THESIS

WARM SEASON TURFGRASSES AS POTENTIAL CANDIDATES TO PHYTOREMEDIATE ARSENIC POLLUTANTS AT OBUASI GOLDMINE IN GHANA

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In partial fulfillment of the requirements

For the Degree of Master of Science

Colorado State University

Fort Collins, Colorado

Summer 2012

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ABSTRACT

WARM SEASON TURFGRASSES AS POTENTIAL CANDIDATES TO PHYTOREMEDIATE ARSENIC POLLUTANTS AT OBUASI GOLDMINE IN GHANA

Ghana, originally known as the Gold Coast prior to March 6, 1957, has generally had a very long history of gold mining dating back over 1000 years. Gold is one of the largest contributors to the economy, including cocoa (Gavin, 2002), accounting for about 38% of total merchandise and 95% of total mineral exports as well as about 80% of all mineral revenue.

Arsenic enters the environment from a variety of sources associated with gold mining, including waste soil and rocks, tailings, atmospheric emissions from ore roasting, and bacterially enhanced leaching. The combination of opencast mining by multi-national mining companies and heap leaching generates large quantities of waste soil and rock (overburden) and residual water from ore concentrations (tailings) into various water bodies in and around Obuasi. Arsenic constitutes the major trace element problem in the Obuasi area. Extremely high concentrations of this element have been observed in ponds (2250µg/L (USEPA)) and drinking water (1400µg/L). These high levels are far above recommended United States Environmental Protection Agency's (USEPA) drinking water guideline of 10µg/L for Arsenic. At least 10% of rural populations rely on Ghana's borehole wells that have Arsenic concentrations exceeding 10µg/L (USEPA).

The basic idea that plants can be used for environmental remediation is very old and cannot be traced to any particular source. However, a series of scientific discoveries combined with an interdisciplinary research approaches have allowed the development of this idea into a promising, cost-effective, and environmentally friendly technology (Pilon-Smits, 2005). This

paper reviews the physiological characteristics of five selected native turfgrasses and one exotic grass found in Ghana and their ability to phytoremediate arsenic pollutants at Obuasi mines.

ACKNOWLEDGEMENTS

I would like to thank Dr. Yaling Qian, my advisor, for the wonderful help and guidance she provided over the course of this project. I would also like to thank Dr. E. Pilon-Smits and Dr. Tony Koski, my committee members and all the members of the Turf Lab especially Sarah Wilhelm for their help, patience and good humor, all of which were invaluable to me throughout this process.

Special thanks to my mom, family and friends for their support, especially Esther and my two wonderful daughters, Akua Boatemaa and Akua Frimpomaa who were and are always ready to provide encouragement, support and much needed laughter.

And to all professors at CSU, I say you guys rock- your classroom instructions were excellent!!!

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CHAPTER 1: INTRODUCTION AND BACKGROUND

1.1 Introduction

"In the country of Ghana gold grows in the sand as carrots do, and is plucked at sunrise" Ibn al-Faqih, C. 900

For centuries, West Africa has been one of the world's most important gold mining regions. Some two billion years ago, following a series of tectonic processes, vast portions of Western Africa folded, faulted, metamorphosed, and were subjected to igneous activity and sedimentary processes, giving rise the region's Birimian and Tarkwaian gold belts (Lunt et al., 1995). Episodes of erosion spanning millions of years led to a re-deposition and reconfiguration of gold-aggregated ores; the resulting gold deposits ranging in complexity and form are suitable for both large- and small-scale mining. As indicated in Fig. 1, one-third of Ghana's landmass has abundant gold deposits. There has been considerable growth in the number of exploration companies ever since gold was discovered under British occupation to the present.

Arsenic contamination of the biosphere from various gold mining and refining operations jeopardize the health and well-being of biological communities. Gold-bearing ores worldwide contain variable quantities of sulfide and arsenic compounds that interfere with efficient gold extraction using current cyanidation technology. Arsenic occurs in many types of gold ore deposits, mainly as arsenopyrite (FeAsS), niccolite (NiAs), cobaltite (CoAsS), tennantite (Cu,Fe)12As4S13], enargite (Cu3AsS4), orpiment (As2S3), and realgar (AsS) (Azcue et al. 1994). Some gold-containing ores in Columbia, South America, and Ghana contain up to 32% of arsenic-bearing minerals, and surrounding sediments may hold up to and as much as 6300 mg As/kg DW (Grosser et al. 1994). In France, a high incidence of neoplasm of the respiratory system among gold extraction and refinery workers was first reported in 1977 and again in 1985, and this appears related to occupational exposure (Simonato et al. 1994).

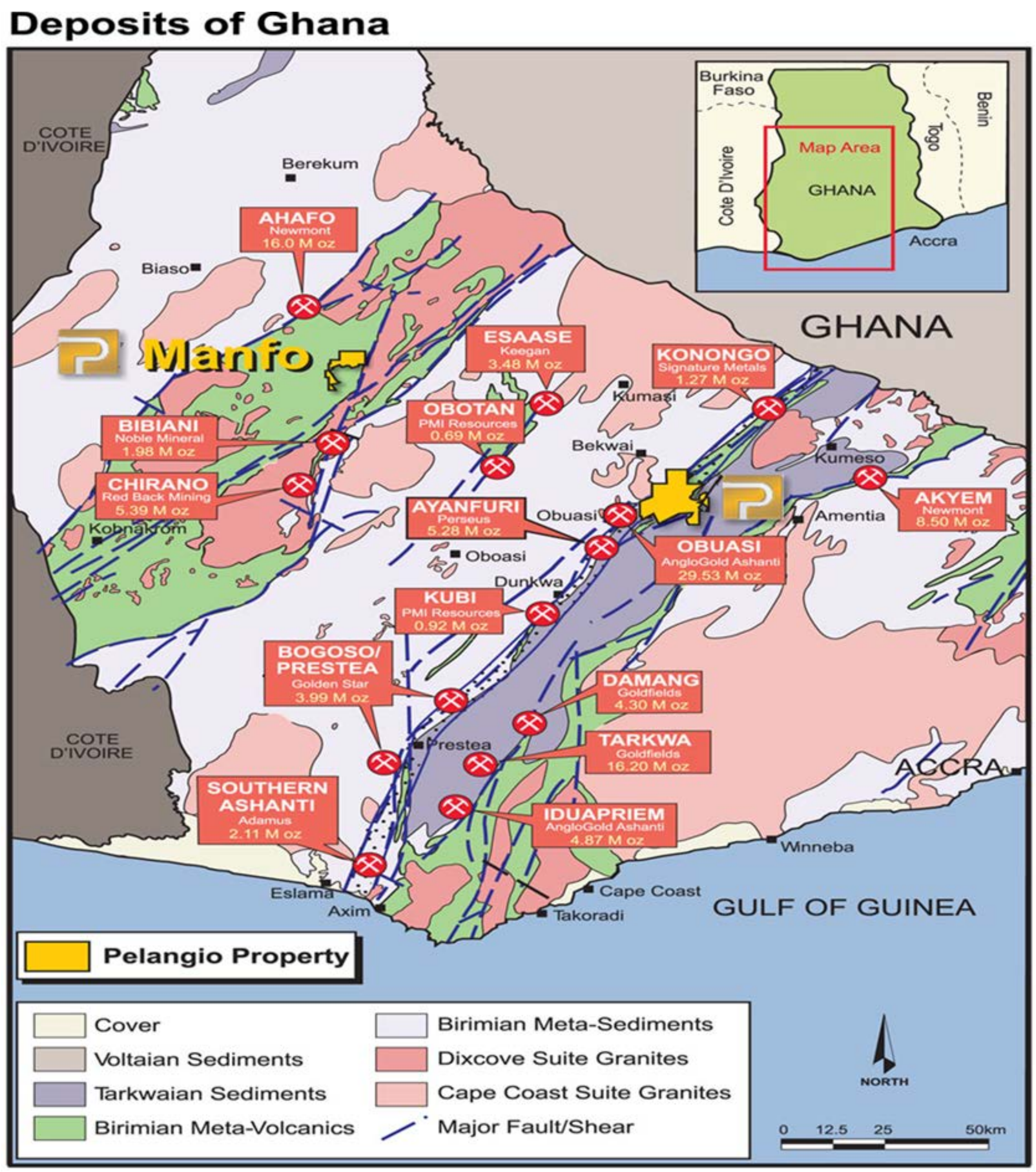

Fig 1: Shown above, one-third of Ghana's landmass is occupied by gold deposits

Mine and smelter workers at this site were twice more likely to die of lung cancer than the general population. The lung cancer excess was strongly associated with exposure to soluble and insoluble forms of arsenic (Simonato et al. 1994). In Zimbabwe, arsenic exposure was implicated in lung cancer increase of gold miners (Boffetta et al. 1994).

The purpose of this paper is to review morphological and physiological characteristics of five selected adapted turfgrasses and one exotic grass, to determine if amendments or use of metal chelators could enhance arsenic uptake by selected species as potential candidates for arsenic phytoremediation, and review effective methods to dispose of arsenic sequestered grass clippings. Most of this review focuses on the phytoremediation of the arsenic pollutants in soil, particularly in the area of metal phytoextraction, which, arguably, is the focus of major scientific and technological progress in the past several years. This review is relevant for the following reasons:

1. Due to their extensive root system turfgrasses may have the potential to remediate and stabilize minewaste lands. They also have high recuperative capacity
2. Most research work carried out in Ghana, on minetailings is based on rock formations, or effects of Arsenic pollution on rural populations and risk assessments to the environment (Smedley et al, 1996, Golow et al, 1996, Amonoo-Niezar et al, 1995).
3. No research work has been carried out on either phytoremediation using native species or any other plant species in Ghana.

1.1The Obuasi Goldmine

Ghana, known as the Gold Coast during British occupation, has a long history of mining going back many years. The country is well endowed with substantial mineral resources, primarily gold, diamonds, manganese, and bauxite. Obuasi, the capital of the Adansi West Municipality is located on latitude 6.19° N and longitude 1.66° W. It is about 57 km south of Kumasi in the Ashanti Region and about 270 km north-west of Accra the capital city of Ghana as shown in Figure 2. . The area lies in the tropical rainforest belt of southern Ghana. It receives a high annual rainfall of 1785mm, pronounced wet season from March to July and October to November and temperature range of 20^{O} to 30^{O}C. Evapotranspiration is high (ca 1200 mm/yr.), however rainfall exceeds evapotranspiration for about 8 months of the year. Much of the area is comprised of natural forest, but parts have been cleared for agricultural and mining activities. Obuasi is accessible by rail, and by road from all major southern cities and towns in Ghana. Gold mining at Obuasi in Ghana dates back to over five centuries and remains one of the oldest viable mines on the continent of Africa. This long history of mining at Obuasi has generated huge environmental issues in the area. Perhaps, the most significant of the environmental challenges is that of trace element contamination including Arsenic and Mercury.

Arsenic constitutes the major trace element problem in the Obuasi area. Extremely high (maximum) concentrations of this element have been observed in ponds (2250 μg/L) and drinking water (1400μg/L). These high levels are far above recommended United States Environmental Protection Agency's (USEPA) drinking water guideline of 10μg/L for Arsenic. At least 10% of the borehole wells in Ghana's rural regions have arsenic concentrations exceeding 10μg/L. This has been linked to the considerable level of naturally occurring arsenic at Obuasi, as well as liberations from arsenic bearing gold ores during extraction processes. The decision made by the Ghanaian government to gloss over regulatory issues, or lift the embargo on applications submitted by multi-national mining corporations to mine in forest reserves has exacerbated tensions between the authorities, miners, indigenous groups and global environmental watchdog groups.

Fig 2: Map of Ghana Showing location of Obuasi

It is believed that between 1947 and 1992 effluents were discharged without precaution or regulatory oversights, resulting in serious environmental degradation issues. Despite these environmental challenges, the country cannot divulge itself from revenues that accrue from gold.

The mine has undergone extensive expansion and modernization in the last three decades resulting in several open pit mines, underground mining operations and large area depositions of minewastes as shown in Fig 3. Even though there are open pit mines, Obuasi is primarily an underground mine operating at depths up to 1500 meters (equivalent to 1 mile) There are three treatment plants: a sulphide plant treats the ore from underground, a tailings plant which treats the material from the reclamation operations, and an oxide plant batch, that treats remnant open-pit ore and low-grade stockpiles.

Fig 3: Minetailings pond (slurry dam) at Obuasi

1.1.1 Gold Production Methods

Ghana presently has two types of gold mines: small-scale and large-scale. Small-scale miners are primarily self-employed indigenous youth, with little financial backing and limited mining expertise. Within the small-scale sector is a form of illegal mining activity known locally as “galamsey”, a slang coiled from ‘gather them and sell’ or the practice of discreetly gathering ‘gold-rock fragments’ or minerals found either at or just below the soil surface and selling them in contravention to the country's environmental laws. The large scale mines are generally operated by multi-national and foreign owned, companies whose operations are large both in physical size and capacity, utilizing heavy equipment and the latest mining technology. Large-scale mines are estimated to employ 20,000 people in the country. For over 100 years of its existence with open cast method and later mechanical that Ashanti has been mining in Obuasi, it's activities would be classified as a small to medium sized high grade underground mine with the quartz-rich ore extracted from steeply dipping shear structures. The underground operations were initially labor intensive. The company used cut-and-fill as the predominant mining method with hoisting and processing capacity being the main limitations to production levels. In 1946, Goldfields of South Africa constructed the Pompora Treatment Plant (PTP), employing Edwards Roasters to treat the highly refractory arsenopyrite sulphides which in those days constituted some 20 per cent of the feed. This plant went through a number of upgrades, the latest in 1997 which increased output to 150,000 tons per month comprising 80 per cent sulphide material. Following the implementation of the 1986 Minerals and Mining Law in Ghana, designed to encourage foreign investment, Ashanti was able to embark on a series of projects refitting and modernizing that have enabled it to grow to the group operation it is today, with 6 operating mines, producing 1.3 million ounces per annum. Currently the range of mining methods employed across the mine includes mechanized open stoping (accounting for 60% of total mine ore production), sub-level retreat and reclamation (accounting for 20% of total mine ore production), mechanized cut and fill (accounting for 5% of total mine ore production), and stope preparation (accounting for 15% of total mine ore production).

The gold is found in two main ore types:

• Quartz veins which consist mainly of quartz with free gold in association with lesser amounts of generally minor amounts of iron, zinc, lead and copper sulphides. The gold particles are generally fine grained and occasionally are visible to the naked eye. This ore type is generally non-refractory;

• Sulphide ore which is characterized by very fine gold occurring as inclusion in the crystal structure of a sulphide, generally arsenopyrite. Higher gold grades tend to be associated with finer grained arsenopyrite. Other prominent minerals include quartz, chlorite and sericite. Sulphide ore is generally refractory.

1.2 Arsenic Pollution

Even though AngloGold has tried in recent years to reduce Arsenic pollution with efficient gold extraction methods using current cyanidation technology, and conducted environmental impact assessment studies and landscape functional analysis projects, the problems still exist since arsenic, as an inorganic element enters the environment from a variety of sources associated with gold mining, including waste soil and rocks, tailings, atmospheric emissions from ore roasting, and bacterially enhanced leaching. The combination of opencast mining and heap leaching by multi-national mining companies generate large quantities of waste soil and rock (overburden) and residual water from ore concentrations (tailings). The wastes, especially the tailings, are rich sources of arsenic, and some of these ore concentrations (tailings) have been exposed to the environment for more than 50 years.

Arsenic toxicity has become a global concern owing to the ever increasing contamination of water, soil and crops in many regions of the world. Arsenic forms inorganic and organic complexes in the environment, but the two biologically important species are As (V) and As

(III), which are incontrovertible depending on redox status of the environment. Arsenic, with atomic number 33, and situated in Group 15 (or VA) of the periodic table, may exist in four different oxidation states: (-III), (0), (III), and (V), however, oxidized As (III) and As (V) are the most widespread forms in nature. The gold bearing rocks at Obuasi are found largely in association with arsenopyrites and pyrite and mining operations have resulted in significant localized surface water and atmospheric Arsenic pollution. Soils above the mineralized zones often have high Arsenic concentrations, with values between 189 and 1025 mg kg-1 (Bowel et al. 1994). Arsenopyrite is largely restricted to the auriferous belt, but pyrite is commonly recorded in borehole logs throughout the Birimian strata in the Obuasi study area. In arsenic speciation study carried out at Obuasi on dumped minetailings as shown in Fig 2 and 3 showed a concentration of 3050 mg kg-1 As (III) and 6800 mg kg-1 As (V) (Ahmad and Carbo, 2000). Arsenic is ubiquitous in the environment, and is derived from both natural and anthropogenic sources (Junru Wang et al 2002). Arsenic (As) is a nonessential element for plants and its inorganic species are generally highly phytotoxic. Arsenate is the predominant as species in aerobic soils, whereas arsenite dominates under anaerobic conditions (Smith et al., 1998). Arsenate acts as a phosphate analog and can disrupt phosphate metabolism in plants, whereas arsenite reacts with sulfhydryl groups of enzymes and tissue proteins, leading to inhibition of cellular function and death (Meharg and Hartley-Whitaker, 2002).

Mining activities generate a large amount of waste rock and tailings which are deposited on land surface, shown in Fig 4. The land surface becomes damaged and these waste rocks and tailings are often unstable and become sources of pollution. Mined degraded soils are man-made habitats which experience a wide range of problems for establishing and maintaining vegetation.

Fig 4: Minetailings deposits shown by the greyscale arrow in the soil profile is more than 50 years old

The physico-chemical properties of the metal-contaminated soils tend to inhibit soil-forming processes and plant growth, and there is lack of organic matter and its associated nutrients (Wong, 2003).

Arsenic in drinking water is increasingly becoming recognized as a potential health hazard for rural communities in developing countries. High As concentrations have been found in groundwater sources which provide drinking water for millions of people in parts of South America, Mexico, China, Taiwan, India and Bangladesh (Tseng et al., 1968; Nicolle et al., 1989; Cebridn et al., 1994; Chen et al., 1994) (Figure 5).

Arsenic is a recognized toxin and carcinogen. Health problems are most commonly manifested as skin disorders(pigmentation disorders, keratosis, skin cancer), but many other cardiovascular, neurological, hematological, renal and respiratory disorders, as well as lung, bladder, liver, kidney and prostate cancers have been reported (Smith et al., 1992; Morton and

Dunette, 1994). Useful plant species can be exploited to extract, stabilize, or filter as from contaminated soil and water. However, it is becoming apparent that these plant species should be adapted to local environmental conditions (Kra¨mer 2005) and accumulate relatively high tissue concentrations of As (Pivetz, 2001) for phytoremediation to be successfully employed.

Fig.5 Distribution of documented world problems with As in groundwater in major aquifers as well as water and environmental problems related to mining and geothermal sources. Areas in blue are lakes. (Adapted: from Smedley and Kinniburgh, 2002).

1.3 Phytoremediation as a means to reduce arsenic pollution

Phytoremediation, the science of using plants and associated microbes to remediate pollution is a very viable solution. This science is easily embraced by local communities, cheap to implement, and yields or plants can be harvested and metals extracted to help restore agricultural lands to the community; thereby reducing social tensions between locals and multi-national companies.

As previously emphasized, useful plant species may be exploited to extract, stabilize, or filter arsenic from contaminated soil and water and accumulate relatively high tissue concentrations of arsenic (Pivetz, 2001) for phytoremediation to be successfully employed. The basic idea that plants can be used for environmental remediation is very old and cannot be traced to any particular source. However, a series of scientific discoveries combined with an interdisciplinary research approach have allowed the development of this idea into a promising, cost-effective, and environmentally friendly technology (Pilon-Smits, 2005). Phytoremediation can be applied to both organic and inorganic pollutants, present in solid substrates (e.g. soil), liquid substrates (e.g. water), and the air. The term 'hyperacccumulator' is a term for plants that actively take up exceeding large amounts of one or more heavy metals from the soil. Moreover, the heavy metals are not retained in roots but are translocated to the shoot and accumulated in above ground organs, especially leaves, at concentrations100-1000-fold higher than those found in non-hyperaccumulating. They show no signs of phytotoxicity (Nicoletta Rascio, 2010). They are equally hypertolerant also. About 450 angiosperm species have been identified so far as heavy metal hyperaccumulators, accounting for less than 0.2% of all known species. New reports of these kinds of plants continue to accrue so that it is conceivable many yet unidentified hyperaccumulators may occur in nature. Phytoremediation is currently divided into the following areas:

1. Phytodegradation: the use of plants and associated microorganisms to degrade organic pollutants.
2. Rhizofiltration: the use of plant roots to absorb and adsorb pollutants, mainly metals, from water and aqueous waste streams.

3. Phytostabilization: the use of plants to reduce the bioavailability of pollutants in the environment.

   Phytovolatilization: the use of plants to volatilize pollutants; and the use of plants to remove pollutants from air. The use of native or adapted species as candidates to phytoremediate is a win-win situation both in terms of functionality and aesthetic appeal.

Turfgrasses have been utilized by humans to enhance their environment for more than 10 centuries. The complexity and comprehensiveness of these environmental benefits that improve our quality-of-life are now being quantitatively documented through research (Beard et al: 1994) Grasses have been suggested as effective plants for phytoremediating organic and inorganic contaminants (Schwab et al 1994). Grasses have fibrous root systems, resulting in large root length and surface area per unit volume of surface soil and the fibrous roots would provide a larger surface area for colonization by microorganisms than a taproot plant and would also allow greater interaction between rhizosphere microbial community and the contaminant.

The mining locality is in the tropical rain forest region of Ghana that is characterized by long rainy periods from March to August. The rainy season (loosely called summer) peaks between June and July, averaging 1785 mm per year. This is followed by brief periods of dryness with occasional rain from September to November. The average yearly rainfall is about 1192 mm. The region is associated with moderate average temperatures ranging between 25 ºC (minimum) and 34.5 ºC (maximum). As a result of this favorable climate, various species of warm season turfgrasses thrive very well at Obuasi. At the minetailings site, grasses like *Cynodon dactylon*- Bermudagrass, *Stenotaphrum secundatum*-St Augustinegrass, *Axonopus affinis*-Carpetgrass and *Zoysia japonica*- Zoysiagrass are found loosely growing very well there. As a check to limit environmental degradation and remediate arsenic pollution, phytoremediation technology using these native turfgrass species may be one of the options to remove contaminants to restore the environmental health to these areas.

CHAPTER 2: SIGNIFICANCE OF TURFGRASSES

2.1 Turfgrass:

Turfgrass may be defined as grass species or cultivar maintained as a uniform mowed vegetation or a collection of grass plants that form a ground cover.

The Poaceae is the most ubiquitous of the higher plant groups found on this earth (Gould, 1968). With an estimated 600 genera and 7,500 species, the Poaceae ranks the third with respect to completeness of representation in all regions of the world and to the percentage of the world's total vegetation. Grasses are one of the first vegetation to reappear after disasters, such as volcanic activity, extended droughts, floods, fires, explosions, abandoned urban ghettos, and battlefields. Without the forgiveness of the Poaceae, many ill-advised construction excavations and certain agricultural activities would have had far more disastrous effect on one of our most vital natural resources, 'the earth's surface soil mantle', on which terrestrial plants and animals live. Economically, Poaceae are by far the most valuable of all plant families. They are also ecologically important, dominating several of the natural and artificial landscapes of the world (Bremer, 2002).

To the botanist, grass is a member of the family Poaceae. To the plant physiologist, grass is effective in removing or reducing contamination caused by pollutants. To humans, grasses are the most important of all plants. The cereal grains and corn (*Zea mays* L.), all members of the grass family, serve as food for humans and animals (Beard, 1973). A host of grazing ruminant animals use grasses as their major food source as forage, pasture, and prepared feeds. Bamboo (*Bambusa spp*., *Dendrocalamus spp*., and *Phyllostachys spp*.) is a major building material. Also, grasses of all types represent a large source of biomass for production of methanol, an alternate energy source. Greenhouse and field trials in Australia have shown that vetiver grass is suitable for the rehabilitation of metal contaminated soils and for the treatment of landfill leachate (Truong, 2002).

Despite the fact that the turf industry has blossomed in the United States with milestones in academic and research programs and a rich turf industry history dating over a century ago, with splendid research institutions spanning across the country (Shearman, 2006). Research work on turfgrasses in most sub-Saharan African countries is still lacking. Selection of appropriate plant species would be very important to ensure a self-sustainable turfgrass systems. Turfgrasses that have been researched and known to stabilize soils are *Cynodon dactylon* (Wong, 2003), *Stenotaphrum secundatum*, and a host of others (White et al, 2006). Useful plant species can be exploited to extract, stabilize, or filter arsenic from contaminated soil and water. However, it is becoming apparent that these plant species should be adapted to local environmental conditions (Kra¨mer, 2005) and accumulate relatively high tissue concentrations of arsenic (Pivetz, 2001) for phytoremediation to be successfully employed.

The effectiveness of turfgrasses for surface soil stabilization is the combined result of a high shoot and root density, and high biomass matrix that provides resistance to lateral surface water flow, thus slowing otherwise potentially erosive water velocities. Perennial turfgrasses offer one of the most cost-efficient methods to control water, wind erosion, and soil stabilization.

Such control is very important in eliminating dust and mud problems around homes, factories, schools, and businesses. When this major erosion control benefit is combined with the groundwater recharge, organic chemical decomposition, and inorganic chemical stabilization; the resultant relatively stable turfgrass ecosystem is quite effective in soil and water preservation.

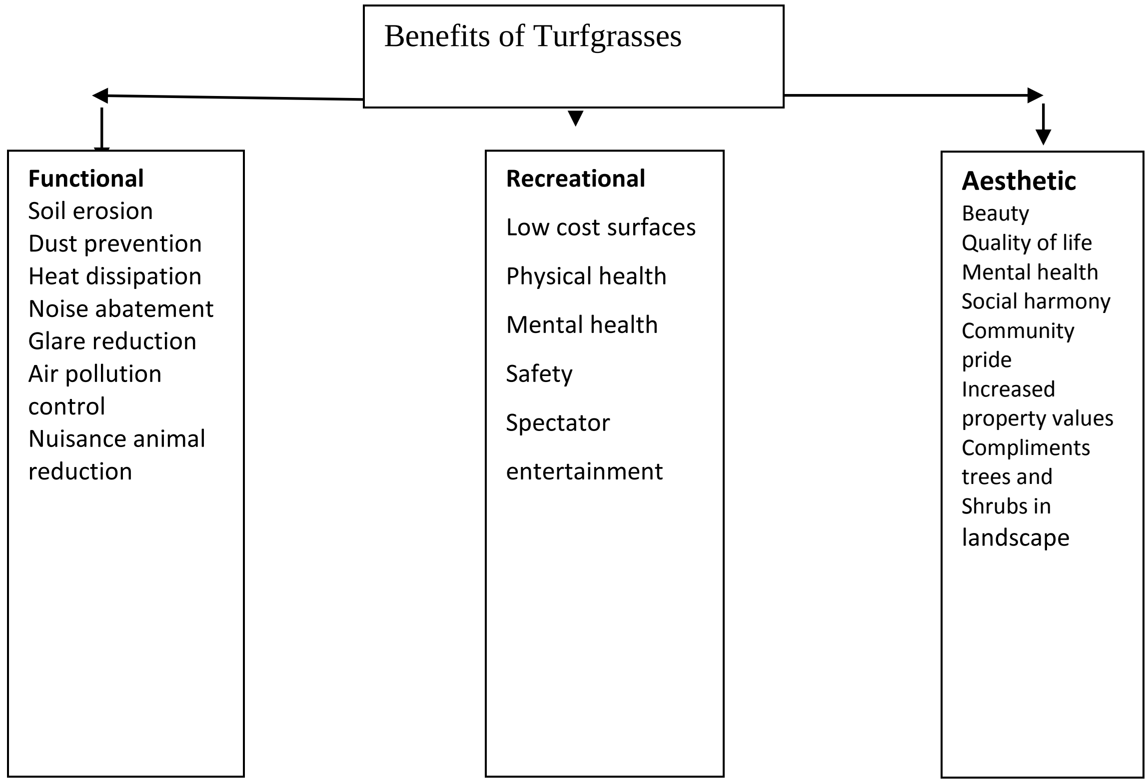

Fig 6: Turfgrasses have functional, recreational and aesthetic benefits. Enumerated in the boxes are some of the stand- out benefits turfgrasses provide

It is significant to note that large populations of diverse soil microflora and microfauna are supported by this same soil-turfgrass ecosystem. These organisms which constitute the largest proportion of biomass decomposer of most soils are able to decompose organic carbon compounds such as grease and fuels, household and industrial hazardous waste oils, paint thinners, organic preservations, and solvents. Fig 6 above shows the benefits of turfgrasses.

2.2 Knowledge Gap

Grasses (Poaceae) are by far the most valuable of all plant families. They are also ecologically important, dominating several of the natural and managed landscapes of the world (Bremer, 2002). The evolutionary history of grasses is complex because of the high level of polymorphism within the family in terms of metabolic pathways, geographical distribution and morphological structure. The origin of the grasses has been dated at c. 75 million years ago (Mya) using the molecular dating method known as nonparametric rate smoothing (Bouchenak-Khelladi et al, 2010). Even though the grass family has been in existence for so many years, plant and turfgrass scientists have made little attempts to reconstruct the biogeographical history of grasses and their ability to phytoremediate both organic and inorganic pollutants. To make phytoremediation work efficiently, a screening study may be performed to identify most suitable varieties of turfgrasses including how agronomic practices could be optimized to maximize biomass production for contaminant uptake. It is interesting to notice that, there are some plants especially grasses that survive, grow and reproduce on natural metalliferous soils as well as on sites polluted with metals as a result of anthropogenic activities. The majority of these species that tolerate heavy metal concentrations that are highly toxic to other plants behave as ‘excluders’. Hyperaccumulator species are distributed in a wide range of distantly related families showing that the hyperacccumulator trait has evolved independently more than once under the spur of selective ecological factors. Compared to trees and shrubs, herbaceous plants especially grasses have characteristics of rapid growth, large biomass (due to sheer numbers of individual plants), strong recuperative ability and effective stabilization of soils and, therefore usually result in excellent restoration effects in degraded and mined lands, particularly in the tropics and subtropics with high precipitation and temperatures. A host of grasses in the family Gramineae and Cyperaceae like vetiver, clover, rye grass, bermudagrass, switchgrass, ryegrass and tall fescue etc. have all shown promising results as natural hyperaccumulators in some few studies. Planting perennial grasses could easily be developed as an economic phytoextraction technique because of their low input requirements and they do not require replanting every year. Ideal species for phytoremediation are Brassiaceae - in the genera Brassica, Alyssum and Thalapsi: Salicaceae –particularly Willow and Poplar trees. Plant surveys have produced a promising list of natural hyperaccumulators that are able to colonize mine tailings, but few turfgrasses have been examined to evaluate their potential to phytoremediate pollutants.

2.3 Native/Introduced Turfgrasses in Ghana

The ancient history of our modern grass species may seem irrelevant in this age with high-performance hybrids, test-tube cultivars and genetic engineered varieties. It is wise to remember, however, that nature has had a head start of many millions of years in which to influence the characteristics of these grasses on today's golf courses, homes and public playgrounds. The modern turfgrass industry has grown rapidly in the past three decades. For example, it contributes substantially to the United States national economy, with numerous employment opportunities. However, virtually all turfgrass cultivated in Ghana or West Africa originated from somewhere else except bermudagrass. Turfgrass germplasm and species development are still lacking in Ghana, Nine (9) turfgrass species (Table 1) and a host of unnamed grass species were profusely spread, and most Ghanaians considered them as weed or turf depending on economic status, social status or education.

It is difficult to classify grasses in Ghana as native, adapted or introduced. It is believed that all species were introduced from the grasslands of East Africa.

Turfgrasses in Ghana		
Ghana Bermudagrass (*Cynodon dactylon*)	St Augustinegrass (*Stenotaphrum secundatum*)	Zoysiagrass (*Zoysia japonica*)
Carpetgrass (*Axonopus affinis*)	Centipede grass (*Eremochloa ophiuroides*)	Buffalograss (*Buchloe dactyloides*)
Golden falsegrass (*Chrysopogon acciculatus*)	African Foxtail grass (*Cenchrus ciliaris*)	Kikuyu grass (*Pennisetum clandestinum*)

Fig 7: Some known turfgrasses and nonturfgrasses found in Ghana

CHAPTER 3: PHYTOREMEDIATION

3.1 Relevance of Phytoremediation in Ghana

Phytoremediation is a promising new technology that uses plants (Fig 8) to degrade, assimilate, metabolize, stabilize or detoxify metals, hydrocarbons, pesticides, and chlorinated solvents. In short, it is a means of cleaning up polluted soils and has gained popularity during the last decade due to its convenience and low cost of installation, maintenance and management. It is also widely considered to be not only an innovative but also an economical and environmentally compatible solution to many engineering and environmental issues across the world. Heavy metal contamination in soils is an increasingly urgent problem throughout the world, and the clean-up of these soils is expensive, costs time and it is very difficult to undertake. Unlike organic contaminants, heavy metals are generally immutable, not degradable and are persistent in soils. Soils on the other hand have a natural capacity to attenuate the bioavailability and movement of heavy metals through them by means of different mechanisms such as precipitation, adsorption, and redox reactions. However when the concentrations of these heavy metals become too high to go through natural attenuation processes as indicated above, the metals become immobilized, resulting in serious contamination of the environment. Currently there is an increase in world population, and unpleasant disposal of industrial effluents, especially in the developing countries, causing soil pollution. Utilization of these lands for agricultural purposes and urban development requires a safe and efficient decontamination process. Various physical and chemical techniques to decontaminate soils like vitrification, landfilling, chemical treatment and electrokinetics have been undertaken during the last 25 years, costing millions of dollars by governments all over the world. However, all of them are labor intensive, costly, and have potential environmental impacts with particular regard to the modification of landscape and soil agronomic properties. Moreover, these techniques cannot be applied to thousands of hectares of land contaminated with inorganic heavy metals. These technologies (physical and chemical treatment techniques) result in rendering the soil biologically dead and useless for plant growth. They remove all flora, fauna, and microbes including useful nitrogen fixing bacteria and phosphorous-enhancing mycorrhizal fungi. Many sites around the world, especially third world countries remain contaminated with no remediation in sight simply because it is too expensive to clean them up with the available technologies. Since the cost of phytoremediation is low due to the use of solar- driven (plants), it is believed that poorly resourced countries in the world will embrace this new technology to reduce or eliminate organic and inorganic contaminants found in the soil.

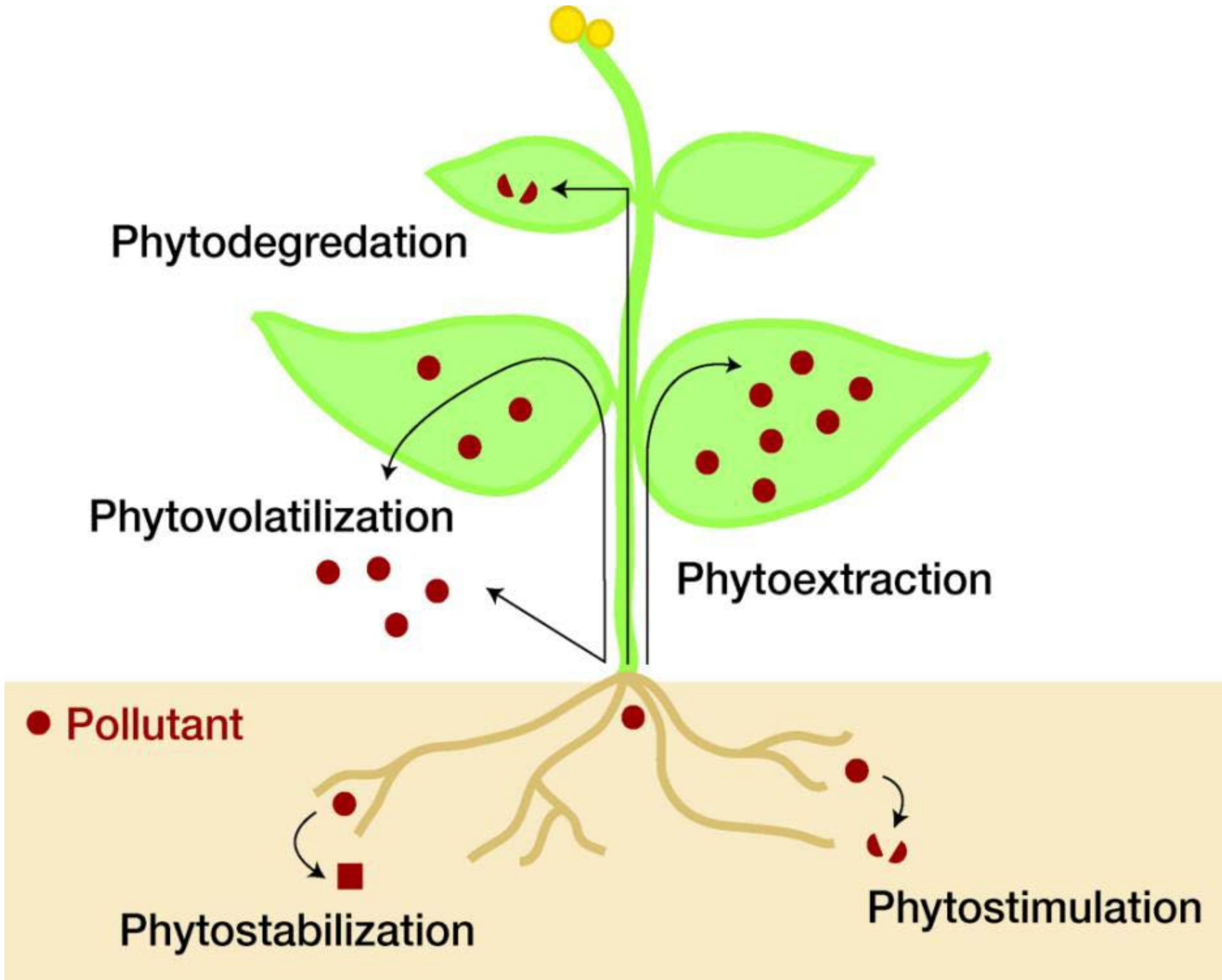

Fig 8: Plant-pollutant interactions: phytoremediation principles.

3.1 Methodology used /strategies for remediation

Phytoremediation takes advantage of the fact that plants have extensive rooting systems which explore large volumes of soil, (with dynamic oxidation and reduction processes) support larger microbial populations in the rhizosphere (the region immediately surrounding the root) than in the surrounding bulk soil. Plant roots produce exudates that directly influence the activities of rhizobacteria populations. Despite the flexibility and adaptability that these various plant-associated remediation pathways provide, it is the interactions between these pathways as well as the biochemical and ecological interactions between the plant/microbe/environment continuum that give rise to the complexity surrounding phytoremediation. To develop phytoremediation strategies for arsenic or other heavy metals, screening of high biomass plant species for rapidly growth, and ability to accumulate heavy metals should be the underlying goal. According to Shahandeh et. al (2000) thirty six different plant species were screened for agronomic importance, size, dry matter production, and tolerance for Cr(III) and Cr(VI) and other inorganic metals including arsenic uptake. Out of 33 indigenous plants evaluated for arsenic phytoremediation trials in Vietnam, (Bui Thi et al. 2011), a new species of plant, *Pityrogramma calemlanos* L exhibited excellent phytoaccumulation qualities compared to *Pteris vittata* L, a species previously known for effective arsenic phytoremediation. It is also important to screen indigenous plants species at the metal contaminated sites before going for exotic species. For phytoextraction to occur, the contaminants must also be bioavailable, which means that the contaminants are ready to be absorbed by plant roots, and the contaminants must be found as free metal ions and/or soluble metal complexes. Plants have evolved three different mechanisms for tolerating high metal concentrations in the soil: 1) excluders prevent metal uptake into root cells, 2) accumulators have specific mechanisms for detoxifying high metal levels accumulated in the cells, and 3) indicators show poor control over metal uptake and transport processes. In fact the group of plant species found in category 3 has been used as indicator species for heavy metal by ecological restorationists.

Plant selection and soil analysis are vital for any phytoremediation strategies to be successfully implemented. For example, assisted phytoextraction or phytoaccumulation is an optimization that, by increasing the metal bioavailable fraction in the soil, enables enhanced metal transport into the aerial parts of plants, thereby reducing soil remediation times. The solubility process of soil-bound metals may be achieved by a number of approaches, including the application of soil acidifiers for metal cations and increasing pH for anions like arsenic, commercial nutrients, or some chelates such as EDTA, DTPA or citric acid (Cao et al, 2009). EDTA, for example, is a low toxicity multidendate chelating agent and is able to form stable complexes with a wide variety of metals to solubilize heavy metals into a soil solution. Methods to prevent the leaching of mobilized heavy metals down the soil profile should however be considered in the phytoremediation design. Agronomic practices may be optimized for these selected species to maximize biomass production and metal uptake. For instance, planting density and fertilization could be optimized to enhance plant productivity (Chaney et al., 2000) and phytoremediation. One of the strategies to improve heavy metal phytoremediation is to increase the synthesis of plants' natural chelators like glutathione (GSH) and phytochelatins (PCs). Reports of over expression of phytochelatins synthase (PCS) by plants showed promising results for arsenic phytoremediation (Rudra et al. 2007).

The choice of using appropriate agents for extracting certain heavy metals from a contaminated soil should be one of the first issues that must be addressed. This solubilization is mainly based on the capacity of organic chelating agents to form water-soluble metal–organic complexes. Here, the solubilization of heavy metals must be enhanced to increase extraction efficiency. According to Schmidt (2000), complexation of heavy metals with various complexing agents typically follows the order EDTA and related synthetic chelates > nitrilotriacetic acid (NTA) > citric acid > oxalic acid > acetic acid. This was shown by several comparative laboratory experiments undertaken by several plant physiologists. It should however be emphasized that the solubilization of semi metals like arsenic is based on increasing the soil pH for increased extraction efficiency. Turfgrass usually plays a significant role in alleviating pollution and protecting environment (Pathan et al, 2003). It has the characteristics of fast growth and strong regeneration capacity, allowing it to be mowed many times in a year. Therefore, with the addition of EDTA, or other chelates and mowing, it will be interesting to examine whether turfgrass can form an “extraction pump system” on a heavy-metal-contaminated medium from which it gradually extracts heavy metals.

Biotechnology has also been used to manipulate plant metal uptake and tolerance properties in several species. Most successful has been plants capable of volatilizing mercury from soil contaminated with methyl-mercury. In genetic engineering model of phytoremediation, a foreign piece of DNA is stably inserted in the genome of a cell which is then regenerated into a mature transgenic plant. The piece of DNA can come from any organism, from bacterial to mammals (Pilon-Smits, 2002). There are however potential risks with the use of engineered plants in any environment especially on impacts on species diversity, soil ecosystems and the food chain.

Characteristics and effectiveness of grass species

3.3 Bermudagrass (*Cynodon dactylon*)

Fig 9: Sample pot grown bermudagrass (credit: www.allspc.com)

This is a highly variable species of turfgrass and the principal species are common bermudagrass (*Cynodon dactylon*) and African bermudagrass (*Cynodon transvaalensis*) Bermudagrass is an aggressive, low-growing and very persistent sod-forming turfgrass. The species is native to Africa. Many of the turf-type bermudagrasses are hybrids of the two

Cynodon species, *C. dactylon* (L) Pers. and *C. transvaalensis*. Plants spread by both above ground (stolons) and belowground (rhizomes) stems. A healthy, actively growing bermudagrass turf is dense, resistant to weed invasion and capable of recovering from injury very quickly. Bermudagrass is one of the most widely studied turfgrasses in the United States, Europe, China and Australia and has more than 50 cultivars. Common bermudagrass is widely distributed between latitudes 45°N and 45°S , penetrating to approximately 53°N latitude in Europe. The climate under which bermudagrass species evolved was tropical and subtropical with typically dry summers that resulted in a deep extensive root system, low evapotranspiration rate, extensive lateral stem development, and superior drought resistance. The modern bermudagrass cultivars for turf have retained these water-conserving characteristics but lack shade adaptation. It has a deep root system; in drought situations with penetrable soil, the root system can grow to over 2 m deep, though most of the root mass is located at the surface 60 cm. In terms of both organic and inorganic pollutant remediation research in literature, bermudagrass has been one of few turfgrasses used. According to Green et al, (1991) on a study on root hairs and root lengths in nine warm season turfgrasses, bermudagrass genotypes had the highest root-hair contribution to total root lengths. If the problem of arsenic bioavailability is overcome with chelator applications and organic or inorganic amendments, then bermudagrass might be a potential candidate for heavy metal phytoremediation. Studies (Mahmud et al, 2008) showed that bermudagrass remediation capacity, determined by calculating the remediation factor (RF), or bioconcentration factor (BF) revealed that the plant species with low metal concentrations in their shoots compensated the remediation effectiveness with more biomass production compared to those species with higher metal concentrations and less biomass production.

St. Augustinegrass (*Stenotaphrum secundatum* [Walt.] Kuntze)

Fig 10: St. Augustinegrass (courtesy Google: www.diylife.com)

St. Augustinegrass is a perennial, course-textured lawn grass that spreads by branching solons, forming a moderate to highly dense canopy. It is used as turfgrass in the tropical and sub-tropical climates. St Augustinegrass is believed to have originated in the coastal regions of the Gulf of Mexico and the Mediterranean and it's currently spread as far as Asia, Africa and Australia where it is now naturalized. It is adapted to very wide range of soil conditions but grows best in slightly acidic conditions with extensive root system.

St. Augustinegrass is suitable for home lawns due to several reasons such as low maintenance costs, shade tolerance, salt tolerance, and growth in a wide range of soils, and competes well with weeds. It is propagated vegetatively by sodding, sprigging, and plugging (Beard, 1973). Because of the absence of rhizomes or other protected stems, it recuperates poorly and has poor wear tolerance. The effectiveness of St. Augustinegrass in arsenic phytoaccumulation or phytoextraction is unknown.

Carpetgrass (*Axonopus affinis*)

Fig 11: Carpetgrass t (Credit: Google, www msucares.com)

Common carpetgrass (*Axonopus affinis*) is a warm season species that may have merit for improvement as a low maintenance turfgrass for use on roadsides and lawns in the southeastern United States and lower latitudes. Cultivation occurs in Australia, Central America, Malaysia, North America, South America, South Korea, and West Africa. The center of origin of this species appears to be Central America, South America, and the West Indies (Greene et. al., 2008). The species was introduced into the United States in the Louisiana area and became a substantial part of improved pastureland. It is now spread across the southern half of United States and Mexico. Limited information is available regarding the types and amounts of variation that exists for this species. Common carpetgrass is stoloniferous, with few rhizomes and is capable of developing a dense turf. It thrives in the acidic, poorly drained soils. Carpetgrass is shallow rooting and sensitive to drought. The roots of mature carpetgrass plants grew to about 0.6 m in contrast to about 2.45 m for bermuda grass (Burton et al . 1954). Biomass production is low so that this species would not be a good candidate for phytoremediation even though it grows in Obuasi.

Golden false beardgrass (*Chrysopogon aciculatus*)

Fig 12: Golden false beardgrass showing inflorescence and shallow root system (Credit: Google, www.discoverlife.org)

While considerable information is available about this popular turfgrass species in the US, very little is known about species that do not thrive in the United States. This plant can be weedy or invasive according to the USDA Animal and Plant Health Inspection Service and is prohibited in a number of states like Arizona and Illinois. Golden false beardgrass is believed to have originated from Asia, particularly China, India and Indonesia. Whilst this species is called golden false beardgrass in the United States and Africa, it is known as lovegrass in Asia. It is common on abandoned cultivations and poor drained soils in the tropics. It is a vigorous creeping grass with stout, tough rhizomes and numerous slender leaves. Golden false beardgrass is one of the few grasses that can withstand heavy grazing. Its creeping rhizomes and the capacity to resist hard grazing make it useful for stabilizing embankments and abandoned mine sites. . Golden false beardgrass is progressively found in patches at Obuasi mine site and may be a good candidate for phytoremediation.

Zoysiagrass (*Zoysia japonica*)

Fig 13: Zoysiagrass t (Credit: Google, www.hampons.com)

Zoysiagrasses, named after an 18th century Austrian botanist, Karl von Zois, are warm season (2n=40) grasses. They originated from hot humid tropical and subtropical regions of China, Korea, Japan and Philippines. Three of five species within this genus are used as turfgrasses. They are lawngrass (*Z. japonica*), manilagrass (*Z. matrella*) and mascarenegrass (*Z. tenuifolia*). Korean lawngrass was introduced in the United States as seed in 1930 from Kokai, North Korea (McCarty, 2010) and has very coarse texture; hairy, light-green leaves and relatively fast growth rate. One disadvantage is that Zoysiagrass has inherent shallower rooting and intermediate evapotranspiration rate, but exhibits a high level of osmotic adjustment compared with bermudagrass (McCarty, 2010). Much research is currently being conducted on breeding, and phytoremediation potentials. Phytoremediation of mine tailings in humid, tropical environments requires establishing a diverse plant community by including drought-, metal-, and salt-tolerant plants that do phytostabilize or hyperaccumulate metals of concern into root and shoot tissues. Candidates for phytostabilization ideally should be native to the area in which the mine tailings are found of which Zoysiagrass fall into this category as they have evolved survival mechanisms appropriate to the harsh climatic conditions at Obuasi. A secondary but also important consideration is that the use of native plants avoids introduction of nonnative and potentially invasive species that may result in decreasing regional plant diversity. To date, many field trials have not taken advantage of native plant diversity, resulting in poor plant colonization and soil conditions.   More research is needed on zoysiagrass's phytoremediation potential.

Vetiver grass (*Vetiveria zizanioides*) now *(Chrysopogon zizanioides*)

Vetiver grass (*Chrysopogon zizanioides*) is a fast growing, perennial grass native to the South and South-East Asian regions. It grows to approximately 96-192cm in height and has long been used in Asia for slope stabilization in agricultural lands because of its deep (up to 267.5), strong root system shown in Fig 10. Traditionally, vetiver grass roots were woven into mats, fans, and essential oils were extracted from them. Vetiver grass has traditionally been used for erosion control in China and India. According to Truong et al (2010), vetiver grass is regarded as a tool for environmental engineering (soil stabilization, dust control, water and soil reclamation, essential oil production etc.) and one of the most versatile crops of the third millennium. It has been shown that vetiver grass does adapt to its environment over time and it is both xerophyte and hydrophyte and, once established, is not affected by droughts or floods.

Fig 14: Deep, extensive and penetrating root system of Vetiver grass,
capable of extending to 3.3m in the first year of growth, and to 4.5m in 3 years.

It has been reported that the total dry weight of vetiver grass grown in 250 mg-As/kg soil significantly decreased arsenic contaminant levels due to the high accumulation of arsenic in the plants roots and shoots, especially in leaves (Truong and Baker, 1998). In Australia, vetiver grass has been used to stabilize excessive mining waste in highly saline, alkaline and acidic tailings of coal and gold mines. In a greenhouse study intended to provide baseline information on the capacity of Vetiver grass to tolerate and accumulate arsenic from pesticide –contaminated soils of varying physical and chemical properties, Rupali et al (2011) observed that at 225mg/kg As concentration, vetiver showed minor yellowing of leaves and small decrease in biomass.

The unique characteristics of vetiver grass can be summarized as follows:

• Adaptability to a wide range of soil and climatic conditions;

• Can be established in sodic, acidic, alkaline, and saline soils;

• Tolerant to drought due to deep and extensive root system;

• Mature plants are tolerant to extreme heat (50◦C) and frost (−10◦C);

• Vetiver can withstand burning, slashing, and moderate tractor traffic;

• Resistant to infestations from most pests, diseases, and nematodes;

• Absence runners or rhizomes, and only spreads by tillering.

To find a cost-effective method for improving the growth of vetiver grass within arsenic contamination environment, and thus enhance its phytoremediation capacities, Singh et al, (2007) explored the use of organic amendments, Mycorrhizae and Azotobacter in a study to improve growth, survival and extraction of arsenic by vetiver grass. Arsenic accumulation was found in all parts of the vetiver grass which grew in the environment with 500 mg As/kg soil. The total arsenic accumulation in vetiver grass reached 286 mg/kg after six-months. The application of organic amendments with dairy waste, Mycorrhizae and Azotobacter indicates that Vetiveria zizanioides could be used to remove arsenic from contaminated soils. The vetiver system is a proven technology, according to Truong (2000). Its effectiveness as an environmental protection tool has been demonstrated worldwide. It is a cost effective, environmental friendly and practical phytoremediation tool for the control and attenuation of heavy metal pollution when appropriately applied.

CHAPTER 4: HARVESTING AND DISPOSAL

Heavy metals make significant contribution to environmental pollution as a result of human activities. Some heavy metals like Co, Cu, Zn, and Se are essential or beneficial micronutrients for microorganisms, plants and animals whilst others like As, Pb, Cd and a host of radionuclides are toxic with no known biological or physiological function. One of the main drawbacks of heavy-metal phytoremediation is related to the handling and disposal of contaminated plant waste. According to Yang et. al,(2006), the biomass may be confined in landfills or used as compost. However, these options are questionable because metals could be liberated to surrounding environments by leaching, runoff, and other natural processes to pollute soils, surface water, and groundwater and threaten human and animal health. After each cropping, plants harvested and removed from the site and this leads to accumulation of huge quantity of hazardous biomass. This hazardous biomass should be stored or disposed appropriately so that it does not pose any risk to the environment. Biomass is stored solar energy in plant mass; it is also termed as materials having combustible organic matter. Biomass contains carbon, hydrogen and oxygen, it is known as oxygenated hydrocarbons. The main constituents of plant biomass materials are lignin, hemicellulose, cellulose, minerals, and ash.

Seeking an alternative method which would allow us either to detoxify plant biomass in order to use it as biofertilizer or mulch (if the heavy metal in question is not toxic to plants) or to recover these heavy metals for confinement or recycling is not an easy task to undertake. The feasible way to recover arsenic from turfgrass clippings is to incinerate leaf biomass and extract the mineral from the ash. In a comparative study, Yang et al (2009) selected ammonia–ammonium chloride solution as the leaching agent because this compound has been successfully used to recover heavy metals from low-grade ores for a long time. According to Singh et al

(2005), one of the conventional and promising routes to utilize biomass products by phytoremediation in an integrated manner is through thermochemical conversion process, that is combining biomass generation and its commercial utilization as an energy source, thus turning phytoextraction into profit making operation and the remaining ash may be used as bio-ore as shown in the schematic diagram in Fig 8. In short, this is also the basic principle of phytomining.

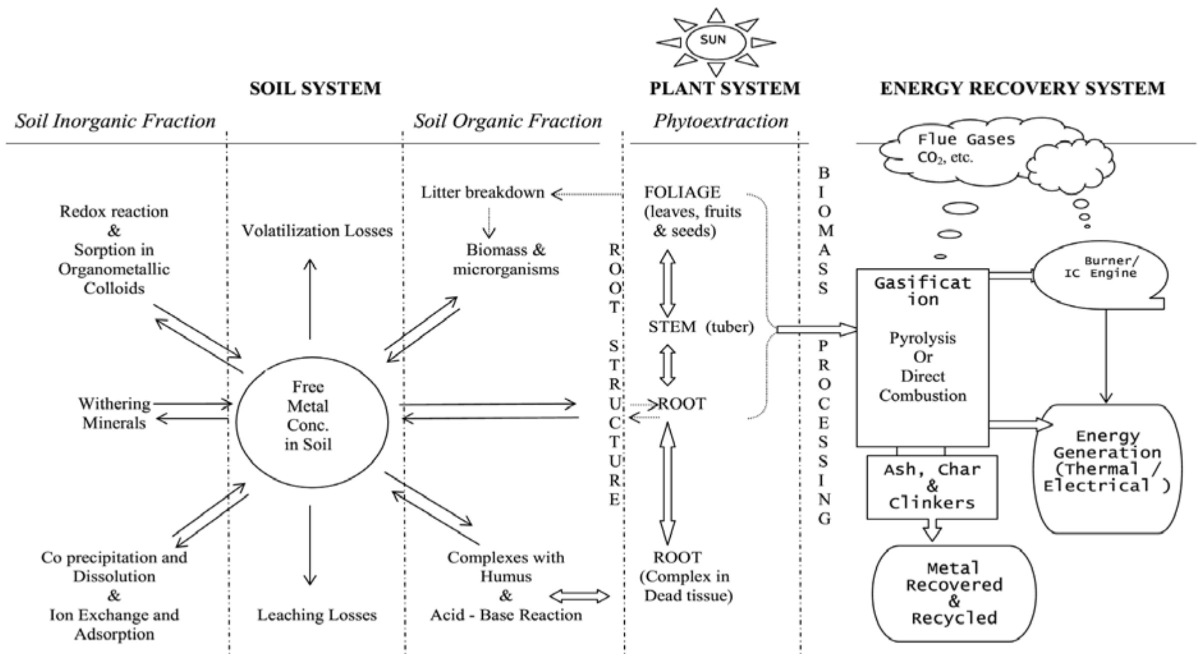

Fig 8 The Soil, Plant and Energy Recovery System depicting the key components concerned with the mass transfer and dynamics of Phytoextraction (Adapted from Ghosh & Singh 2005)

Conclusion and future directions

Heavy metal pollution has now become a major environmental concern because it can contaminate water, soil and crops, and consequently affect human health. To remediate heavy metal contaminated sites, application of conventional methods such as landfilling or excavation and extraction have little impact, owing to high energy input and engineering costs. Phytoremediation, where plants are used to uptake and accumulate heavy metals in above ground biomass, harvested and removed from the site is a panacea to this cycle of problems. Over 400 plants have been reported as metal hyperaccumulators which accumulate more heavy metals in their aboveground biomass than the threshold limits and this number continues to increase as plant researchers increase efforts to find ways to deal with the environmental problems. For many centuries, turfgrasses have played a vital role in protecting our environment and people of all generations have been willing to devote time and resources to enhance their quality of life and recreational opportunities. Phytoremediation is an emerging technology and at this stage, additional research and information is needed to consolidate this science through turfgrass biotechnological research to enable these relatively inexpensive groundcover plants to be used as clean-up tools. Vetivergrass, Bermudagrass, St. Augustinegrass and Zoysiagrass may be considered based on this review as potential candidates for heavy metal phytoremediation.

For soils contaminated with heavy metals like arsenic in Obuasi, the chemical form of this toxic metal may aggravate toxicity based on the prevailing pH and nutrient status. Various remedial technologies may have been developed around the world but each technology is site specific. Therefore a comprehensive site analysis, soil analysis (pH range) and Arsenic speciation studies must be undertaken to assess the actual concentrations of this heavy metal pollution. Unlike organic components, heavy metals cannot be degraded. Remediating the pollution they cause can only be envisioned, as their immobilization in a non-bioavailable form, or their re-speciation into less toxic form should also be the ultimate goal here. Plant analysis including adapted turfgrasses and indigenous forbs, shrubs, smaller, and bigger trees should be undertaken. Both laboratory and greenhouse studies on various phytoremediation technologies should be carried out before a full scale project is commenced. To make phytoremediation work efficiently, a screening study may be performed to identify most suitable varieties of turfgrasses including how agronomic practices could be optimized to maximize biomass production for contaminant uptake. In view of the enormous cost involved, the contaminated sited must be zoned according to the depths of metal pollution

Zone 1: This should apply to areas of shallow arsenic pollutant depths. Adapted turfgrasses may be used for both phytoextraction and phytostabilization

Zone 2: Turfgrasses, shrubs and trees may be used for deeper depths of contaminant pollution. Complexing agent like EDTA may be used for induced phytoextraction

Zone 3: Wetlands including ponds and rivers could be ‘cleaned’ with vetiver grass, bamboo and other adapted or even exotic plants.

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