JOURNAL OF DEGRADED AND MINING LANDS MANAGEMENT
ISSN: 2339-076X (p); 2502-2458 (e), Volume 4, Number 3 (April 2017): 807-814
DOI:10.15243/jdmlm.2017.043.807

Review

Revegetating Bagacay Mining Site: A review of potential tropical species for phytoremediation of non-essential heavy metals

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Abstract: Post-mining activities in Samar left serious environmental issues. Albeit it is used to provide prosperity to its constituents, mining in the area brought with it negative impacts. Bagacay Mine, an abandoned mining area in the province was left with enourmous amount of heavy metals. This include As (6-693 ppm), Cu (9-5,279), Pb (22-354 ppm), Hg (1-5 ppm), Zn (<1-7,138 ppm) and Fe (5,900-373,500 ppm). The area was then reforested with *Swietenia macrophylla, Leucaena leucocephala, Acacia mangium, Bambusa blumeana* and *Thysanolaena maxima* but only 1 percent survived. This paper touches the nature and effects of the non-essential heavy metals and metalloids present in the area as well as the mechanism of phytoextraction. Additionally, tropical metallophytes which can be used for phytoremediation activities in the future were introduced and reviewed.

Keywords*: heavy metals, Bagacay mine, metallophytes, phytoremediation*

Introduction

Post mining activities in Samar left serious environmental issues. Albeit it used to provide prosperity to its constituents (Holden, 2012), mining in the area brought with it negative impacts. Twenty-four years after it was abandoned, bagacay mine turned into a great example of destructed nature. By the time it was abandoned, there were no existing firm policies relative to remediation and rehabilitation of mining sites prior to its closure. As justified, the bagacay mine was left with enormous amount of heavy metals. When left in contact with the soil, these heavy metals are considered to be the worst kind of pollutants. Its presence hinders the normal functioning of soil ecosystems and plant growth (Khan et al., 2008). These made the area barren and still devoid of vegetation.

In 2004, the National Policy Agenda on the Revitalization of Mining in the Philippines stressed to prioritize the remediation and rehabilitation of abandoned mines of which the Bagacay Mine ranked first. An initial assessment was conducted and soil samples revealed that the area was contaminated with very high levels of Iron (Fe), Copper (Cu), Zinc (Zn), Lead (Pb) and Arsenic (As). Samples on the midstream and downstream portions of the area were also discovered to contain rather considerable amount of Mercury (Hg). In 2005, a reforestation activity was conducted. Said reforestation made use of plants such as Mahogany (*Swietenia macrophylla),* Ipil-ipil *(Leucaena leucocephala),* Mangium *(Acacia mangium),* Bamboo *(Bambusa blumeana) and* Tigergrass *(Thysanolaena maxima).* In the end, the measure undertaken resulted to around 1% survival rate of the species planted (MGB-MESD, 2006). To note, the previous activity conducted uses the concept of phytoremediation. However, direct reforestation of said plants on the area would still be in question for the following reasons: (a) although, species selected in the reforestation were proven to thrive in low-nutrient soils, the implementing agency failed to conduct a review on each species' performance on heavy metal contaminated soil; (b) the soil samples revealed that the area do not just contain excessive essential metals but a combination of diverse essential and toxic metals or metalloids in substantial amount. The existence of these toxic pollutants impedes the survival of the plants in the area. Therefore, addressing a solution to this context is a practical imperative.

This study reviewed the effects of the non-essential heavy metals present in the abandoned mine. Considerable heavy metal tolerance of plants with high metal accumulation capacity would make the phytoremediation efficient (Davies, 2013). Thus, heavy metal tolerant and hyperaccumulator species used for phytoremediating mines in the tropics that can potentially bring successful phytoremediation projects in the area were also looked into. In general, the study provides prudent aid for the phytoremediation measures to be implemented in the future.

Materials and Methods

The paper is all based on secondary information using the systematic review as defined by Zurynski (2014). The review involves identification of publications, focusing on those which are relevant to the thesis statement, critical appraisal of publications, analyses of data reported in publications being used and combining results from relevant publications.

The paper uses open source peer-reviewed publications specifically those which are related to phytoremediation studies. On the other hand, the paper has also used literature published in the including news articles to enrich discussions about the issues regarding the subject under assessment. Publication date was not considered a criterion.

Results and Discussion

Bagacay mine contaminants

According to MGB-MESD (2006), Bagacay mine contains enormous amounts of heavy metals. This includes As (6-693 ppm), Cu (9-5,279 ppm), Pb (22-354 ppm), Hg (1-5 ppm), Zn (<1-7,138 ppm) and Fe (5,900-373,500 ppm) with first five belonging to metals and metalloids commonly subjected to phytoremediation (phytoextraction) which uses hyperaccumulators (Ensley, 2000).

Phytoremediation

Phytoremediation was derived from the greek word “phyton” meaning “plant” and “remedium” meaning “to correct”. It is defined as any remediation method (e.g. phytoextraction, phytovolatization) that uses plants to mitigate pollutant concentrations and remove, degrade or extract toxic substances in contaminated environment (Arbaoui et al., 2013; Dickinson et al., 2009; Prasad et al., 2004; Salt et al., 1998). This green technology is being widely used in the present because of its overall cost effectiveness (Watanabe, 1997; Salt et al., 1998; Kabata-Pendias and Pendias, 2001). Although it is cost effective, phytoremediation carries with it some disadvantages which need to be considered when applying this technology as shown in Table 1.

Phytoextraction

Phytoextraction is a phytoremediation technique that uses pollutant accumulating plants. Such plants extract and translocate pollutants to its above ground parts. The plants concentrate the soil contaminants in their above ground biomass, so that the contaminant-enriched biomass can be properly disposed or harvested. It is the most difficult yet the most effective phytoremediation technique and works best with the use of hyperaccumulators (Kramer, 2005). It is mainly applied to metals like Cadmium (Cd), Nickel (Ni), Copper (Cu), Zinc (Zn) and Lead (Pb) but can also be used for other elements like Arsenic (As) and organic compounds (McGrath, 1998).

Non-essential heavy metals

The term ‘‘heavy metals’’ have been commonly refered to as the metallic elements with relatively high density and is toxic or poisonous even at low concentration (Lenntech Water Treatment and Air Purification, 2004) But, technically, heavy metals are those elements with molecular mass greater than 5.0 g/cm^3 (Sherameti and Varma, 2011). Heavy metals like iron (Fe), zinc (Zn), Copper (Cu), manganese (Mn), cobalt (Co) and molybdenum (Mo) are essential for growth of organisms with the first three present in the Bagacay mine. Other heavy metals like lead (Pb), mercury (Hg), cadmium (Cd), uranium (U), thallium (Tl), chromium (Cr) and silver (Ag), with first two present in Bagacay mine, are toxic to organisms and are therefore considered as “non-essential” heavy metals. Arsenic (As), which is also present in the area, and selenium (Se) are non-heavy metals. However, since they share toxicity features with heavy metals, these two elements are usually referred to as “metalloids” in some publications.

Arsenic

Arsenic (As) is a ubiquitous trace metalloid that can be derived from both anthropogenic and natural inputs. It is toxic and carcinogenic, which has caused severe environmental and health problem worldwide (Gonzaga et al., 2006). Arsenic concentration only lies below 10 ppm in a non-contaminated soil (Adriano, 1986; Matschullat, 2000) and can reach up to 30,000 ppm in a contaminated soil (Vaughan, 1993). Concentration higher than 40 ppm may pose a threat to human and is already critical for plant species like rice (*Oryza sativa*) (Sheppard, 1992; Dudka and Miller, 1999). Arsenic is commonly associated with ores (e.g. copper, lead and gold) and can be released during mining and smelting processes (Rathinasabapathi et al., 2006; Adriano, 2001).The most important arsenic ores are arsenical pyrite or arsenopyrite (FeAsS), Realgar (AsS), and Orpiment (As_2S_3) (Gonzaga et al., 2006). Although no study has been conducted in tracing its origin, it can be said that the most probable source of arsenic is the enormous amount of ores in the Bagacay Mine. Most parts of the site were also observed to be barren. Presence of arsenic in the area contributes to this situation. Arsenic, in its other oxidation state, can be a phosphate analog. Its chemical behavior is akin to that of phosphorus. In all of its studies so far, arsenate is transported via phosphate transport pathways (Asher and Reay, 1979; Lee, 1982; Meharg and Macnair, 1992). Arsenate is one of the two inorganic (arsenic combined with oxygen, chlorine, or sulfur) states of arsenic present in soil (Harper and Haswell, 1988).

Table 1. Advatages and limitations of phytoremediation (Laghlimi et al., 2015)

Advantages	Limitations
Cost	***Time***
– Low Capital and Operating Cost;	– Slower compared to other techniques and seasonally dependent;
– Metal Recycling provides further economic advantages.	– Hyperaccumulators tend to grow slow in actual operation.
Performance	
– Permanent treatment solution;	– Not capable of 100% reduction;
– Capable of remediating bioavailable fraction of contaminants;	– Very high contaminant concentration may be toxic to plants;
– Capable of mineralizing organics;	– Soil phytoremediation is applicable only to surface soils;
– Potential to treat site contaminated with more than one type of pollutant;	– Restricted to sites with low contaminant concentration;
– It is restricted to rooting depth of remediative plants;	– Requires technical strategy, expert project designers with field experience that choose the proper species and cultivars for particular metals and regions.
– Highly-specialized personnel is not required;	
– Can be used for site investigation or after closure.	
Application	
– *In situ* application avoids excavation and transport of polluted media;	– The presence of multiple types of heavy metals and organic contaminants may pose a challenge;
– Relatively easy to implement.	– Climatic conditions are limiting factor.
Environment and Population Impact	
– Reduce risk of spreading the contamination;	– Metals can be transported back to the soil due to decomposition;
– Eliminate secondary air or waterborne wastes;	– Use of invasive alien species can affect biodiversity;
– Public acceptance due to aesthetic reasons.	– Risk of food chain contamination in case of mismanagement and lack of proper care.

Arsenate prevails in aerobic conditions. Albeit, Pierce and Moore (1982) revealed that it is less toxic than the other species (Arsenite), its bioaccumulation disrupts phosphate metabolism in the event known as hydrolytic process which initiates by replacing phosphate with arsenate (Oremland and Stolz, 2003). Arsenite on the other hand causes indirect plant death. It reacts with enzymes and plant tissue proteins which inhibits its function (Meharg and Whitaker, 2002; Leonard and Lauwerys, 1980). It also induces intrachromosomal homologous recombination

(Helleday et al., 2000) and generates reactive oxygen species (Chou et al., 2004). United States Environmental Protection Agency (USEPA) regarded these inorganic arsenic (Arsenate and Arsenite) as major environmental pollutant based on their evaluation (USEPA, 2001; Johnson and Derosa, 1995). Extraction of this metalloid increases the feasibility of revegetating the area. For now, remediation technologies for removal of arsenic in the area are expensive. Thus, the use of phytoextraction has become an option for its rehabilitation.

Lead

Lead (Pb) is an extremely persistent anthropogenic heavy metal that accumulates in soils, sediments, and water (Traunfeld and Clement, 2001; Sharma and Dubey, 2005). It has no biological function and it is toxic to living organisms even at low concentrations (Antosiewicz 1992; Xiong 1998; Fahr et Al, 2013). Lead uptake affects plant processes. Photosynthesis was found to be most affected by lead contamination (Singh et al., 1997). Mining contributes to the presence of high Pb levels in an area (Mukai, et al., 2001; Sharma and Dubey, 2005) and this will never return to normal without remedial action (Traunfeld and Clement, 2001). The remediation of lead affected areas are carried out by narrow range of technologies (Salt et al., 1995). Among these technologies, phytoremediation provides better hopes for the clean-up of lead contaminated soils (Hussain et al., 2013).

Mercury

Mercury (Hg) was known for the Minamata incident (1950). It caused 2,265 casualties just because of their direct exposure to the heavy metal (Zahir et al., 2005). It has been a priority toxic substance in many countries (Gaudet et al., 1995). Its high solubility in water and easy shift to gaseous phase (Clarkson and Magos, 2006) aggravates its ability to spread and remain in an area (Yang et al., 2008). Among metals, Hg is unique being the only one to exist in a volatile liquid form, in room temperature. Its liquid form releases a monoatomic gas commonly referred to as Hg vapour. This species plays a vital role in the global heavy metal cycle for it can exist as a cation with an oxidation state of Hg^{+} (mercurous) and Hg^{2+} (mercuric) (Boening, 2000; Clarkson and Magos, 2006). Among the two, mercuric is a more pervasive cation since it is formed from vapour Hg and from organic compunds of Hg. This properties made Hg^{2+} a keystone in Hg cycle and the in the toxicology of this heavy metal in living organisms.

Phytotoxicity of Hg can be through alteration of cell membrane permeability , high affinity to react with the sulphydryl (SH) groups, affinity for reacting with phosphate groups, and the replacement of essential ions and its ability to disrupt functions involving critical or non-protected proteins (Patra and Sharma, 2000; Patra et al., 2004). It is also known to interrupt antioxidant defense system by modulating enzymatic and non-enzymatic antioxidants (Sparks, 2005; Villasante et al., 2005; Israr et al., 2006). According to Boening (1999), Hg exposure can also reduce photosynthesis, transpiration rate, water uptake, chlorophyll synthesis and can cause loss of potassium, magnesium, manganese , which explains the changes in cell membrane permeability (Azevedo and Rodriguez, 2012), and accumulation of iron.

Metallophytes in the tropics

Each plant species has a specific threshold value for each heavy metal it absorbs (Ernst, 1982). Plants specifically adapted to life on heavy metal-rich soils (“heavy metal soils”) are termed metallophytes. Metallophytes exhibit phytoremediation techniques to survive. For a high chance of success in any phytoremediation activity, metallophytes that will be used should be well adapted to the climate in the area. Thus, metallophytes to be used in the Bagacay mine should be tropical species.

Ferns

There were promising reports about these species. *Pteris vittata (Pteridaceae)*, one species of fern, is tolerant of soil conditions with up to 1,500 ppm of arsenic and can efficiently translocate the heavy metal from roots to fronds (Ma et al., 2001). Using phytoextraction, it extracts a pollutant from a surrounding area and accumulates it in a harvestable part of a plant (Blake, 2006). *Pteris vittata* is unique as an effective hypperaccumulator. It is versatile, resilient, grows rapidly with large biomass, and is perennial in nature. And like other hypperaccumulators, this fern has an efficient root uptake system, efficient root to shoot translocation, and much-enhanced tolerance to arsenic inside plant cells (Wang et al., 2002). Aside from *Pteris vittata*, other *Pteris* species like *Pteris cretica, Pteris longifolia, Pteris umbrosa, Pteris multifada,* and *Pteris oshimensis* are also capable hypperaccumulators. (Zhao et al., 2002; Wang et al., 2006).

Another species of fern that has been studied thoroughly in the field of green remediation is the

Athyrium wardii (*Woodsiaceae*), a perennial plant that grows in fascicles. These fern also has suitable features for phytostabilization because of its well-developed root system, high biomass, and ability to maintain high content of Pb in its root tissue (Zou et al., 2010). Unlike the *Pteris vitatta*, *A. wardii* uses the method of phytostabilization. Phytostabilization is a type of phytoremediation were the metals are sequestered in the roots and rhizosphere (Mendez and Maier, 2008). According to Zou et al. (2010), they were able to identify a Mining Ecotype (ME) of *A. wardii* species growing in Lead-Zinc Mine tailings in Sichuan Province of China and was able to accumulate as much as 15, 542 ppm of lead in its roots. Further, selection of the ME *A. wardii* should be considered because study revealed that the response of ME was quite different from the Non-mining Ecotype of this species. ME showed less decline in biomass and less damage when subjected to Pb stress (Zou et al., 2010).

Indian Mustard

Several *Brassica (Brassicaceae)* species were already evaluated as potential phytoextracting plants (Van Ginneken et al., 2007; Gall and Rajakaruna, 2013). The Indian Mustard (Brassica juncea), a non-hyperaccumulating species for extracting heavy metals belongs to this genus. Among non-hyperaccumulating crops with high shoot dry matter yields, the Indian Mustard was identified as a species able to accumulate Cd, Cu, Ni, Zn, Pb and Se in its above-ground parts (Haag-Kerwer et al., 1999). It is tolerant to heavy metals, fast growing and produces relatively large amount of above-ground biomass. These characters made these species a target for phytoremediation potential studies (Bhuiyan et al., 2011). Being cultivated mainly for its oil, its use in removing the heavy metals in the mine can be a good solution to bring back the economic value of the area (Witters et al., 2012).

Vetiver

Vetiver (*Chrysopogon zizanioides*) grass is known for its effectiveness in erosion control. Discovering that vetiver can tolerate extreme climatic and soil conditions, to include heavy metals (Troung, 1996; Troung and Baker, 1998; Zheng et al., 1998; Roongtanakiat and Chairoj, 2001), many studies on the use of vetiver in phytoremediation occured. Later, it was discovered that vetiver is a non-hyperaccumulator (Greenfield, 2002; Roongtanakiat, 2006). In the study of Alves et al. (2016), vetiver showed dry matter production at Lead (Pb) concentrations higher than 350 ppm.

Conclusion

Phytoremediation does not just answer the problem of the abandoned bagacay mine but also solves the current mining problems being faced by the nation. Thus, intensive research for each tropical metallophytes should be conducted. Although the paper focused on the available tropical species for removing non-essential heavy metals in the area for it to be considered in the next phytoremediation activities to be done, it was not able to provide a metallophyte for the removal of mercury (Hg). To date, mercury (Hg) accumulators and hyperaccumulators are still to be discovered. Further, extracting the excessive amount of essential heavy metals in the area should be studied.

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