthetic activity due to reductions in chlorophyll contents.

It seems that Cd induces similar symptoms to Fe deficiency. It also has its own mechanism of cell toxicity, which has specific targets such as aminos acid residues in multiprotein complexes. In addition, Fe deficiency increases susceptibility of multiprotein complexes to toxic effect of Cd (Qureshi et al., 2010; Basa et al., 2014).

This suggests that Cd not only causes micronutrient deficiency, but also triggers stress and induces cell damage. The primary consequence of toxic effect of Cd is on absorption and assimilation processes of essential minerals. For example, changes in water relations, plant anatomy and morphology decreases growth and development may occur. Also, photosynthetic metabolism of plant species, conformational and functional alteration of enzymes, proteins, especially cytosolic can happen (Verbruggen et al., 2009; Choppala et al., 2014; Liu et al., 2015).

In plants with lack of Cd tolerance mechanism, this ion is easily translocated by xylem current to intracellular spaces reaching chloroplasts, which affect their structure and function. Chloroplasts are one of the major sites of action of abiotic stresses including toxicity by Cd and other metals and semimetals (Anjum et al., 2016).

The main targets of metal in this cell compartment are two enzymes involved in CO₂ fixation process, essential for photosynthesis, ribulose -1,5- biphosphate carboxylase/Oxygenase (RuBisCo), which affects photosystem I and II activity.

Cd reduces RuBisCo activity and cause damage in its structure by replacing Mg²⁺ ion present in catalytic center, which appears like an important cofactor for carboxylation reaction. Cd can also displace RuBPCase activity to oxygenation reactions, which induces photorespiration (Tran and Popova, 2013; Wang et al., 2014). Processes such as gas exchange, water balance and stomatal conductance are reduced (Choppala et al., 2014; Wang et al., 2014; Luo et al.,

2016; Rizwan et al., 2016; Rahman et al., 2017) due to Cd toxicity.

Cd has a great effect on Chl a/Chl b II protein complex and light energy uptake, in part by inducing a reduction in chloroplast density or by displacing Mg²⁺ ion from chlorophyll tetrapyrrolic, leading to functionality with considerable reduction in content of chlorophyll pigments act in cellular protection against cytotoxic compounds to plant metabolism (Krupa, 1988; Tran and Popova, 2013).

In this process, Cd can replace Ca²⁺ ions in Ca/Mn clusters constitute reaction sites of water oxidation complex (OEC), causing no function and blocking electron transport. The toxicity of Cd to PSII reactions results from structural changes promoted by metal in electron transport proteins, plastoquinones (Qb), inducing low photosynthetic regulation (Sigfridsson et al., 2004; Tran and Popova, 2013).

Therefore, Cd inhibits photosynthesis by reducing photosystem II activity, which eventually suppresses quantum production and electron transport. It leads to an increase in concentration of cytotoxic compounds to plant species such as ROS that cause oxidative stress (Tran and Popova, 2013; Choppala et al., 2014; Pereira et al., 2017).

Use of phytoextraction in trees

Vegetables are able to adapt various growth environments and few places are devoid of their presence. Some species have ability to interact with other organisms such as arbuscular mycorrhizal fungi and nitrogen that fixes bacteria, which facilitate adaptation of plants to saline, acid, poor or rich in fertility. In this situation, plants that have good biomass production and ability to extract MP from soil and translocate them to aerial part are considered as MP phytoextractors. Phytoextraction consists of using plants to decontaminate polluted soils by heavy metals and organic products.

This technology reduces MP contents to levels safe and not harmful to human health, preventing spread of contamination through food chain and improving chemical, physical and microbiological attributes of soil. The feasibility of this technology is low cost of implementation, despite time required to have positive effects.

After absorption by root system and translocation of MP to aerial part of plants, harvested biomass can have several destinations such as biogas production or incineration. Incinerated plant biomass can be used for recovery of MP, fixing MP on bricks or disposed on deserted land (Ashraf et al., 2013). In trees, seasonality, age and phenology are factors that affect accumulation of MP.

The accumulation of MP (Cd, Co, Cu, Cr, Ni, Pb and Zn) in trees of *Salix viminalis* has been studied throughout plant age. Thus, two and three years old plants were more efficient in promoting phytoextraction, besides tolerating stress by MP and presenting ability to adapt in comparison to first year of evaluation.

In the first year of evaluation, plants presented high MP accumulation in relation to third one, supposed to dilution effect due to expressive plant growth (Dinelli and Lombini, 1996; Mleczek et al., 2009; Pulford and Watson, 2003).

In another study effect of plant seasonality and age on MP accumulation in *Salix fragiles* plants cultivated in contaminated sediment areas was evaluated. There were less extraction capacity of four and six years old species compared to one and two years old plants.

These results were related to effect and dilution, availability of Cd in root zone and root activity (Mertens et al., 2006). Seasonal variations in Cd content of leaves of *Evodiopanax innovans* are reported with leaf age, budding in April until leaf fall in November (Takenaka et al., 2009).

Phytoextraction as mechanism of decontamination of soil polluted by MP has advantage of low or zero energy use, except for solar energy being used by plants for photosynthesis. Plants can be easily monitored against microorganisms because some species can grow in soils with levels of toxic elements, in which microorganisms would not grow.

Plants promote improvements in physical, chemical and microbiological quality as they increase porosity, fertility and water infiltration as well as provide and recycle nutrients. On the other hand, phytoextraction does not fully reduce concentration of soil pollutants. Phytoextractors must have good biomass production and ability to extract pollutants from soil. A disadvantage of phytoremediation is positive results take longer if compared to other MP remediation technologies.

In general, trees with phytoextraction potential for Cd have phytoextraction capacity in substrates with variable levels of Cd, but depends on soil type, pH, organic matter content and trees (table 2).

Potential phytoextractor of mahogany

Mahogany (*Swietenia macrophylla* King) is considered one of main neotropical species (Figure 3) due to great commercial value of its wood. It belongs to family of Meliaceas, having a trunk with 3.7 m in diameter and height of 20 - 27 m in height before forming branches, with capsule like fruits and samaroid seeds (Lima Júnior and Galvão, 2005).

However, as a result of decades of illegal logging, this species has been in serious danger of extinction as its natural renewal does not occur in same speed as commercial demand (Souza et al., 2008; Souza et al., 2010; Free et al., 2014; Negreros-Castillo et al., 2018).

This species, besides being great timber seems to tolerate toxicity of Cd (Fan et al., 2011) and survive contamination by crude oil petroleum (Pérez-Hernández et al., 2013). Despite experimental evidence on phytoremediation potential of mahogany, studies on tolerance of this species to Cd toxicity still incipient.

Preliminary data shows that mahogany has little tolerance to increasing concentrations of Cd in nutrient solution with negative impact of Cd on growth of young mahogany plants. In general, concentrations above 25 µM cadmium chloride reduce growth (Figure 4). However, under concentrations ≤ 25 µM Cd, plants did not show significant decreases in growth variables.

This suggests that this specie has efficient mechanisms of accumulation and compartmentalization of Cd in tissues, which may guarantee tolerance and survival in environments contaminated with Cd. These results, although preliminary, match findings of Fan et al. (2011) suppositing of phytoextraction capacity of *Swietenia macrophylla*.

Final considerations

In several countries, anthropogenic activity has significantly contributed to soil pollution and heavy metal water resources, particularly, through activity of mineral

exploration and improper disposal of products that include heavy metals such as batteries and cell phones.

This fact has raised great concern from environmental agencies that signal increased environmental contamination by heavy metals. These agencies look for techniques that provides decontamination that are not expensive and sustainable. Thus, phytoremediation is viable alternative because it is not costly. It is simple and only requires resources already available in environment such as water and sun. Also, does not impose a frequent need for monitoring the contaminated areas. Studies are required on tolerance level, which is closely related to specific pattern of physiological, biochemical and nutritional response of species to type of heavy metal. Cadmium is seventh most harmful pollutant. Studies on phytoremediation by trees is mostly restricted to some temperate species.

Moreover, there is few studies about endemic trees in Amazon region with cadmium phytoremediation potential, given that anthropic activity such as agriculture, mineration, illegal gold exploitation and disorderly growth of cities. The pollutants become more intense, contributing to release of heavy metals in soil and water resources.

In this scenario, this review studies biochemical, physiological and nutritional mechanisms of plant species, especially *Swietenia macrophylla*, based on previous studies showing as a potential for cadmium phytoremediator.

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