2016

Arsenic Speciation and Phytoremediation Modeling for Environmental Management

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Recommended Citation

Marlborough, Sidney Joseph, "Arsenic Speciation and Phytoremediation Modeling for Environmental Management" (2016). *LSU Doctoral Dissertations*. 2062.
https://repository.lsu.edu/gradschool_dissertations/2062

ARSENIC SPECIATION AND PHYTOREMEDIATION MODELING FOR ENVIRONMENTAL MANAGEMENT

A Dissertation

Submitted to the Graduate Facility of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Environmental Science

by
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May 2016

ACKNOWLEDGMENTS

I dedicate this dissertation to my mother and father who have always supported me in my academic endeavors. My father passed before I finished my work and cannot be a part of my celebration, but I know that he is always with me. I would like to acknowledge the support of my family and committee. Dr. Wilson has been a friend and mentor for over 10 years. Throughout my life I have been guided by God and I am thankful for all I have been given and have achieved. My wife, Aimee Marlborough and children, Zoe, Madeline, and Zack.

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ABBREVIATIONS AND DEFINITIONS

ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
ATP	Adenosine triphosphate
CTSPAC	Mathematical model for coupled transport of water, solutes, and heat in the soil-plant-atmosphere continuum
HQ	Hazard quotient
ITRC	Interstate Technology and Regulatory Council
LOAEL	Lowest observed effect level
mg/kg	Milligrams per kilogram or parts per million
MCL	Maximum Contaminant Level
NOAEL	No observed effect level
NRC	National Research Council
PCL	Permissible concentration limit
PKM	Phytoremediation kinetic model
ppm	Parts per million
ppb	Parts per billion
Risk based corrective action	Corrective action strategies based on identifying exposure pathways and receptors to protect human health and the environment
TCEQ	Texas Commission on Environmental Quality
TRV	Toxic risk value
TRV LOAEL	Toxic risk value based on the lowest observed effect level
TRV NOAEL	Toxic risk value based on the no observed effect level
UCL	Upper Confidence Limit
USGS	United States Geological Survey
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

ABSTRACT

Arsenic has been used throughout recorded history but during the industrial revolution widespread use led to global environmental impact. The two forms that should be considered in environment management are arsenate and arsenite. The calculations of environmental risk for arsenic exposure relies the toxicity of arsenite however, in well aeriated surface soils arsenate may be the predominate form. Ecological risk assessments based on arsenite studies will lead to restrictive remediation requirements that do not adequately reflect the level of risk. Arsenate resembles phosphate and as such has a greater affinity for phytoremediation. Phytoremediation is one of the most viable and cost effective cleanup techniques developed. Different mathematical approaches have been implemented to characterize phytoremediation systems to address concerns with performance. A system dynamic model is presented to describe solute transport in groundwater coupled to sorption by plant roots, translocation into plant stems, and evapotranspiration. The model was tested and assessed using published and peer-reviewed experimental data, to assess its capability to mimic phytoremediation processes. The model is consistent with previous research establishing the extraction process as a constringent factor for this cleanup technique. The model included modules that can estimate rainfall, seasonal temperature and growth. The modules allow for the independent verification of data before input into the model. The implementation of phytoremediation model can provide information about: pollutant-media-plant interaction, pollutant concentration and flow rate through the plant.

CHAPTER 1
INTRODUCTION AND REVIEW OF LITERATURE

1.1 BACKGROUND

Risk assessment is the process to determine the potential hazards of a chemical to the human health and or ecological systems. The risk is based on the toxicity of a contaminant as a function of probable or maximal exposure. A remediation design is based on the risk characterization of a particular contaminant and will detail the final remedial goals that must be achieved to consider the site closed.

Phytoremediation is the installation of plants, like trees, to clean up contamination in various environmental media. Plants can be used to sequester, degrade, or remove contaminants. In the early 90's, phytoremediation began to be evaluated in the field and promised significant decreases in operational costs over conventional systems (U.S. Environmental Protection Agency, 1996). There is a potential for impressive economic benefits from using plants for remediation. Plants are a green alternative to standard methodologies. The root systems can enhance microbial degradation over non rooted soil. Plant based systems are aesthetically pleasing and provide social and environmental benefits to the public beyond simple cleanup.

The science surrounding phytoremediation expanded with the discovery of hyperaccumulators that could extract metals from soils and allow for less tolerant plants to flourish. Scientists also have found that plants can be useful in absorbing or degrading organic contaminants by metabolizing them into less harmful products. More recently, environmental scientists have applied deep rooted tree technologies to the remediation of groundwater contaminants. The deep root system forces the preferential path of growth into the groundwater zone so that root pull water directly from the contaminated source.

A number of mechanisms have been suggested to illustrate how deep rooted trees may be useful in the remediation of arsenicals during phytoremediation:

- Plant tissues have the ability to accumulate and store contaminants. Poplars have the ability to uptake and store heavy metals in roots and then translocate these to stems and leaves (Hinchman, 1996).

- Poplars can provide a hydraulic control of aqueous contaminants through uptake of water. Mature poplars have been shown to transpire from 50 to 300 gallons of water per day based on climate and soil types conditions (Chappell, 1997).

Contaminated water can be taken into the plant itself by direct uptake and stored or respired depending on the chemistry of the contaminant. Plant transpiration of water effects hydraulic control of the site during the growing season. Transpiring trees have been shown to depress water tables and therefore prevent contaminant migration off-site. Phytoremediation is broad class of bioremediation techniques that consists of various treatment strategies and application ideas. Remedial project managers have to ability to select from a large variety of phytoremediation techniques to solve the specific problem at hand.

Use of Deep Rooted Poplars in Phytoremediation

Phytoremediation offers the following benefits for the remediation of soil and groundwater:

- Low installation, operational and maintenance cost.
- Low ecological impact and positive public perception.
- Poplars have been studied extensively and have been shown to remove and respire metals.
- Poplars are fast growing with rates as high as 3-6 meters/yr (Schnoor et al., 1995).
- Rapid growth couples with the ability to transpire significant quantities of water.

A systematic analysis for the design of phytoremediation systems for groundwater capture and contaminant control does not exist. Tools are needed to evaluate phytoremediation effectiveness that can be applied to existing sites and case studies. A discussion of previous research will be presented in the literature review section. The research addresses the need for water and contaminant transport models that can incorporate removal contaminants and water from a given natural process and current and future site conditions.

1.2 OBJECTIVES

Until now, little research has been done on the characterization of the ecological risk of arsenate and arsenite as separate constituents; most risk based corrective actions consider a total arsenic concentration. Therefore, it is important to focus on the species of arsenic found at a specific site to accurately consider remedial goals. In particular, the following questions addressed are:

- Is assessing arsenic risk based on species present a suitable method to evaluate ecological risk protective of target?
- How does evaluation of risk based on metal species compare to standard evaluations?

The second goal of this research is to develop and validate a model that simulates the transport of arsenic and water by plants via plant uptake kinetics. The model will be implemented using the STELLA modeling package to simulate phytoremediation processes. The specific objectives are identified:

- Develop a stochastic model for the removal of contaminants by poplars from soil-groundwater systems. The model will be constructed and tested using the STELLA.
- Develop modular components to address plant growth and site specific seasonal changes.

1.3 INTRODUCTION

The need to clean existing contaminated sites has become a focus of many organizations due to the substantial risks such sites pose. Governmental agencies and industry continue to look for efficient and cost effective technologies that can be used to remediate contaminated sites. Heavy metals like arsenic are among the most prevalent forms of contamination found at impacted sites, and the remediation of soil is one of the most technically difficult to complete (Cunningham et al., 1997). In order to select the appropriate remediation technology at any given site, an environmental assessment has to be conducted. The results of the assessment can be used to generate risk based corrective action plan to address the hazards to human health and the environment. Sites and specific hazards can be ranked based on their level of risk to impact the human health through exposure at a point of contact.

Dealing with risk based corrective action and phytoremediation is inherently complex. The risk based corrective action or risk assessment, is used to evaluate the acceptable limits for contact with both an individual contaminant and combined risk of multiple contaminants. Environmental management decisions are usually made with limited information and must be projected over large time frames. There are many factors involved in the risk assessment and remediation of a site and not all may be known in the beginning. Environmental managers have to review the available knowledge from both a scientific and managerial viewpoint to make informed decisions and implement the most appropriate assessment and remedial options to mitigate the environmental contamination at a subject site

Widespread water and soil contaminations created by natural releases of arsenic from aquifers have been identified in many parts of the world (Smedley and Kinniburgh, 2002). Use of arsenical pesticides and medicinal compounds have led to extensive worldwide contamination. Chronic arsenic exposure accounts for the increased risk of various disorders such as cardiovascular abnormalities, diabetes, mellitus, neurotoxicity, nephrotoxicity, cancer and possible hepatotoxicity (Singh et. al., 2011). The detection of arsenic contaminated locations throughout the United States and worldwide has increased the interest in studying the dynamics of arsenic in soil and groundwater. Unfortunately, a lack of assessment and remediation technologies for arsenic contaminated land and groundwater still remains.

1.4 ARSENIC

1.4.1 Sources of Arsenic

Natural

Arsenic is a naturally occurring element with a molecular weight of 74.9216 and atomic number of 33. Inorganic arsenic is steel-gray in physical appearance and resembles metal, but it is classified as a transition element or metalloid to distinguish it from a true nonmetal (Mandal and Suzuki, 2002). Arsenic has four valence states: -3, 0, +3, and +5. In natural environments, trivalent arsenite [AsO_3^{3-}, As(III)] and pentavalent arsenate [AsO_4^{3-}, As(V)] species are the most commonly observed, though As(-III) in the form of arsine gas (AsH_3) may be found in the atmosphere. Elemental arsenic (As^0), gray colored and very insoluble, is rarely found by itself and is usually combined with any of several other elements, including oxygen, hydrogen, sulfur, and iron in inorganic forms, as well as carbon and hydrogen in organic arsenicals. Arsenic is widespread in nature and ranks twentieth in crustal abundance, fourteenth in seawater, and twelfth in the human body (Mandal and Suzuki, 2002).

Arsenic is a component in more than 245 minerals, mostly ores containing sulfide, as well as copper, nickel, aluminum and other metals. Arsenic’s relatively high concentration in the rock reservoir can be attributed to its ability to readily substitute for Fe, Al or Si in the crystalline structure of some minerals. The actual concentration is highly variable and depends largely upon the type of rock. Sedimentary rocks tend to have considerably more arsenic than igneous or metamorphic rocks. The main carrier of arsenic in rocks and most types of mineral deposits is iron pyrite (FeS_2), which may contain >2000 mg/kg of arsenic (Mandal and Suzuki, 2002).

Arsenic can also be found in soil, freshwater and marine environments, in the biota inhabiting these milieus, and in the atmosphere (Woolson, 1983). Relative concentrations of arsenic in natural reservoirs are listed in Table 1. Other than arsineferous rocks, the major reservoirs for arsenic are oceans and soils. Arsenic is mobile in the environment. Once released from rocks and soils, arsenic is cycled among land, air and water (Matschullat, 2000; Miteva, et al., 2005).

Table 1.1 Calculated Ratios of Arsenic Concentrations in Natural Reservoirs with Respect to Soils

Reservoir	Approximate Ratio with Respect to Soil
Rocks	25,000
Oceans	4
Soil	1
Biota	0.0005
Atmosphere	0.000001

(Nriagu, J.O., Arsenic in the Environment, Pt. I 1979)

Typically, the weathering of rocks converts arsenic sulfides to arsenic trioxide (As_2O_3), which can then enter the arsenic cycle as dust or by dissolution in rain, rivers, or groundwater. Volatile arsenicals, such as arsine and trimethylarsine [$(CH_3)_3As$], formed by microbial and abiotic processes, enter the atmosphere from land and water and are returned by rain and atmospheric fallout. Oxidized arsenicals are converted back to sulfides by anaerobic processes occurring on land and in water sediments. Water plays a critical role in the transport of arsenic in the environment. (Nimick, et al., 1998; Ning, 2002)

Anthropogenic

According to the National Resource Council of Canada, anthropogenic input of arsenic to the environment is at least three times the amount contributed by natural weathering processes. In 1999, the U. S. Geological Survey reported that global production of arsenic was approximately 41,500 metric tons, with the United States importing 30,000 metric tons from foreign producers, mainly China. Since 1985, no arsenic producers have operated in the United States. Until 1985, arsenic was only produced as a byproduct of high-arsenic copper ore smelting at the ASARCO facility in Tacoma, Washington (Washington Department of Ecology, 2012). With the closure of that facility, imported quantities of arsenic have steadily risen. About 97% of all arsenic produced globally enters end-product manufacture as arsenic trioxide (As_2O_3). As_2O_3 (a trivalent species) is a product of smelting operations and is the material used in synthesizing most arsenicals (Adriano, 2001).

Arsenic released from anthropogenic sources is often deposited directly or indirectly into soils. Humans and many ecosystems may be closely connected with soils, and the accumulation of arsenic in edaphic systems is an important concern. Arsenic has been added to soils in many ways: about 41% has come from commercial product wastes, about 23% comes from coal combustion by-products, 14% from atmospheric fallout, 10% from mine tailings, 7% from smelters, 3% from agriculture, and 2% from manufacturing, urban and forestry wastes. Together, these combine to total more than 82×10^6 kg/yr of arsenic released into soils (Matera and Le Hecho, 2001).

Agriculture

In the U.S., more than 90% of total arsenic consumption is used for agricultural purposes. These include production of wood preservatives (74% of total), herbicides, insecticides, algicides, fungicides, desiccants, anti-parasitic medications and growth stimulants for plants and animals (Agency for Toxic Substances and Disease Registry, 2007, Azcue and Nriagu, 1994). The widespread agricultural use of arsenicals over several decades has left behind a legacy of highly contaminated soils in orchards and farmlands. Some old orchard fields contain up to 2500 mg/kg of total residual arsenic (average arsenic levels in soils range from 0.1 to 40 mg/kg (mean = 6 mg/kg)), raising concerns over the possibility of food chain and ground water contamination from residual arsenic in these soils (Agency for Toxic Substances and Disease Registry, 2000).

Smelting Operations

Smelting operations represent another significant source of arsenic release into the environment and are the largest single contributor of arsenic to the atmosphere. As arsenic is a natural contaminant in lead, zinc, gold and copper ores, it can be released during the smelting process (Leonard, 1991). The dust and flue gases produced by smelters often contaminate soils with arsenic downwind from the operation (Bhattacharya, 2007).

Fossil Fuel Combustion

Fossil fuel combustion is the second most important anthropogenic source of arsenic release, particularly the burning of coal materials. Coal is known to be a concentrated source of arsenic and coal combustion releases significant quantities of arsenic into the environment. Arsenic usually occurs in the form of arsenopyrite in coal, and its combustion releases arsenic as fly ash particles or in a gaseous form. Furthermore, the physical translocation of coal from subterranean (reducing) conditions to the oxidizing environment found at the surface leads to rapid oxidation of arsenic-containing minerals and the subsequent release of arsenic to surface soil and waters (Bhattacharya, 2007).

Other Anthropogenic Sources

While the agriculture field consumes most of the As_2O_3 produced, other uses are found in the manufacture of glass and in the textile industry. Arsenic is also being used in increasing amounts by the electronics industry, where it is used to form semiconductor compounds and as a doping agent to confer semiconductive properties on silicon or germanium (Bissen and Frimmel, 2003). Volatile arsines are used for this purpose and may represent a hazard to workers and the local environment.

1.4.2 Environmental Fates of Arsenic

The mobilization and accumulation of arsenic are largely controlled by its speciation and the reactions it undergoes. Oxidation-reduction, adsorption-desorption, precipitation-dissolution and biotic transformations all influence the fates of arsenic in the environment. In areas of high oxidation-reduction potential (Eh), high dissolved oxygen, and neutral to basic pH, such as those encountered in many surface waters, arsenate [As(V)] usually predominates in the form of $H_2AsO_4^-$ (at $pH<7$) or $HAsO_4^{2-}$ (from pH 7.5 to 11) (Dobran and Zagury, 2005).

Arsenates are generally less toxic, less soluble and less mobile than the trivalent species arsenite. Arsenates are less mobile than arsenites due in part to their stronger adsorption to sediments. This adsorption process depends largely on arsenic concentrations, sediment characteristics, dissolved oxygen and pH. An important mechanism of arsenic adsorption onto sediments is the interaction of arsenates with hydrous iron- and manganese oxides (Dobran and Zagury, 2005; Ning, 2002; Goh and Lim, 2005). Under oxidizing conditions, arsenic tends to sorb to, and hence be immobilized by, iron and manganese oxyhydroxides (Omoregie, 2013). Under reducing conditions, however, the dissolution of iron and manganese oxides may release bound arsenic back into an aqueous phase as As(V) (Dobran and Zagury, 2005;Ning, 2002; Goh and Lim, 2005). It should also be noted that anions when present (particularly phosphate) can effectively compete with arsenic for adsorption sites. In some cases this may increase levels of leached arsenic (Goh and Lim, 2005).

Arsenicals in flooded soils and water are subject to chemically and microbiologically mediated oxidation or reduction and methylation reactions (Eisler, 1994; Mitchell and Barr, 1995). In areas of low Eh and low dissolved oxygen the trivalent species may be present (H_3AsO_3 - the predominant species at $pH<10$) as they are thermodynamically stable under these conditions

(Smedley and Kinniburgh, 2002). Since As(III) species are generally more mobile, more soluble, and more toxic than As(V), their presence in waters and soil may pose a threat to the environment (Cullen and Reimer, 1989).

In reduced environments such as anaerobic sediments and flooded soils, arsenate may be reduced to arsenite by both abiotic and biotic processes (Jain and Loeppert, 2000; Jekel, 1994; McGeehan and Naylor, 1994). Abiotic arsenate reduction processes may involve the actions of sulfides. Sulfides are strong reductants and are frequently present at significant concentrations in reducing environments (McGeehan and Naylor, 1994; Eisler, 1994). Sulfides play an important role in retaining and remobilizing arsenic from sediments (Goh and Lim, 2005). In the reduced environment, sulfides will scavenge arsenic with the formation of arsenic-sulfide precipitates. These precipitates may persist for extended periods, essentially sequestering soluble arsenic from the environment (Fox and Doner, 2003). Some less stable arsenic sulfides may eventually dissociate, leading to the release of dissolved arsenite (Goh and Lim, 2005).

Biotic arsenate reduction may significantly contribute to the concentration of reduced arsenical species in anoxic environments. Microbial (dissimilatory) reduction of arsenate has been demonstrated in many environments (Newman et al. 1997, Cummings et al., 1999, Tufano et al., 2008). The rates of this microbial reduction may be limited, however, due to the lower bioavailability of sorbed phase arsenic (iron- and manganese oxide-bound arsenic) (Bhattacharya, 2007). In turn, reduced arsenite may be methylated by soil and sediment microorganisms into methylarsinic acid or dimethylarsenic acid. These compounds may then be further methylated to trimethyl species, and these may volatilize to the atmosphere. Methylated arsenicals are eventually mineralized back to inorganic species (Hughes et al., 2011).

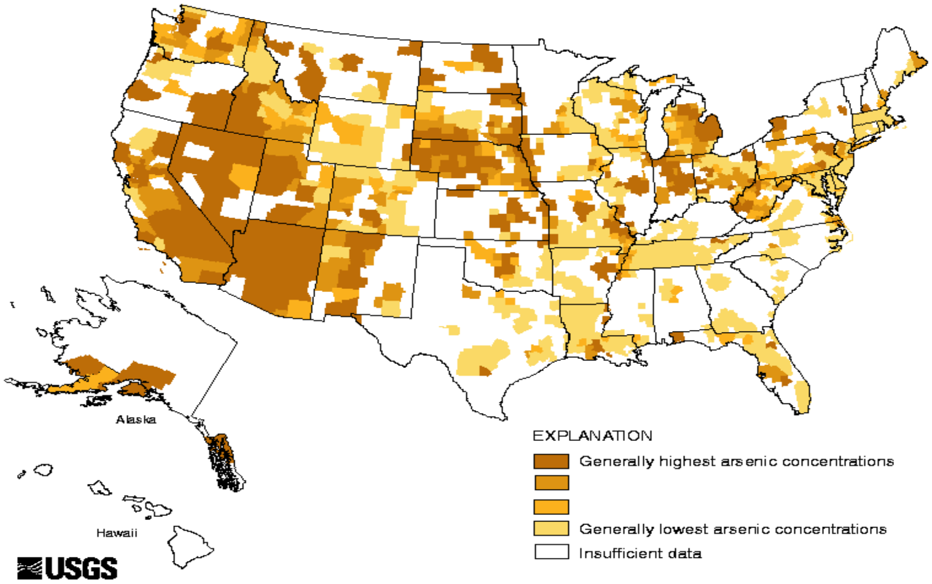
1.4.3 Effects of Arsenic on Human Health and Ecosystems

Arsenic: Human Health Effects

Despite the use of arsenic in human medicines for nearly 4,000 years, and some evidence suggesting that it may be an essential trace-nutrient in the human diet, arsenic has been classified as a human carcinogen by the International Agency for Research on Cancer and the U.S. Environmental Protection Agency (Agency for Toxic Substances and Disease Registry, 2000; Hughes et al., 2011). This classification was based upon studies that have decisively linked arsenic intake to various cancers in humans (Cullen and Reimer, 1989; Dermatas, et al., 2004; Hudson-Edwards et al., 2004). Human exposure to arsenic occurs primarily from water, food, and air through ingestion and/or inhalation of arsenical compounds.

Exposure Via Water

Water supply systems are the major source of human exposure to arsenic. Arsenic is generally in the inorganic form in most water systems, occurring predominantly as As(V) in surface waters and as As(III) in groundwater containing high levels of total arsenic. Arsenic may be encountered in water from wells drilled in into arsenic-rich ground strata or where geochemical conditions favor arsenic dissolution and release into rivers, lakes and other bodies of water. It may also be found in water contaminated by industrial or agrochemical wastes. The US Geological Survey (USGS) has identified ground water with naturally high levels of arsenic throughout the United States (Figure 1.1). One quarter of the U.S. counties where data were available, 10 percent or more of samples had arsenic concentrations exceeding 10 µg/L (USGS). This is significant because in 2001 the U.S. Environmental Protection Agency decreased the Maximum Contaminant Level (MCL) for arsenic in drinking water from 50 ug/L to 10 ug/L for community water systems and non-transient, non-community water systems in the United States. Residents of the counties colored darkest brown in Figure 1.1 may have groundwater exceeding new standards for arsenic (USGS).



🟫 Arsenic concentrations exceeding 10 µg/L in 10 percent or more of samples.
🟧 Arsenic concentrations exceeding 5 µg/L in 10 percent or more of samples.
🟧 Arsenic concentrations exceeding 3 µg/L in 10 percent or more of samples.
🟨 Fewer than 10 percent of samples exceeding 3 µg/L.
⬜ Counties with insufficient data in the USGS data base to make estimates.

Figure 1.1 Arsenic occurrence in ground waters of the United States. USGS Fact Sheet 063-00.

Exposure Via Food

Food ingestion is an important source of arsenic exposure. Humans may consume food contaminated with arsenical pesticides or grown with arsenic-contaminated water or in arsenic-rich soil (Chen and Lin, 1994). Certain foodstuffs are known to contain considerably more arsenic than most other foods. Unusually high concentrations of arsenic are found in many types of seafood. Marine crabs, lobster, shrimp, and cod typically contain arsenic levels of 10-40 ppm, and there have been instances where mussels contained as much as 120 ppm of arsenic. Marine organisms can contain arsenic at much higher levels than terrestrial organisms, there are no documented cases of arsenic poisoning by ingestion of marine organisms in the literature. This is explained by the fact that the major arsenical in most marine organisms is arsenobetaine, a water-soluble, trimethylated organoarsenical that poses little risk to the organism or its consumer (Abernathy, 2001). Thus, many factors should be weighed when analyzing the dangers of arsenic in foods destined for human consumption. Local and traditional diets, individual eating habits and preferences, and the form of arsenic typically found in a given food group must all be considered. It is estimated that more than 80% of arsenic consumed in food is in an organic form, which has lower toxicity (Agency for Toxic Substances and Disease Registry, 2007). Milk and meat products, however, have substantially higher inorganic arsenic concentrations than do fruits, vegetables and fish (Agency for Toxic Substances and Disease Registry, 2007; Hughes et al., 2011).

Exposure Via Air

Smelting operations and the burning of coal and arsenic-treated wood are major sources of atmospheric arsenic contamination. Arsenic particulates mainly consist of inorganic arsenic compounds, mainly in the As(III) oxidation state (Smedley and Kinniburgh 2001). According to the U.S. Environmental Protection Agency, the concentration of arsenic in the air is usually only a few ng/m^3, with the average national exposure in the United States estimated to be at 0.006 µg As/m^3 (ASTDR, 2007). Exposures may be considerably higher, however, in polluted areas near smelters or power plants that burn fossil fuels of high arsenic-content. Specific occupations may place some individuals at risk for exposure to arsine gas (AsH_3), the most toxic of all arsenicals (Hughes et al., 2011). Absorption of inhaled arsenicals varies between 30 to 85%, depending upon the arsenical species in question (World Health Organization, 2001).

Bioavailability

Bioavailability is key in determining exposure outcomes. It is dependent on the ability of arsenic to be liberated from ingested sources like food, soil and water (Caussy et al., 2003a).

Bioavailability information about arsenic is primarily obtained from animal studies and human exposure. Results of the studies conducted indicate that most (90%) ingested inorganic arsenic salts are absorbed in the gut (Pomroy et al., 1980; Vahter and Norin, 1980; Freeman et al., 1995). This is because of similarities between phosphate (PO_4) and arsenate (AsO_4) ion absorption. Phosphate is a crucial macronutrient and is primarily absorbed in the gut. Arsenate seems to follow similar phosphate metabolic pathways.

1.4.4 Modes of Toxicity for Arsenic Species

Different arsenic-containing compounds vary considerably in their toxicity to mammals (Agency for Toxic Substances and Disease Registry, 2007). While some species are highly toxic (AsH_3), others are considered essentially non-toxic at any level of exposure (arsenobetaine) (Hughes et al., 2011). A general ranking of arsenical toxicity, from highest to lowest, is as follows: Arsine gas>inorganic trivalent compounds>organic trivalent compounds>inorganic pentavalent compounds>organic pentavalent compounds>elemental arsenic (Agency for Toxic Substances and Disease Registry, 2007). Factors other than speciation may also influence toxicity. These include physical state, solubility, particle size, the rate of absorption into cells, the rate of elimination, fitness of the patient and an individual's genetic background (Hughes et al., 2011; World Health Organization, 2001).

While the specific reactions involved in biotransformation of arsenic in humans are not well characterized, metabolism of arsenicals is believed to proceed in two steps. After entering a cell, arsenate [As(V)] is reduced to arsenite [As(III)]. This reduction occurs primarily in the kidneys. Arsenite is then methylated to form monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). Methylation reactions are believed to take place in the liver (Agency for Toxic Substances and Disease Registry, 2007; Abernathy, 2001).

Arsenate [As(V)], arsenite [As(III)], and methylated organoarsenicals are the most common forms of arsenic observed in most environments and are the forms most likely to be exposed to humans (Agency for Toxic Substances and Disease Registry, 2007; Hughes et al., 2011; Abernathy, 2001). As the toxicity of these species differs significantly, the modes of toxicity for each are described below.

Arsenate

Although ingested arsenate [As(V)] is believed to be reduced to arsenite [As(III)] in human bodies, the kinetics of this reduction have not been clearly established (Freeman et al., 1993). Thus, the toxic effects of arsenate should be considered. Arsenic, like phosphorous, is in Group V of the periodic table, and arsenate is an analog of inorganic phosphate. As(V) is thought to be capable of uncoupling oxidative phosphorylation by a mechanism based upon the competitive substitution of arsenate for phosphate. This results in the formation of an unstable arsenate ester that is rapidly hydrolyzed. The high-energy bonds of adenosine triphosphate (ATP) are not conserved due to this arsenolysis. As a result, there is no net formation of ATP from glycolysis, with potentially lethal consequences (Meharg, 2002).

Arsenite

The toxicity of arsenite [As(III)] is based upon its high affinity for sulfhydryl (-SH) groups. Sulfhydryl groups (also known as thiol groups) are found in proteins that contain cysteine residues and in other important biochemicals. The reaction between arsenite and enzymatic sulfhydryl groups leads to inactivation of a variety of enzymes, which is believed to be the cause of the overt toxicity of arsenite. Although many enzymes are susceptible to arsenite-mediated deactivation, those enzymes involved in the tricarboxylic acid cycle (Kreb’s cycle) are particularly sensitive (Carbonell et al., 1998). In most cases, enzyme activity can be restored by administration of monoand dithiols. British anti-lewsite (2,3-dimercaptopropanol), a widely used antidote for arsenic poisoning, very effectively blocks the action of arsenites on sensitive enzyme systems (Agency for Toxic Substances and Disease Registry, 2007; Hughes et al., 2011).

Organoarsenicals

Organoarsenicals are generally much less toxic than the inorganic species (Hughes et al 2011). In rare cases, however, toxic effects are associated with some organic arsenicals. In these instances, toxicity is primarily due to in-vivo reactions that convert specific organic species (i.e. methylarsonous acid) to trivalent arsenite. As(III) can then react with sulfhydryl groups as described above (Agency for Toxic Substances and Disease Registry, 2007). Occasionally, a massive organoarsenical overdose may also result in acute arsenic poisoning (Agency for Toxic Substances and Disease Registry, 2007).

Conversion of inorganic As(V) or As(III) into organic forms (specifically methylated species) is a detoxifying mechanism in mammalian systems. Methylated arsenicals are rapidly removed from body tissues. This is in striking contrast to mercury, where methylation is a highly detrimental process. Hepatic methyltransferases carry out the rapid conversion of As(III) to MMA and DMA. Murine models have shown that DMA was present in plasma only 12 minutes after injection of inorganic arsenic (Hughes et al., 2011). There may be a threshold for arsenic concentration in humans, below which no ill effects are observed. This is presumably due to detoxification by hepatic methyltransferase enzymes (Rosen et al., 2014). It is theorized that above a certain limit these enzymes become overwhelmed and can no longer efficiently detoxify ingested arsenic (World Health Organization, 2001). Interestingly, animals previously exposed to sub-lethal doses of arsenic may develop tolerance to arsenic on re-exposure. This is probably due to increased efficiency of in-vivo methylation processes (Hughes et al., 2011).

1.4.5 Effects on Freshwater and Marine Ecosystems

A general model for arsenic behavior in freshwater and marine ecosystems is very difficult to deploy. Different ecosystems contain diverse types of biological communities and may have specific blends of both geochemical and biological controls over arsenic speciation and accumulation. Thus, only when a given system has been adequately described can arsenic behavior and its potential impacts be identified (Agency for Toxic Substances and Disease Registry, 2007).

In freshwater, increased concentrations of arsenic are found in hot springs, in thermally active ground water locations or in areas containing rocks with high arsenic content, and in waters with high dissolved salt content. The majority of the other elevated concentrations reported in lakes, rivers and sediments are most likely due to anthropogenic sources, which include smelting and mining operations, combustion of fossil fuels, sewage sludge wastes, and arsenical defoliants, herbicides and pesticides (Hughes et al., 2011).

In lacustrine systems, arsenic may accumulate in lake sediments by routes that transfer arsenic from the water column to particulate forms that may be deposited on the lake floor. Sorption to iron and manganese oxides, as well as incorporation into algal biomass are two such processes. Deposited arsenicals may then be immobilized and buried or partially remobilized into the overlying water. Soluble sulfides may also play a role in arsenic deposition to sediments. Arsenic-sulfides may store arsenic in the sediments, sequestering it from biological uptake (Bhattacharya et al., 2007). Eutrophication of lacustrine systems has been shown to affect the concentration and speciation of arsenic in lake water (Carbonell, 1998).

The great variability and dynamic nature of marine ecosystems makes its difficult to propose a general model for arsenic behavior in these systems. Some attention has been paid to the effects of arsenic in marine food chains, however. The most important route for arsenic entrance into marine food webs is through the uptake of arsenic by phytoplankton and attached macroalgae. The levels of arsenite, MAA (monomethylarsonate) and DMAA (dimethylarsonate) are elevated in the photic zone of marine waters, suggesting that phytoplankton are producing these arsenicals from arsenate. Invertebrates and vertebrates show little uptake of arsenic from water. The relatively high uptake of arsenic by algae provides a pathway for arsenic into higher trophic levels, as the organoarsenicals formed within algae are available to herbivorous organisms. Studies have shown that arsenic incorporation into higher trophic levels is low, however. In feeding experiments conducted in Chesapeake Bay, only 7 to 10% of the arsenic contained within phytoplankton tissues (and only 1% overall) was incorporated into invertebrates grazing on the phytoplankton (Agency for Toxic Substances and Disease Registry, 2007). The few studies done on freshwater food chains mirror these results.

The absence of arsenic from higher trophic levels should not be assumed to mean that these levels are free from potential harm. Arsenic is an example of a contaminant that has its primary effects at the lower trophic levels, with cascading, indirect consequences to higher trophic levels. Phytoplankton are the most sensitive link in the food chain, with some species showing evidence of growth reductions at arsenate concentrations as low as 3 ug/l. Concentrations of 5 to 10 ug/L have been shown to cause significant reductions in growth and shifts in phytoplankton species composition because of variations in arsenic sensitivity in these species. Shifts in the relative abundance of phytoplankton species can have highly detrimental effects if higher trophic levels are feeding selectively with respect to phytoplankton species, size or shape. Thus, ecosystem-level impacts may be caused by changes in the composition of the autotrophic community (Agency for Toxic Substances and Disease Registry, 2007).

1.4.6 Remediation of Arsenic

The remediation or removal of arsenic from contaminated waters has been the focus of much scientific attention. The widespread occurrence of arsenic in U.S. ground waters, as well as concerns over the mass-poisonings of the people of Bangladesh and India by long-term arsenic ingestion have led to development of many technologies designed to remove arsenic from drinking water (World Health Organization, 2000). The development of specific technologies for removal of arsenic from soils and sediments has received much less attention.

1.5 RISK ASSESSMENT

The environmental protection agency defines risk as the chance of harmful effects to human health or to ecological systems resulting from exposure to an environmental stressor. All chemical substances can produce adverse health effects at some level of exposure. The dose makes the poison. Risk is the likelihood that an adverse health effect will result from an exposure to a dose of chemical. Risk is a function of both toxicity and exposure, and without exposure there is not risk. Risk assessment is a process designed to answer questions about how toxic a chemical is, what the probability that use will cause harm is, and how to characterize that risk. Environmental risk assessment is a scientific process that identifies and evaluates threats to the environment, in particular to living organisms, their habitats and ecosystems.

The risk assessment process, includes various steps that meant to identify and evaluate risks, risk impacts, and evaluate risk mitigation measures. Risk management is the decision-making process that entails consideration of the site information along with risk related information to develop, analyze, and compare options and to select the appropriate response to a potential health hazard. Using experience and judgment, the (risk) manager must determine a level of risk that is acceptable. The scope of risk assessment varies widely (Paton, 1993).

Risk assessment is used both as a predictive tool and as a management tool during the implementation and post implementation stages of a project to monitor actual impacts and to intervene in the management of impacts if necessary. When conducting a risk assessment, a qualitative evaluation must be performed to illustrate the complete or reasonably anticipated to be complete ecological exposure pathways that will be evaluated in the assessment. This qualitative evaluation is known as a site conceptual model. The site conceptual model graphically depicts the movement of contaminants from the sources through media to the feeding guilds or to the selected ecological receptors of those guilds. Based on knowledge of the fate and transport of site-specific inorganic arsenics in soils and the toxicity to terrestrial wildlife, a conceptual model can be developed. Migration through subsurface soils, to groundwater and subsequent surface water bodies is unlikely with inorganic arsenic. Therefore, surface soils of the upper 6 feet are the most important medium of ecological concern at the sites contaminated with arsenic.

Ecological Risk Assessment

The concept of ecological risk has emerged as a distinct field of risk assessment that goes beyond evaluating environmental and ecosystem impacts. Ecological risk is based on the understanding that ecosystems can biodegradation and remove contaminant from soil and water without significant impact based on site conditions. The objective of an ecological risk assessment is to estimate the possibility of adverse impacts on one or more trophic levels of the ecosystem due to exposures to environmental stressors. Ecological risk assessment draws widely on the standard procedures of environmental impact assessment and evaluation. Sensitive receptor species specific to the site may not have toxicity test data and must use standard tests animal data. Although these procedures constitute a low cost, pragmatic means of evaluating the toxicity of a potentially hazardous chemical, they do not directly evaluate the sub-lethal toxicity, or other adverse effects on organisms exposed to complex mixtures of pollutants in the highly fluctuating conditions that prevail in the environment (Kanzawa et al., 1997; Kortenkamp & Altenburger, 1998).

The distribution of observed concentrations should be used when evaluating ecological risk. The distributions of effective concentrations can be used to evaluate exposure pathways for plants, vertebrates, invertebrates, and microbial species. The exposure distributions are evaluated over area since soil composition varies little over time, but contaminants may not be equally distributed throughout the area. The distributions indicates the proportion of locations in an area where concentrations of the chemical are expected to be toxic to a particular proportion of species in the site community. Expert judgment plays a significant role because ecosystems are complex and do not lend themselves entirely to experiments or modelling.

1.6 METHODS OF REMEDIATION

Site contamination occurs as a result of industrialization processes, which means that it is a problem mainly experienced in developed countries or those countries currently undergoing economic transition or rapid urbanization. The total number of contaminated sites identified as requiring remediation worldwide has been estimated to be well over a million. Conservative estimates given by each country are in the high hundreds of thousands. A study conducted in the last 10 years suggests that the global remediation market is worth between 12 and 35 billion dollars (Industry Canada, 2005). The actual dollar amount could be much higher based on unassessed contaminated sites and remediation value that countries have not identified or completely assessed.

Within the United States, the Environmental Protection Agency has recognized an estimated 30,000 sites as candidates for immediate treatment (Ensley, 2000). These sites have been polluted with inorganic contaminants, organic contaminants, or a mixtures of both. The projected cost for remediation of sites that have been contaminated with heavy metals over a five year period exceeds $7.1 billion (Ensley, 2000). The high cost of cleanup of hazardous waste residue is caused, in part, to a lack of remedial efficiency and the high cost of available technologies. Existing conventional remediation techniques are based on civil and chemical engineering technologies including a wide variety of physical, chemical, thermal and combined treatments coupled with technologies to accelerate or reduce mass transport in the contaminated matrix. Many of these conventional remediation technologies are inadequate despite the billions of dollars spent on cleanup. The lack of available remedial technologies that can restore contaminated sites at reasonable cost has increased the pressure to limit waste cleanups to sites that pose the greatest risks to human health and the environment.

Metals can be found at most waste sites and are technologically difficult to remove from soils, unlike many organic contaminants, most heavy metals cannot be removed from the environment by chemical or biological transformation, although it may be possible to reduce the toxicity of arsenic by influencing speciation (National Research Council, 1999). Sources of anthropogenic metal contamination include smelting, electroplating, gas exhaust, energy and fuel production, the application of fertilizers, pesticides and municipal sludges to land, and industrial manufacturing (Blaylock and Huang, 2000; Cunningham et al., 1997; Raskin et al., 1994). The following section describes some of the conventional remediation technologies that are used to clean heavy metal polluted environments.

1.6.1 Conventional Remediation Technologies

Excavation and Landfill

The excavation of soil and subsequent landfill disposal is the most widely used method of cleaning sites that have been contaminated with heavy metals. A major criticism of this method is that contaminants are simply moved from one site to another without trying to destroy or stabilize onsite. Transport from the site location increase the likelihood of environmental release during uncontrolled movement. Landfills are designed to isolate the contaminated material from the surrounding environment so that liquid or gaseous interchange is minimized or controlled (Wood, 1997). Different techniques are commonly used at landfill sites to aid isolating the hazardous materials away from exposure points. Specifically, landfill caps reduce the amount of water infiltration and suppress the downward migration of contaminants, whereas underground vertical barriers like engineered liners inhibit lateral movement.

Impermeable or Containment Barriers

Impermeable barriers have been used to fully surround a source of groundwater contamination to isolate contaminants. They are a widely used as way of preventing the movement offsite of metals in groundwater (National Research Council, 1999). Engineered liners and compacted clays are used as a barrier at landfills to isolate the contaminated mass from the outside environment (Wood, 1997). This method may include the use of caps, horizontal / vertical walls, liners or a combination of all. The primary function of an impermeable cover is to retard the downward migration of metals by controlling the infiltration of water. Covering the cap with soil media can encourage vegetative growth and help to prevent the exposure of at-risk receptors. The cap usually consists of certain impermeable clays, lime, fly ash, concrete or asphalt, or synthetic membranes or geotextiles. The lateral movement of groundwater can be controlled by underground vertical barriers used around the perimeter of a contaminated site. Vertical barriers have been composed of clay mixtures, concrete, steel sheet piling, and synthetic membranes (Wood, 1997). Contaminants are not removed so that sites where barrier technologies have been installed normally have mandated long term or permanent deed restrictions that responsible parties must consider.

Permeable Reactive Barriers

A permeable reactive barrier (PRB) is a passive treatment zone of reactive material which is installed through which a dissolved contaminant plume must flow, typically under natural gradient (Interstate Technology & Regulatory Council, 2011). Metal contaminants are immobilized within the barrier as groundwater flows through the treatment zone. Reactive barriers can be created using any material that react with inorganic contaminants including zero valent iron (ZVI), emulsified zero valent iron (EZVI), zeolites, organophylic clays, slag, peat, apatite, polymer gels, or limes. Treatments specific to the remediation of arsenicals include ZVI, zeolite, slag, and ZVI-carbon combinations. PRBs require a comprehensive hydrologic characterization with the design based on a detailed understanding of subsurface heterogeneity and not on average values of hydraulic parameters (Korte, 2001). They are often used to treat localized areas where the possibility of contaminant plumes moving off site pose high risk to the surrounding environment. Where metals are concerned, sorption or precipitation within a reactive barrier can be regarded as restricting contaminant migration rather than as a permanent solution to the problem (Interstate Technology & Regulatory Council, 2011).

In-Situ Vitrification

In situ vitrification can be used to treat areas with high levels of organic or inorganic soil contamination. Soils are heated to temperatures between 1600 and 2000°C using an electric current passed between multiple electrodes placed in the ground to melt contaminated soil. When cool, the vitrification product is a chemically stable, leach-resistant, glass and crystalline material similar to obsidian or basalt rock (Wood, 1997). Volume reduction of the soil matrix is about 20-40%, as has been demonstrated at Superfund sites (Interstate Technology & Regulatory Council, 2011). Heavy metal contaminants are secured inside of the vitrified product and subsequently, removed and disposed of in an approved permitted landfill. While the vitrified product has significant positive long term characteristics, the technology is expensive and normally reserved for contamination that is not readily remediated by other methods.

Solidification and Stabilization

Solidification and stabilization refers to general category of processes used to treat both solid and liquids.

- Solidification suppresses the movement of contaminants in soils, sludges, and liquids by reducing their solubility or by decreasing the permeability of the matrix and encapsulating contaminants (Wilk, 2007).

- Stabilization reduces the solubility of a material through a chemical reaction, which may or may not change the physical nature of the material (Environmental Protection Agency, 2000).

The successful application of this technology is dependent on the capability of the media to mix with the stabilizing agent (National Research Council, 1999). The primary materials used in matrix stabilization are portland-type cements, pozzolanic materials, lime, silicates, clays, and polymers (Wood, 1997; National Research Council, 1999). The solidified matrix may require long-term monitoring, if left on site, to ensure that leaching of contaminants does not occur. This remediation method has only been in practice for about 20 years and so no long-term data are available.

In Situ Redox Manipulation

In situ redox manipulation reduces the mobility and at times toxicity of heavy metals that are a toxic risk in their oxidized form but not in reduced form (National Research Council, 1999). This remedial technique can be used to treat metals in soil and groundwater that may not be easily accessible from the surface. Redox manipulation requires the injection of chemical reducing agents below ground and/or the activation of naturally-occurring iron-reducing bacteria with nutrients, in order to create reducing conditions. Some of the more commonly injected reducing agents include ZVI, aluminum, sodium and zinc metals, and some specific iron compounds (Wood, 1997). Long-term monitoring and periodic retreatment may be necessary to minimize the possibility of contaminant mobilization by reoxidation (National Research Council, 1999).

Soil Flushing

The concept of soil flushing is similar to soil washing as it pertains to releasing contaminants from the solid phase of a soil and concentrate them in a liquid phase, which can be recovered and treated as waste water. Both remedial techniques use washing or extracting solutions, but soil flushing is an *in situ* process where the bulk soil mass is left onsite. The process of soil flushing involves the use of extracting chemicals, which are applied to the contaminated soil by surface flooding, sprinklers, leach fields, or by vertical or horizontal injection walls (National Research Council, 1999). The flushing solutions are recovered for disposal or treatment after leaching through the soil. This method is seldom used by itself as a complete clean-up method. Leachate recovery techniques that specialize in the recovery of the contaminant-rich water will commonly be used in conjunction with soil flushing.

Soil Washing

One of the major problems with the dig and haul methodology is that the majority of the soil being disposed of in a landfill consists of soil mass and not the actual contaminant. It is expensive to place large volumes of soil in a controlled landfill and it reduces the amount of space available for other materials. Soil washing is a process where contaminants bound to soil particles are separated from soil using a water-based system (Wood, 1997; CL:AIRE, 2007). The benefit of consolidating contaminants is that costs associated with disposal and treatment are decreased based on the reduction in volume of process residues. Contaminated soil is excavated from the site and taken to a washing facility where it is screened to remove debris and then treated with washing agents such as acids or chelates which displace or extract contaminants from soil particles (Dennis et al., 1994; National Research Council, 1999). The resulting leachate is concentrated with the contaminant and can be treated as waste water (Wood, 1997), which is a less expensive approach than the disposal of the total soil mass.

1.6.2 Bioremediation

Bioremediation and phytoremediation contain similar concepts but are two completely different remedial methods. Although both use living organisms to alter contaminated environments, bioremediation involves the manipulation of microbial populations, and phytoremediation concerns the use of higher plants. Bioremediation refers to a process through which metal contaminants are modified as a direct result of microbial activity (National Research Council, 1999). The objective may be to mobilize, immobilize, or reduce the toxicity of metals in soil or water depending on the ultimate goals of remediation (Smith et al., 1994). If reducing conditions are maintained by the addition of suitable substrates, such as oxygen and nutrients, inorganic contaminants will remain in their highly insoluble, immobile forms (National Research

Council, 1999; Wood, 1997). However, the immobilization of some contaminants should be viewed as a temporary fix and not a final solution to the problem.

Of the disadvantages of conventional remediation methods, cost is the primary driving force behind the search for alternative remediation technologies. Some micro-organism-based remediation techniques, such as bioremediation, show potential for their ability to degrade and detoxify certain contaminants. Although these biological systems are less amenable to environmental extremes than other traditional methods, they have the perceived advantage of being more cost-effective (Cunningham et al., 1997). Bioremediation is most applicable for sites that have been contaminated with organic pollutants, and as such, this condition has been the focus of the majority of bioremediation research. Because heavy metals are not subject to degradation, several researchers have suggested that bioremediation has limited potential to remediate metal-polluted environments. In contrast, plants are known to sequester certain metal elements in their tissues (Marschner, 1995) and may prove useful in the removal of metals from contaminated soils (Chaney, 1983).

1.6.3 Phytoremediation

Conventional remediation technologies are used to clean the vast majority of metal-polluted sites. The reason is because they are fast, relatively insensitive to heterogeneity in the contaminated matrix, and can function over a wide range of oxygen, pH, pressure, temperature, and osmotic potentials (Cunningham et al., 1997). However, they also tend to be clumsy, costly, and disruptive to the surrounding environment (Cunningham and Ow, 1996). Over the past decade there has been increasing interest for the development of plant-based remediation technologies known as phytoremediation, which have the potential to be low-cost, low-impact, visually benign, and environmentally sound (Cunningham and Ow, 1996).

Phytoremediation is a word formed from the Greek prefix “phyto” meaning plant, and the Latin suffix “remedium” meaning to clean or restore. The term actually refers to a diverse collection of plant-based technologies that use either naturally occurring or genetically engineered plants for cleaning contaminated environments (Flathman and Lanza, 1998). The primary motivation behind the development of phytoremediative technologies is the potential for low-cost remediation (Ensley, 2000). Although the term phytoremediation is a relatively recent invention, the practice is not (Brooks, 1998a; Cunningham et al., 1997).

Some plants, which grow on metalliferous soils, have developed the ability to accumulate massive amounts of the indigenous metals in their tissues without exhibiting symptoms of toxicity (Baker and Brooks, 1989; Baker et al., 1991; Reeves and Brooks, 1983). Chaney (1983) was the first to suggest using these “hyperaccumulators” for the phytoremediation of metal-polluted sites. However, hyperaccumulators were later believed to have limited potential in this area because of their small size and slow growth, which limit the speed of metal removal (Comis, 1996; Cunningham et al., 1995; Ebbs et al., 1997).

By definition, a hyperaccumulator must accumulate at least 1000 $\mu g\ g^{-1}$ of Co, Cu, Cr, Pb, or Ni, or 10,000 $\mu g\ g^{-1}$ (i.e. 1%) of Mn or Zn in the dry matter (Reeves and Baker, 2000; Wantanabe, 1997). Some plants tolerate and accumulate high concentrations of metal in their tissue but not at the level required to be called hyperaccumulators. These plants are often called moderate metal-accumulators or moderate accumulators (Kumar et al., 1995). The lack of viable plant alternatives for phytoremediation reduced the amount of phytoremediation research conducted between the mid 1980’s and the early half of the 1990’s. The search for plants for phytoremediation centered on the Brassica family, to which many hyperaccumulators belong (Cunningham et al., 1995). Through the work of various researchers, particularly Kumar et al.

(1995) and Dushenkov et al. (1995), several high-biomass, metal-accumulating species were identified. Phytoremediation research gained momentum after the discovery of these plants, and most of our understanding of this emerging technology has come from research reports published since 1995.

Phytoremediation consists of a collection of four different plant-based technologies, each having a different mechanism of action for the remediation of metal-polluted soil, sediment, or water. These include:

- rhizofiltration, which involves the use of plants to clean various aquatic environments;
- phytostabilization, where plants are used to stabilize rather than clean contaminated soil;
- phytovolatilization, which involves the use of plants to extract certain metals from soil and then release them into the atmosphere through volatilization; and
- phytoextraction, where plants absorb metals from soil and translocate them to the harvestable shoots where they accumulate.

Although plants show some ability to reduce the hazards of organic pollutants (Carman et al., 1998; Cunningham et al., 1995; Gordon et al., 1997), the greatest progress in phytoremediation has been made with metals (Blaylock and Huang, 2000; Salt et al., 1995a; Watanabe, 1997). Phytoremediative technologies which are soil-focused are suitable for large areas that have been contaminated with low to moderate levels of contaminants. Sites which are heavily contaminated cannot be cleaned through phytoremediative means because the harsh conditions will not support plant growth. The depth of soil which can be cleaned or stabilized is restricted to the root zone of the plants being used. Depending on the plant, this depth can range from a few inches to several meters (Schnoor et al., 1995). Phytoremediation should be viewed as a long-term remediation solution because many cropping cycles may be needed over several years to reduce metals to acceptable regulatory levels. This remediation technology is competitive with, and may be superior to existing conventional technologies at sites where applicable. Phytoremediation is not the solution for all hazardous waste problems but is rather a tool that can be used, possibly in conjunction with other clean-up methods, to remediate polluted environments.

Rhizofiltration

Metal pollutants in industrial-process water and in groundwater are most commonly removed by precipitation or flocculation, followed by sedimentation and disposal of the resulting sludge (Ensley, 2000). A promising alternative to this conventional clean-up method is rhizofiltration, a phytoremediative technique designed for the removal of metals in aquatic environments. The process involves raising plants hydroponically and transplanting them into metal-polluted waters where plants absorb and concentrate the metals in their roots and shoots (Dushenkov et al., 1995; Flathman and Lanza, 1998; Salt et al., 1995a; Zhu et al., 1999). Root exudates and changes in rhizosphere pH also may cause metals to precipitate onto root surfaces. As they become saturated with the metal contaminants, roots or whole plants are harvested for disposal (Flathman and Lanza, 1998; Zhu et al., 1999). Most researchers believe that plants for phytoremediation should accumulate metals only in the roots (Dushenkov et al., 1995; Flathman and Lanza, 1998; Salt et al., 1995a). Dushenkov et al. (1995) explains that the translocation of metals to shoots would decrease the efficiency of rhizofiltration by increasing the amount of contaminated plant residue needing disposal. In contrast, Zhu et al. (1999) suggest that the efficiency of the process can be increased by using plants which have a heightened ability to absorb and translocate metals within the plant. Despite this difference in opinion, it is apparent that proper plant selection is the key to ensuring the success of rhizofiltration as a water cleanup strategy.

Dushenkov and Kapulnik (2000) describe the characteristics of the ideal plant for rhizofiltration. Plants should be able to accumulate and tolerate significant amounts of the target metals in conjunction with easy handling, low maintenance cost, and a minimum of secondary waste requiring disposal. It is also desirable for plants to produce significant amounts of root biomass or root surface area. Several aquatic species have the ability to remove heavy metals from water, including water hyacinth (*Eichhornia crassipes* (Mart.) Solms; Kay et al., 1984; Zhu et al., 1999), pennywort (*Hydrocotyle umbellata* L.; Dierberg et al., 1987), and duckweed (*Lemna minor* L.; Mo et al., 1989). However, these plants have limited potential for rhizofiltration, because they are not efficient at metal removal, a result of their small, slow-growing roots (Dushenkov et al., 1995). These authors also point out that the high water content of aquatic plants complicates their drying, composting, or incineration. Despite limitations, Zhu et al. (1999) indicated that water hyacinth is effective in removing trace elements in waste streams. Terrestrial plants are thought to be more suitable for rhizofiltration because they produce longer, more substantial, often fibrous root systems with large surface areas for metal sorption. Sunflower (*Helianthus annuus* L.) and Indian mustard (*Brassica juncea* Czern.) are the most promising terrestrial candidates for metal removal in water. The roots of Indian mustard are effective in the removal of Cd, Cr, Cu, Ni, Pb, and Zn (Dushenkov et al., 1995), and sunflower removes Pb (Dushenkov et al., 1995), U (Dushenkov et al., 1997a), ^{137}Cs, and ^{90}Sr (Dushenkov et al., 1997b) from hydroponic solutions.

Rhizofiltration is a cost-competitive technology in the treatment of surface water or groundwater containing low, but significant concentrations of heavy metals such as Cr, Pb, and Zn (Ensley, 2000). The commercialization of this technology is driven by economics as well as by technical advantages, including 1) applicability to many problem metals, 2) ability to treat high volumes, 3) lesser need for toxic chemicals, 4) reduced volume of secondary waste, 5) possibility of recycling, and 6) increased likelihood of regulatory and public acceptance (Dushenkov et al., 1995). However, the application of this plant-based technology may be more challenging and susceptible to failure than other methods of similar cost. The production of hydroponically grown transplants and the maintenance of successful hydroponic systems in the field will require the expertise of qualified personnel, and the facilities and specialized equipment required can increase overhead costs (Prasad and Freitas, 2003). Perhaps the greatest benefit of this remediation method is related to positive public perception. The use of plants at a site where contamination exists instills the perception of cleanliness and progress to the general public in an area that would have usually been perceived as polluted (Dushenkov et al. 1995).

Phytostabilization

Phytostabilization, also known as phytorestoration, is a plant-based remediation technique that stabilizes wastes and prevents exposure pathways via wind and water erosion; provides hydraulic control, which suppresses the vertical migration of contaminants into groundwater; and physically and chemically immobilizes contaminants by root sorption and by chemical fixation with various soil amendments (Berti and Cunningham, 2000; Cunningham et al., 1995; Flathman and Lanza, 1998; Salt et al., 1995a; Schnoor, 2000). Sometimes there is no immediate effort to clean metal-polluted sites, either because the responsible companies no longer exist or because the sites are not of high priority on a remediation agenda (Berti and Cunningham, 2000). The conventional method by which metal toxicity is reduced is by in-situ inactivation, a remediation technique that employs the use of soil amendments to immobilize or fix metals to the soil by changing the soil's physical and chemical characteristics to increase adsorption and binding. Although metal migration is minimized, soils are often subject to erosion and still pose an exposure risk to humans and other animals. Unlike other techniques, the goal of phytostabilization is not to remove metal contaminants from a site, but rather to stabilize them and reduce the risk to human health and the environment by limiting transport. This technique is actually a modified version of the in-place inactivation method in which the function of plants is secondary to the role of soil amendments.

The most comprehensive and up-to-date explanation of the phytostabilization process is offered by Berti and Cunningham (2000). Before planting, the contaminated soil is plowed to prepare a seed bed and to incorporate lime, fertilizer, or other amendments for inactivating metal contaminants. Soil amendments should fix metals rapidly following incorporation, and the chemical alterations should be long lasting if not permanent. The most promising soil amendments are phosphate fertilizers, organic matter or bio-solids, iron or manganese oxyhydroxides, natural or artificial clay minerals, or mixtures of these amendments.

Plants chosen for phytostabilization should be poor translocators of metal contaminants to aboveground plant tissues that could be consumed by humans or animals. The lack of appreciable metals in shoot tissue also eliminates the necessity of treating harvested shoot residue as hazardous waste (Flathman and Lanza, 1998). Selected plants should be easy to establish and care for, grow quickly, have dense canopies and root systems, and be tolerant of metal contaminants and other site conditions which may limit plant growth. The research of Smith and Bradshaw (1979) led to the development of two cultivars of *Agrostis tenuis* Sibth and one of *Festuca rubra* L. which are now commercially available for the phytostabilization of Pb-, Zn-, and Cu-contaminated soils.

Phytostabilization is most effective at sites having fine-textured soils with high organic-matter content but is suitable for treating a wide range of sites where large areas of surface contamination exist (Berti and Cunningham, 2000; Cunningham et al., 1995). However, some highly contaminated sites are not suitable for phytostabilization, because plant growth and survival is not a possibility (Berti and Cunningham, 2000). At sites which support plant growth, site managers must be concerned with the migration of contaminated plant residue off site (Schnoor, 2000) or disease and insect problems which limit the longevity of the plants. Phytostabilization has advantages over other soil-remediation practices in that it is less expensive, less environmentally evasive, easy to implement, and offers aesthetic value (Berti and Cunningham, 2000; Schnoor, 2000). When decontamination strategies are impractical because of the size of the contaminated area or the lack of remediation funds, phytostabilization is advantageous (Berti and Cunningham, 2000). It may also serve as an interim strategy to reduce risk at sites where complications delay the selection of the most appropriate technique for the site.

Phytovolatilization

Some metal contaminants such as As, Hg, and Se may exist as gaseous species in the environment. In recent years, researchers have searched for naturally occurring or genetically modified plants that are capable of absorbing elemental forms of these metals from the soil, biologically converting them to gaseous species within the plant, and releasing them into the atmosphere. This process is called phytovolatilization, the most controversial of all phytoremediation technologies. Mercury and Se are toxic (Suszcynsky and Shann, 1995; Wilber, 1980), and there is doubt about whether the volatilization of these elements into the atmosphere is safe (Watanabe, 1997). Selenium phytovolatilization has been given the most attention to date (Banuelos et al., 1993; Lewis et al., 1966; McGrath, 1998; Terry et al., 1992), because this element is a serious problem in many parts of the world where there are areas of Se-rich soil (Brooks, 1998b). However, there has been a considerable effort in recent years to insert bacterial Hg ion reductase genes into plants for the purpose of Hg phytovolatilization (Bizily et al., 1999; Heaton et al., 1998; Rugh et al., 1996, 1998). Although there have been no efforts to genetically engineer plants with enhanced abilities to volatilize As, studies have looked at plants and their ability to metabolize arsenic into arsine gas (Mirza et al., 2011).

According to Brooks (1998b), the release of volatile Se compounds from higher plants was first reported by Lewis et al. (1966). Terry et al. (1992) report that members of the Brassicaceae are capable of releasing up to 40g Se $ha^{-1}day^{-1}$ as various gaseous compounds. Some aquatic plants, such as cattail (*Typha latifolia* L.), are also good for Se phytoremediation (Pilon-Smits et al., 1999). Unlike plants that are being used for Se volatilization, those which volatilize Hg are genetically modified organisms. *Arabidopsis thaliana* L. and tobacco (*Nicotiana tabacum* L.) have been genetically modified with bacterial organomecurial lyase (*merB*) and mercuric reductase (*merA*) genes (Heaton et al., 1998; Rugh et al., 1998). These plants absorb elemental Hg(II) and methyl mercury (MeHg) from the soil and release volatile Hg(O) from the leaves into the atmosphere (Heaton et al., 1998).

The phytovolatilization of Se and Hg into the atmosphere has several advantages. Volatile Se compounds, such as dimethylselenide, are 1/600 to 1/500 as toxic as inorganic forms of Se found in the soil (DeSouza et al., 2000). The phytovolatilization process removes the contaminant from the soil and releases the less toxic volatile form decreasing site contamination and minimizing air impact. The volatilization of Se and Hg is also a permanent site solution, because the inorganic forms of these elements are removed and the gaseous species are not likely to be redeposited at or near the site (Atkinson et al., 1990; Heaton et al., 1998). Sites that utilizing this technology should not require extensive management after the initial planting. This remediation method has the added benefits of minimal site disturbance, less erosion, and no need to dispose of contaminated plant material (Heaton et al., 1998; Rugh et al., 2000). Heaton et al. (1998) suggest that the addition of Hg(O) into the atmosphere would not contribute significantly to the atmospheric pool. However, those who support this technique also agree that phytovolatilization would not be wise for sites near population centers or at places with unique meteorological conditions that promote the rapid deposition of volatile compounds (Heaton et al.,1998; Rugh et al., 2000). Unlike other remediation techniques, once contaminants have been removed via volatilization, there is a loss of control over their migration to other areas. Despite the controversy surrounding phytovolatilization, this technique is a promising tool for the remediation of Se and Hg contaminated soils.

Phytoextraction

Phytoextraction is the most commonly recognized of all phytoremediation technologies, and is the focus of the present research work. The terms phytoremediation and phytoextraction are sometimes incorrectly used as synonyms, but phytoremediation is a concept while phytoextraction is a specific cleanup technology. The phytoextraction process involves the use of plants to facilitate the removal of metal contaminants from a soil matrix (Kumar et al., 1995). In practice, metal-accumulating plants are seeded or transplanted into metal-polluted soil and are cultivated using established agricultural practices. The roots of established plants absorb metal elements from the soil and translocate them to the above-ground shoots where they accumulate. If metal availability in the soil is not adequate for sufficient plant uptake, chelates or acidifying agents may be used to liberate them into the soil solution (Huang et al., 1997a; Lasat et al., 1998). After sufficient plant growth and metal accumulation, the above-ground portions of the plant are harvested and removed, resulting the permanent removal of metals from the site. The remaining root structure can either allowed to continue growth or new plants can be installed.

As with soil excavation, the disposal of contaminated material is a concern. Some researchers suggest that the incineration of harvested plant tissue dramatically reduces the volume of the material requiring disposal (Kumar et al., 1995). In some cases valuable metals can be extracted from the metal-rich ash and serve as a source of revenue, thereby offsetting the expense of remediation (Comis, 1996; Cunningham and Ow, 1996). Phytoextraction should be viewed as a long-term remediation effort, requiring many cropping cycles to reduce metal concentrations (Kumar et al., 1995) to acceptable levels. The time required for remediation is dependent on the type and extent of metal contamination, the length of the growing season, and the efficiency of metal removal by plants, but normally ranges from 1 to 20 years (Blaylock and Huang, 2000; Kumar et al., 1995). This technology is suitable for the remediation of large areas of land that are contaminated at shallow depths with low to moderate levels of metal- contaminants (Kumar et al., 1995; Wantanabe, 1997).

Many factors determine the effectiveness of phytoextraction in remediating metal-polluted sites (Blaylock and Huang, 2000). The selection of a site that is conducive to this remediation technology is of primary importance. Phytoextraction is applicable only to sites that contain low to moderate levels of metal pollution, because plant growth is not sustained in heavily polluted soils. Soil metals should also be bioavailable, or subject to absorption by plant roots. The land should be relatively free of obstacles, such as fallen trees or boulders, and have an acceptable topography to allow for normal cultivation practices, which employ the use of agricultural equipment. As a plant-based technology, the success of phytoextraction is inherently dependent upon several plant characteristics. The two most important characters include the ability to accumulate large quantities of biomass rapidly and the ability to accumulate large quantities of environmentally important metals in the shoot tissue (Blaylock et al., 1997; Cunningham and Ow, 1996; Kumar et al., 1995; McGrath, 1998). It is the combination of high metal accumulation and high biomass production that results in the most metal removal. Ebbs et al. (1997) reported that *B. juncea*, while having one-third the concentration of Zn in its tissue, is more effective at Zn removal from soil than *T. caerulescens*, a known hyperaccumulator of Zn. This advantage is due primarily to the fact that *B. juncea* produces ten-times more biomass than *T. caerulescens*. Plants being considered for phytoextraction must be tolerant of the targeted metal, or metals, and be efficient at translocating them from roots to the harvestable above-ground portions of the plant (Blaylock and Huang, 2000). Other desirable plant characteristics include the ability to tolerate difficult soil conditions (e.g., soil pH, salinity, soil structure, water content), the production of a dense root system, ease of care and establishment, and few disease and insect problems. Although some plants show promise for phytoextraction, there is no plant which possesses all of these desirable traits. Finding the perfect plant continues to be the focus of many plant-breeding and genetic-engineering research efforts.

Metal Availability in Soil

A major factor influencing the efficiency of phytoextraction is the ability of plants to absorb large quantities of metal in a short period of time. Although the total soil metal content may be high, it is the fraction that is readily available in the soil solution that determines the efficiency of metal absorption by plant roots. Soil pH is a major factor influencing the availability of elements in the soil for plant uptake (Marschner, 1995). Under acidic conditions, H^+ ions displace metal cations from the cation exchange complex (CEC) of soil components and cause metals to be released from variable-charged clays to which they have been chemisorbed (i.e. specific adsorption; McBride, 1994). The retention of metals to soil organic matter is also weaker at low pH, resulting in more available metal in the soil solution for root absorption. These authors and others report that acid chelates the soil, thereby enhancing its solubility and availability in the soil solution. Soil pH is a major effect on both metals availability and plant selection based on environmental tolerances.

Plant Selection

As a plant-based technology, the success of phytoremediation is inherently dependent upon proper plant selection. As previously discussed, plants used for phytoremediation must be fast growing and have the ability to accumulate large quantities of environmentally important metal contaminants in their shoot tissue (Blaylock et al., 1997; Cunningham and Ow, 1996; Kumar et al., 1995; McGrath, 1998). Many plant species have been screened to determine their usefulness for phytoremediation.

Poplar Trees

Poplar trees from the genus Populus (family Salicaeae) have been broadly studied for biomass and phytoremediation. Poplars are closely related to willows and cottonwoods (Tuskan et al., 2004). Poplar trees are commonly used for groundwater remediation because they are fast growing and can survive in a broad range of climates. They can also draw large amounts of water through soil and directly from aquifers through deep rooted planting techniques. As such, the poplar has the capacity to draw a greater amount of dissolved contaminant and reduce the risk of off-site exposure. Phytoremediation has a cost advantage over other treatment technologies because it relies on the use of the natural growth processes of plants with minimal operational and maintenance costs.

Poplar trees are typically used in phytoremediation of pollutants because they are long lasting (between 25 and 50 years), fast growing, hardy, and transpire large quantities of water

(Schnoor et al., 1995). Poplar trees can grow six to eight feet per year, reaching heights of 30 to 45 feet depending on species. For the first two years of the trees life the expected transpiration could be 200 gallons per tree per year (Matso, 1995). Grown poplars can uptake up to 100 liter per day of groundwater (Sutherson, 1997).

Poplar root distribution can increase the transfer of oxygen throughout the root zone. This increases the equilibrium balance of arsenic, favoring arsenate and uptake through the plant system. Poplars can be adapted to various climates and coupled with deep rooting techniques, can be used to draw water from deep underground. The removal of groundwater can create a hydraulic depression that stops the transport of contaminants.

As in a natural pump and treat system, the tree root system of a poplars will transpire water and draw down the water table in the areas below the tree. However, a disadvantage of phytoremediation is that the roots must be able to reach the contaminated groundwater for remediation, therefore, making phytoremediation an unfeasible remedial technology for deep contaminated aquifers. Some companies such as Treemediation® have patented systems to treat deep contaminated soil and groundwater (Quinn et al., 2000). Table 1.2 lists recorded and estimated evapotranspiration rates by poplar trees (Chappell, 1997).

Hybrid forms of the poplar tree have been utilized at sites with chemical contamination of soil and groundwater. Most hybrid varieties are fast-growers, perennial, long-lived (25-50 years) and tolerant adverse conditions (Schnoor et al., 1995). Poplar roots can extend towards the water table and establish root mass that can potentially consume rather large quantities of water. In amenable soils and temperate conditions, hybrid poplars can grow 2 meters in the first growing season and reach a height of 5 to 8 meters after 3 years (Schnoor et al., 1995).

Table 1.2 Estimates of evapotranspiration rates by hybrid poplars

Rate	Source
100 to 200 L/day/tree (~26 to 53 gallon/day) for 5 year old trees	Newman et al (1997)
100 L/day/tree for a 5 year old tree under optimal conditions	Stomp et al (1994)
13 gallons per day (estimated) when trees are calculated as low-flow	Sheldon Nelson (1996)
1.6 to 10 gpd/tree (observed) sap flow rates for young hybrid poplars at the Aberdeen Proving grounds in Maryland	Compton (1998)

In summary, the advantages of hybrid poplar trees as phytoremediation tools include:

- Extremely fast growing;
- Tolerates poor agronomic conditions;
- Tolerant of high organics concentrations;
- High levels of water uptake; and
- Amenable to directed path root growth.

Hybrid poplars are responsive to remediation designs that focus on increased root depth by preferential path designs. The advantages listed allow for hybrid poplars to be utilized in diverse conditions and with different types of contaminates.

Advantages of Phytoremediation

Phytoremediation can cost about a tenth of conventional remediation technologies (U.S. Environmental Protection Agency, 2000). Initial capital costs is the largest expenditure for the system with minimal costs associated with operation and maintenance. Utilizing phytoremediation as a polishing step to conventional remediation methods reduces both cleanup time and operations and maintenance costs. The cost of phytoremediation is 10-50% of the cost of mechanical, thermal, or chemical treatments (Flathman and Lanza, 1998). Phytoremediation can be permanent in situ solution, as most conventional methods result in the transfer of contaminants from one medium to another.

Limitations of Phytoremediation

Despite the diversity in types, the application of phytoremediation technology is limited by a number of factors. The limitations are that contamination must be shallow (unless using deep rooting technologies), the site must be a large enough to apply agronomic techniques, there must be sufficient remedial time, and its effectiveness is affected by contaminant variability, weather variability, animal and insect damage, and the presence of toxic chemicals and salt. Phytoremediation can only work at sites that are well suited for plant growth. This means that the concentration of pollutants cannot be toxic to the plants, and the pollution cannot be so deep in the soils or groundwater that plant roots cannot reach it. As a result, phytoremediation may be a good strategy for sites conducive to plant growth with shallow to moderate contamination. At sites with high initially toxic concentrations, phytoremediation could be used as a polishing step or may not be a viable option.

Costs of Phytoremediation

In the United States the costs of remediation is estimated to be surpassing 700 billion dollars for the tens of thousands of contaminated sites that need to be cleaned-up (Revkin, 2001). So far, 410 Superfund Sites (32%) on the National Priority List (NPL) have been remediated of hazardous waste to levels safe for human health and the environment. The most common technologies used in these clean-up projects was excavating and removing hazardous soil and solid waste (45%), covering the landfill with a protective cap (39%) and pumping and treating contaminated groundwater (34%). Cost estimates for excavation and disposal range from $270.00 to $460.00 per ton depending on the nature of hazardous materials and methods of excavation. Approximate industry costs for capping a contaminated site are $175,000 to $225,000 per acre (www.frtr.gov). These technologies are costly and instead of eliminating contamination, they either move the waste restrict access to the public.

1.7 MODEL DEVELOPMENT

Visualization and graphics have made a huge impact on the ability of environmental managers to simulate dynamic systems. As computers have become more accessible and software easier to use has resulted in areas of modeling that would have been unthinkable just a few years ago. Phytoremediation modelling based on biotic components is a relatively new challenge. These models have only become really useful, however, in connection with computer applications. Mathematical models and simulation software (including numerical analysis) are therefore strongly dependent on each other. Mathematical models are utilized in environmental science to help to evaluate different scenarios and to make a decision based on all the available information. Human rational can promote errors and/or biases (Sterman 1989), particularly in complex systems.

Within the past forty years, mathematical approaches have been used to illustrate the soil-plant interaction. These can be applied to modeling phytoremediation systems specific to long term evaluations. Mathematical algorithms and software solutions have been employed to understanding phytoremediation processes. These models are mathematically intensive and very specialized. The stochastic approach has provided differential equation solution sets as defined by models for compartmentalization of the plant physiology (Ouyang 2007, Ouyang 2008).

The most important concerns about phytoremediation are: 1) bioavailability; 2) uptake rate by roots; 3) proportion of contaminant “fixed” within the roots; 4) rate of xylem loading/ translocation to shoots; and 5) cellular tolerance to toxic contaminants (Environmental Protection Agency, 2000; Sarma, 2011; Deuren, 2006). It is possible to have all of these compartments constructed using STELLA, considering the internal interactions of the contaminant according to the plants' metabolism and uptake of water.

STELLA

STELLA (Strongly Typed Lips Like Language; system thinking software of Isee Systems) is a commercially available, dynamic software that implements pictographic modeling representation based upon four basic components: stocks, flows, connectors and converters. The key features of STELLA consist of the following four tools: (1) Stocks, which are the state variables for accumulations. They collect whatever flows into and out of them; (2) Flows, which are the exchange variables and control the arrival or the exchanges of information between the state variables; (3) Converters, which are the auxiliary variables. These variables can be represented by constant values or by values depending on other variables, curves or functions of various categories; and (4) Connectors, which are to connect among modeling features, variables, and elements. STELLA has been widely used in biological, ecological, and environmental sciences (Hannon and Ruth, 2001; Peterson and Richmond, 1996; Costanza et al., 2004; Aassine and El Jai, 2002).

1.8 SUMMARY OF LITERATURE REVIEW

The pollution of soil and water with heavy metals is an important environmental concern today. Contaminant metals are among the most recalcitrant forms of contamination found at waste sites, and their remediation in soils are some the most technically difficult. The projected cost for remediation of areas containing heavy metals pollutants by conventional means is in the tens of billions and will only increase as time progresses**.** The high cost of existing cleanup technologies led to the search for new cleanup technologies that have the potential to be low-cost, low-impact, visually benign, and environmentally sound. Phytoremediation is a concept that involves the use of plants to clean or stabilize contaminated environments. Phytoremediation is another tool to be used alone or in conjunction with existing remediation technologies. However, in areas that have been contaminated with low to moderate levels of heavy metals phytoremediation has some advantages over conventional cleanup methods, the primary one being low cost.

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CHAPTER 2
ARSENIC SPECIATION
DRIVING RISK BASED CORRECTIVE ACTION

This chapter has been written as a journal article[1] and is presented in its entirety. This chapter aims to demonstrate that arsenate and not arsenite is the more appropriate species on which to base remediation at sites with certain soil conditions, such as well drained, upland soils.

2.1 ABSTRACT

The toxicity of arsenic depends on a number of factors including its valence state. The more potent trivalent arsenic [arsenite (As^{3+})] inhibits a large number of cellular enzymatic pathways involved in energy production, while the less toxic pentavalent arsenic [arsenate (As^{5+})] interferes with phosphate metabolism, phosphoproteins and ATP formation (uncoupling of oxidative phosphorylation). Environmental risk based corrective action for arsenic contamination utilizes data derived from arsenite studies of toxicity to be conservative. However, depending upon environmental conditions, the arsenate species may predominate substantially, especially in well aeriated surface soils. Analyses of soil concentrations of arsenic species at two sites in northeastern Texas historically contaminated with arsenical pesticides yielded mean arsenate concentrations above 90% of total arsenic with the majority of the remainder being the trivalent arsenite species. Ecological risk assessments based on the concentration of the trivalent arsenite species will lead to restrictive remediation requirements that do not adequately reflect the level of risk associated with the predominate species of arsenic found in the soil. The greater concentration of the pentavalent arsenate species in soils would be the more appropriate species to monitor remediation at sites that contain high arsenate to arsenite ratios.

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[1] Marlborough, S.J. and Wilson, V.L. 2015. Arsenic Speciation Driving Risk Based Corrective Action. Sci. Total Envir. 520 (2015) 253–259.

Highlights

- Arsenic speciation in aerated soils indicates a substantial bias for arsenate
- Seasonal rainfall and short term flooding does not affect the ratio of arsenite to arsenate in well-drained soils.
- Remediation should be focused on arsenate instead of arsenite in well aerated soils
- Increased arsenate in soils may increase effectiveness of phytoremediation

Keywords: Allometric Scaling, Arsenic Speciation, Ecology, Remediation, Risk Assessment, Aerated Soils, and Shrew

2.2 INTRODUCTION

Arsenic contamination is an issue of concern worldwide and it is a considerable risk factor in various countries including Bangladesh, Taiwan, India, Mexico, China, Chile, Argentina, Russia, Great Britain and USA (Adriano, 2001; World Health Organization, 2001). As a natural element, arsenic is widespread and ranks twentieth in crustal abundance, fourteenth in seawater, and twelfth in the human body (Agency for Toxic Substances and Disease Registry, 2007; Ahuja, 2008). In the last century, arsenic based pesticides, herbicides, and insecticides were applied throughout the United States that subsequently led to considerable contamination of domestic and agricultural land (Agency for Toxic Substances and Disease Registry, 2007; Bhattacharya et al., 2007). Arsenic has been released into the environment in both organic and inorganic forms. The two arsenic species most important to toxicology are also the most commonly observed in natural environments, trivalent arsenic [arsenite (As^{3+})] and pentavalent arsenic [arsenate (As^{5+})]. Arsenite is considered to be the significantly more potent than arsenate due at least in part to the more rapid cellular uptake of the trivalent moiety (Agency for Toxic Substances and Disease Registry, 2007; Dopp et al., 2004; Jain and Loeppert, 2000).

Arsenic interferes with over 200 enzymes involved in cellular energy production and metabolism (Agency for Toxic Substances and Disease Registry, 2007; Dopp et al., 2004; Singh et al., 2011). Arsenite rapidly binds to sulfhydryl groups of proteins resulting in increases in reactive oxygen species and inhibiting enzyme functions, while the less acutely toxic pentavalent arsenate is more effective at perturbing phosphoproteins and ATP production (Hughes, 2011).

In the U.S., more than 90% of total imported arsenic is for agricultural purposes. These include production of wood preservatives (74% of total), herbicides, insecticides, algicides, fungicides, desiccants, anti-parasitic medications and growth stimulants for plants and animals (Woolson, 1975; Agency for Toxic Substances and Disease Registry, 2007). The widespread agricultural use of arsenicals over several decades has left behind a legacy of highly contaminated soils in orchards and farmlands. Some old orchard fields contain up to 2500 mg/kg of total residual arsenic (average arsenic levels in soils range from 0.1 to 40 mg/kg (mean = 6 mg/kg)), raising concerns over the possibility of food chain and ground water contamination from residual arsenic in these soils (Agency for Toxic Substances and Disease Registry, 2007; Woolson, 1977; World Health Organization, 2001).

Different arsenic-containing compounds vary considerably in their toxicity to mammals (Agency for Toxic Substances and Disease Registry, 2007; Ng et al., 1998). While some compounds are highly toxic (AsH3), others are considered essentially non-toxic (arsenobetaine and arsenocholine, also known as “fish arsenic”) (Agency for Toxic Substances and Disease Registry, 2007; Agency for Toxic Substances and Disease Registry, 2009). A general ranking of arsenical toxicity, from highest to lowest, is as follows: Arsine gas > inorganic trivalent compounds > organic trivalent compounds > inorganic pentava-lent compounds > organic pentavalent compounds > elemental arsenic (Woolson, 1977). Factors other than speciation may also influence toxicity. These include physical state, solubility, particle size, the rate of absorption into cells, the rate of elimination, fitness or health of the patient and an individual's genetic background (Agency for Toxic Substances and Disease Registry, 2007; Agency for Toxic

Substances and Disease Registry, 2009; Dopp et al., 2004). Arsenate and arsenite are the most common forms of arsenic observed in most environments and to which humans are most commonly exposed (Adriano, 2001; Agency for Toxic Substances and Disease Registry, 2007; Agency for Toxic Substances and Disease Registry, 2009; Ahuja, 2008).

The remediation or removal of arsenic from contaminated waters has been the focus of much scientific attention. The widespread occurrence of arsenic in U.S. ground waters, as well as concerns over the mass-poisonings of the people of Bangladesh and India by long-term arsenic ingestion have led to development of many technologies designed to remove arsenic from drinking water (Ahuja, 2008; Jekel, 1994; Tassi et al., 2004). The development of specific technologies for removal of arsenic from soils and sediments has received much less attention.

Arsenic speciation analysis can be useful in understanding the redox potential of soil. Soils contaminated with arsenic that are aerobic will favor arsenate over arsenite, as illustrated in the data. Arsenate can follow the same metabolic pathway as phosphate and has been shown in other studies to increase plant growth. The concentration of arsenate in soils can be utilized to design a phytoremediation system focused on uptake kinetics of phosphate. Proper installation of phytoremediation systems can increase available oxygen in the soil to change the redox potential. As arsenate is removed from the soil by uptake through the plant, remaining arsenite will be oxidized to arsenate and taken up by the plant system. Plants contaminated with arsenic generally confer less of a risk of toxicity to mammals due to metabolism of inorganic arsenic into less toxic organic forms (Agency for Toxic Substances and Disease Registry, 2007; Agency for Toxic Substances and Disease Registry, 2009).

Arsenite

The toxicity of arsenite (As^{3+}) is based upon its high affinity for sulf-hydryl (–SH) groups (Agency for Toxic Substances and Disease Registry, 2007; Davidson et al., 1986; Yan-Chu, 1994). Sulfhydryl groups (also known as thiol groups) are found in proteins that contain cysteine residues and in other important cellular compounds. The reaction between arsenite and enzymatic sulfhydryl groups leads to inactivation of a variety of enzymes, which is believed to be the cause of the overt toxicity of arsenite. Although numerous cellular enzymes are susceptible to arsenite-mediated deactivation, those enzymes involved in the tricarboxylic acid cycle (Kreb's cycle) are particularly sensitive (Agency for Toxic Substances and Disease Registry, 2007; Agency for Toxic Substances and Disease Registry, 2009; Momplaisir et al., 2001; Rochette et al., 1998). In most cases, enzyme activity can be restored by administration of mono- and dithiols. British anti-Lewisite (2,3-dimercaptopropanol), a widely used antidote for arsenic poisoning, effectively blocks the action of arsenite on sensitive enzyme systems (Adriano, 2001; Agency for Toxic Substances and Disease Registry, 2007; Agency for Toxic Substances and Disease Registry, 2009; Ahuja, 2008).

Arsenate

Arsenic, like phosphorous, is in Group V of the periodic table, and the pentavalent arsenate is an analog of inorganic phosphate (Agency for Toxic Substances and Disease Registry, 2007; Carbonell et al., 1998; Hughes et al., 2011). Arsenate (As^{5+}) is thought to be capable of uncoupling oxidative phosphorylation by a mechanism based upon the competitive substitution of arsenate for phosphate. This results in the formation of an unstable arsenate–phosphate ester that is rapidly hydrolyzed. The high-energy bonds of adenosine triphosphate (ATP) are not conserved due to this arsenolysis (Hughes et al., 2011; Jekel, 1994). The resulting substantial reductions in the formation of ATP may lead to significant toxicity with potentially lethal consequences. Additionally, absorbed arsenate is reduced metabolically to arsenite in human tissues (Agency for Toxic Substances and Disease Registry, 2007; Agency for Toxic Substances and Disease Registry, 2009; Hughes et al., 2011; Singh et al., 2011). Although the kinetics of the tissue based reduction of arsenate to arsenite have not been clearly established, the health impacts of exposure to arsenate may be compounded by the combined mechanisms of action of both arsenite and arsenate (Ouypornkochagorn and Feldmann, 2010). Human health and ecological risk assessments normally focus on the toxicity of total inorganic arsenic without considering the difference in toxicity of the two main species (Texas Commission on Environmental Quality, 2014a; Texas Commission on Environmental Quality, 2014b; U.S. Environmental Protection Agency, 1998).

The present study focuses on two contaminated sites in Texas, in areas of historical industrial activity. These two sites are located in areas of upland soils with a high redox potential. Chemical investigations revealed that both sites contained elevated levels of arsenic in the surface soil. Site one located in College Station, Texas was operated as a drilling service facility from 1952 to 1994 producing products and services for cementing and stimulating oil and gas production wells. Site two located northeast of Houston was used as a formulating facility for pesticides from the 1940s and 50s until the 1970s. Arsenic was the primary contaminant in surface soil for both properties.

A feeding guild is the term used to refer to broad groups of related ecological receptors (e.g., omnivorous mammals) that represent the variety of species potentially exposed to arsenic at the affected sites. Feeding guilds are based on a shared function within an ecosystem (i.e., same feeding strategy), similar potential for exposure, and physiological and/or taxonomic similarity.

The ecologic receptor group animal for the ecological risk assessment for this study was the Least Shrew (*Cryptotis parva*). The ecological receptor is used to define the food web specific to the impacted habitat evaluated in the risk assessment. The selection of the ecological receptor is determined by ecological relevance, exposure potential, sensitivity, social or economic importance, connection to protected species and available data. The Least Shrew is abundant and has a high population density, thus making up a large portion of the diet of owls, hawks, and snakes (Otteni et al., 1972; Schmidly, 2004). The Least Shrew is the smallest mammal in Texas and occurs in grasslands in eastern and central portions of the state (like those found at the subject sites) (Schmidly, 2004). It feeds on snails, insects, sow bug, and other small invertebrates. The diets of these invertebrates and their burrowing behavior result in a high potential of direct and indirect exposures to arsenic in surface soils. The availability of natural history and toxicological information also supports selection of the Least Shrew as a measurement receptor (Otteni et al., 1972; Schmidly, 2004).

Both sites in Texas were assessed using arsenic speciation data to calculate a risk based remedial goal. Arsenic speciation analysis of soil provides insightful information associated with risk assessment, fate and transport, and chemical equilibrium within the substrate.

2.3 METHODOLOGY

The methodology for this research consisted of three parts. First, soil sampling and speciation analysis from two similar sites located in Texas. Then measures of arsenite and arsenate toxicity were reviewed and compared to the toxicity of total arsenic associated with the receptor species. Finally, an ecological remediation goal was calculated for arsenic based on the concentration of arsenite versus arsenate that would be protective of the least shrew.

Site Locations

Site one is comprised of an approximately 18.4-acre tract of vacant land in College Station, Texas. This subject property appears to have been first developed in the 1940's and 1950's, and was historically utilized as an arsenical pesticide formulation facility. Details regarding the composition of pesticides including arsenicals used at this facility were not recorded in the site history and are not available. The facility ceased operations sometime in the 1970s. Topographic and flood plan maps and geologic studies, the soils at the site are primarily upland and well drained. Contamination at the site has been weathered for over 50 years.

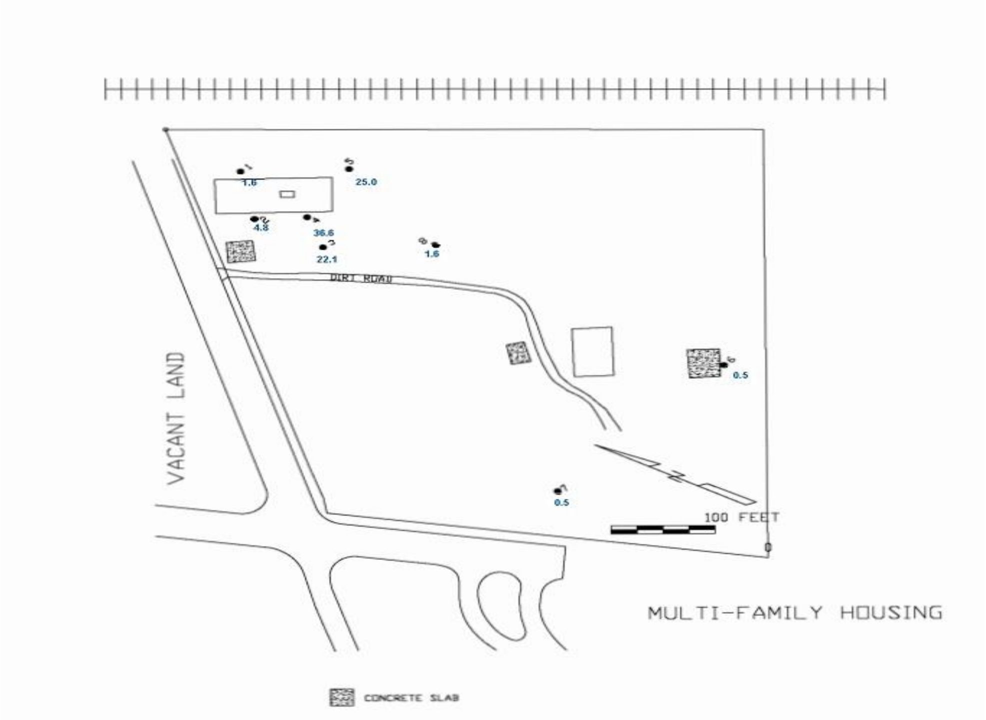
Site two is comprised of approximately 5 acres of currently vacant land in Texas northwest of College Station. The property was first developed in the 1950s, and was historically utilized as a drilling services facility. The facility was operated from 1954 to 1994 and offered services for cementing and stimulating oil and gas wells. The facility included a bulk cement plant, a dry chemicals storage building, an acid plant, truck wash facility and maintenance shop. Arsenic contamination at the site was most likely from oilfield equipment cleaning and sediment piling as indicated by an increase in concentration near the truck wash facility.

An extensive assessment of the properties of both sites was performed initially, analyzing only for total As. Following the identification of areas of high As contamination, new sample wells were drilled and samples were obtained for As speciation determinations. Only the samples and locations of sample wells that were analyzed for arsenite and arsenate are presented here (Figure 2.1).

Sampling and Analysis

Soil samples were taken from soil borings using direct push technology with the soil cores collected utilizing discrete samplers and acetate liners. Undisturbed, continuous soil samples

A) Arsenic contaminated Site One.



B) Arsenic contaminated Site Two

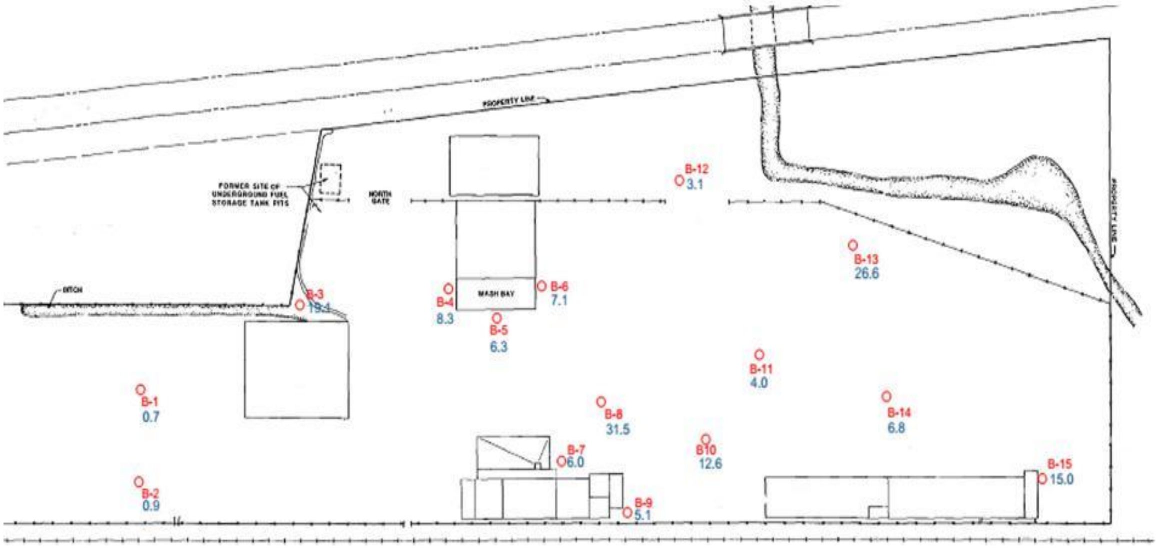


Figure 2.1. A) Arsenic contaminated site one. The location of this property is in an area near College Station, TX, with a history of over 40 yrs of use in the oil industry. This is a natural area of upland soil. The numbers noted below each sample well number denote the total As (ppm) content of the soil. B) Arsenic contaminated site two. This property is northeast of Houston, TX, with a history of 20 - 30 yrs of formulating arsenical pesticides. This is a natural area of upland soil. The values below each sample well number denote the total As (ppm) content of the soil.

down to 4 feet were collected from the boreholes. Each soil sample was visually classified in accordance with American Society for Testing and Materials (ASTM) Method D2488 and documented on a boring log using the Unified Soil Classification System.

Soil samples were extruded in the field immediately following retrieval of each sampler. A representative portion of each soil sample was carefully trimmed to remove the smear zone formed during sample acquisition and soil samples were collected using clean sample containers appropriate for the method. Soil samples collected for arsenic and arsenic speciation analysis were collected from 0–1 ft below ground surface (bgs). Samples for arsenic speciation were frozen and shipped by Federal Express for next day delivery. Total arsenic samples were collected at the same time in 4 ounce jars and cooled to 4 °C.

The soil samples were analyzed by Frontier Global Sciences, Inc., for arsenite and arsenate by soil leach and analysis by hydride generation-cryo trapping-gas chromatography-atomic absorption spectrometry according to USEPA Method No. 1632. Total arsenic was analyzed by USEPA Method No. 6010A. The quality assurance/quality control (QA/QC) samples were run after every 10 specimens. The relative percent difference (RDP) from duplicates was 2.4% and 1% for arsenite and arsenate, respectively. Two samples from each site were spiked and analyzed for percent recoverable. The percent of recoverable spike was 105% for arsenite and 93% for arsenate, which is within calibration boundaries.

Allometric Scaling

Allometry is the scaling of physiological rates or quantities to relative growth and size (mass or volume) of one animal species relative to another animal species (Sample and Arenal, 1999). This is based on the premise that the excretion and metabolism of toxic chemicals are a function of metabolic rate, which, in turn, varies as a function of body weight.

Allometric scaling is a commonly used method to extrapolate toxic responses observed in mammalian test species to the wildlife endpoint species of interest. It is based on biological properties varying proportionally with body weight such that: A = a · (BW) · b, where A = biological attribute, a = intercept, BW = body weight, and b = allometric scaling factor (Davidson et al., 1986). The U.S. Environmental Protection Agency recommends the application of a 0.75 scaling factor for extrapolation of carcinogenicity data from test animals to humans (Ruby et al., 1999). For wildlife risk assessment, Sample et al. (1996) applied scaling factor of 0.75 to mammalian toxicity data (Sample et al., 1996). Based on a toxicity value for a given test species (A_t), an allometric scaling factor (b), and the body weights of the test species and a selected wildlife species (e.g., BW_t and BW_w, respectively), then the unknown toxicity value for a particular wildlife species (A_w) may be estimated (Ruby et al., 1999; Sample and Arenal, 1999):

$$A_w = A_t * ({}^{BW_t}/_{BW_w})^{1-b} \qquad (1)$$

Body weights of the selected ecological receptor Least Shrew (sensitive species) and two test species (rat & mouse) used in Eq. (1) were 0.0075 kg, 0.03 kg, & 0.35 kg, respectively as reported in The Mammals of Texas (Online edition), published by the Texas Parks and Wildlife Department. The toxic risk value $_{(TRVNOAEL)}$ is equal to the allometrically scaled NOAEL for the endpoint species (Sample and Arenal, 1999). The dose to the target species is described in the following equation,

$$\text{Dose} = [(IR_{food} \bullet C_{food} \bullet EMF_{food}) + (IR_{soil} \bullet C_{soil})] / BW \qquad (2)$$

where IR_{food} is the food ingestion rate (dry weight basis), C_{food} is the concentration , EMF_{food} is the exposure modification factor for food (bioaccumulation factor), IR_{soil} is the soil ingestion rate (kg dry soil/kg body weight-day), BW is the bodyweight of the ecological receptor and C_{soil} is the 95%

upper confidence limit of the contaminant concentration in soil. The hazard quotient (HQ) compares the exposure (e.g. dose) to a TRV:

$$HQ = \text{Exposure} / TRV = \text{Dose} / TRV \qquad (3)$$

The permissible concentration level (PCL) was derived by dividing the representative soil concentration by the appropriate HQ (Schmidly, 2004):

$$\text{NOAEL PCL} = \text{Representative soil concentration} / \text{NOAEL HQ} \qquad (4)$$

$$\text{LOAEL PCL} = \text{Representative soil concentration} / \text{LOAEL HQ} \qquad (5)$$

where the representative soil concentration is based on the 95% upper confidence level of the data and the no observed adverse effect level (NOAEL) HQ and lowest observed adverse effect level (LOAEL) HQ are based on the TRV_{NOAEL} and $TRV_{LOAEL,}$ respectively.

Eqs. (4) and (5) were used to calculate the NOAEL and LOAEL for each species (Texas Commission on Environmental Quality, 2014a; U.S. Environmental Protection Agency, 2011). The final PCL for each species is based on the range created from the NOAEL and LOAEL and the weighted concentrations of both species of arsenic as described in the following equations:

$$P_{III} = As_{III} / [As_{III} + As_{V}] \qquad (6)$$

$$P_{V} = As_{V} / [As_{III} + As_{V}] \qquad (7)$$

$$PCL_{total} = P_{III} \bullet (As_{III}\ PCL) + P_{V} \bullet (As_{V}\ PCL) \qquad (8)$$

Where, P_{III} and P_{V} are the percentages of the total arsenic in soil as arsenite and arsenate, respectively, As_{III} and As_{V} is the average total concentration of each arsenic species, and As_{III} PCL and As_{V} PCL are calculated from equation (4) & (5). The PCL_{total} is the weighted PCL calculated from the percent concentration in soil of each species.

2.4 RESULTS

Following the identification of two sites in Texas heavily contaminated with arsenic from years of industrial use, samples were taken from each site and analyzed for total arsenic. The total arsenic results for eight samples from site one (labeled A1-A8) and fifteen samples from site two (labeled B1-B15) are provided in Table 2.1. Analysis of the soil core profile indicated that arsenic contamination at both sites was bound in the first 6 in. of soil. The boring logs from both sites indicated a one-inch lens of organic material and silt followed by approximately 4 ft of silty-sand. Site two had a 0-1 inch surface of shell and rock mixed with organic material.

Table 2.1: Total concentration of As in 23 soils from two sites

Sample	[As]/mg kg^{-1}
A1	1.62
A2	4.76
A3	22.10
A4	36.63
A5	25.00
A6	0.49
A7	0.51
A8	1.56
B-1	0.74
B-2	0.87
B-3	19.10
B-4	8.30
B-5	6.27
B-6	7.08
B-7	5.99
B-8	31.50
B-9	5.12
B-10	12.60
B-11	4.00
B-12	3.10
B-13	26.60
B-14	6.81
B-15	15.00

Samples A1-8 and B-1-15 were taken from test Sites One and Two, respectively.

Soil properties of the surficial soils were measured at each site. Analysis of organic carbon at sites one and two resulted in an average of 4.0% and 2.7%, respectively. Oxidation-reduction potential (Eh) at both sites was above +450 mV. The average pH at sites one and two were 7.9 and 7.25, respectively. Analytical analyses for chemical speciation of arsenic for site one resulted in an arsenite average of 7.3% (ranged from 0.7% to 26.9%) and an arsenate average of 92.7% (ranged from 73.1% to 99.3%) (Table 2.2). Site two speciation analyses provided an arsenite average of 9.4% (ranged from 2.5% to 16.0%) and an arsenate average of 97.5% (ranged from 84.0% to 97.5%) (Table 2.3).

Table 2.2: Arsenic speciation results obtained for site one

Sample	[As3+]/mg kg-1	[As5+]/mg kg-1	(%) [As3+]	(%) [As5+]
A1	0.05	1.56	3.4	96.6
A2	0.16	4.61	3.3	96.7
A3	0.40	21.69	1.8	98.2
A4	2.41	34.22	6.6	93.4
A5	0.18	24.82	0.7	99.3
A6	0.05	0.45	9.2	90.8
A7	0.14	0.37	26.9	73.1
A8	0.10	1.46	6.2	93.8
		Average%	7.3	92.7
			STDV	8.4

The samples taken at A3, A4, and A5 from site one were located within an area considered central to the pesticide mixing facility. A4 was adjacent to the entrance to the storage facility for processed pesticides as determined from historical aerial photos. The samples taken at B-3, B-8, and B-13 from site two were all located in an area formerly used for equipment wash. The surface soil at this location was formed from the continual deposition of wash debris. The soil samples taken at the above-denoted locations from the two sites contained elevated concentrations of total arsenic.

Samples A6, A7, B-1, and B-2 were taken from soil outside of the contamination zone as a measure of the natural arsenic speciation variability without the influence of exogenous arsenic. As noted in Table 1, these samples contained the levels of total arsenic more in line with the natural background soil arsenic content. Interestingly, sample A7 displayed a much higher portion of arsenite (Table 2.2) and might represent a data outlier, but the opportunity to resample this site was not available. These samples were used to calculate the arsenic speciation ratio as part of the site natural variability.

Table 2.3:Arsenic speciation results obtained for site two

Sample	[As3+]/mg kg-1	[As5+]/mg kg-1	[As3+] (%)	[As5+](%)
B-1	0.12	0.63	16.0	84.0
B-2	0.10	0.77	11.3	88.7
B-3	1.08	18.02	5.7	94.3
B-4	0.71	7.59	8.5	91.5
B-5	0.96	5.31	15.3	84.7
B-6	0.60	6.49	8.4	91.6
B-7	0.75	5.24	12.6	87.4
B-8	1.53	29.97	4.9	95.1
B-9	0.69	4.43	13.5	86.5
B-10	0.68	11.92	5.4	94.6
B-11	0.35	3.65	8.8	91.2
B-12	0.38	2.72	12.3	87.7
B-13	1.26	25.34	4.7	95.3
B-14	0.73	6.08	10.7	89.3
B-15	0.37	14.63	2.5	97.5
		Average %	9.4	90.6
			STDV	4.2

The arsenic contamination at both of the sites has been weathered for over 50 years. Regulatory limits are generally based on the more toxic form of a contaminant and as such are more conservative (100% arsenite).

Arsenite/Arsenate

Using Eqs. (4) and (5) (noted in the Methodology section), the NOAEL and LOAEL for the Least Shrew were calculated using the published values of 0.126 mg/kg/day and 1.26

mg/kg/day, respectively, for arsenite based on reproductive effects in mice (Ruby et al., 1999; Sample and Arenal, 1999). The NOAEL and LOAEL values for the Least Shrew were determined to be 0.14 mg/kg/day and 1.41 mg/kg/day, respectively (Table 4). An acceptable test species LOAEL for arsenate was not found in the literature. LD50 doses for most mammal species tested have been reported to range from 35–100 mg/kg/BW/day (Agency for Toxic Substances and Disease Registry, 2007). The lower end of this range was used as the benchmark. The low value of 35 mg/kg was multiplied by an uncertainty factor of 0.01 based on published recommendations and the guidelines of TCEQ (Texas Commission on Environmental Quality) (Calabrese and Baldwin, 1994; TCEQ (Texas Commission on Environmental Quality), 2014a; TCEQ (Texas Commission on Environmental Quality), 2014b). By this method, the NOAEL for arsenate was calculated to be 0.35 mg/kg and was used in the allometric estimates of NOAEL for extrapolation to the ecological receptor (Table 2.4).

Table 2.4:Allometric scaling of data

Chemical	Endpoint Species	Test Species	Test Species		Estimated for Endpoint Species	
			TRV_{NOAEL} (mg/kg-bw/day)	TRV_{LOAEL} (mg/kg-bw/day)	TRV_{NOAEL} (mg/kg-bw/day)	TRV_{LOAEL} (mg/kg-bw/day)
Arsenite	Least Shrew	mouse	0.126	1.26	0.14	1.41
Arsenate	Least Shrew	mouse	--	--	0.35	35
Arsenite	Least Shrew	rat	0.4	4.0	0.45	4.47
Arsenate	Least Shrew	rat	0.700	7	0.88	8.82

The 95% upper confidence level of the soil data, 32 mg/kg (see Table 2.1), was used as the representative soil concentration for the PCL calculations. The dose is based on the soil concentration with respect to both the ingestion of soil and the assumed diet of the target organism.

The bioavailability of arsenite and arsenate for mice is 62% and 66%, respectively (Davidson et al., 1986; Freeman et al., 1993). The small difference in percent did not impact the end product of the PCL calculations.

The calculated NOAEL PCLs (using Eq. (4)) for arsenite and arsenate were 4 ppm and 26 ppm, respectively (Table 2.5). The NOAEL $_{\text{PCLtotal}}$ was determined to be 24 ppm based on the arsenate concentration of 90% of total arsenic in soils. The calculated LOAEL PCLs (using Eq. (5)) were ten times higher based on the data. The LOAEL $_{\text{PCLtotal}}$ was determined to be 240 ppm based on the arsenate concentration of 90% of total arsenic in soils.

Table 2.5: Calculated PCL values.

Chemical	Hazard quotient (NOAEL)	Hazard Quotient (LOAEL)	PCL_{NOAEL}	PCL_{LOAEL}
Arsenite	7.66	0.77	4	41
Arsenate	1.22	0.12	26	261
Weighted	-	-	24	239

2.5 DISCUSSION

The two contaminated sites identified for this study were aerobic and comprised of well-drained upland soils. Upland soils are generally 50% solid, 25% water and 25% air (Adriano, 2001; Carbonell et al., 1998; Evangelou, 1998; Sparks, 2003). Reduced compounds like arsenite are usually not found in high concentrations in upland soils. The present study illustrates that fact as the results were weighted heavily toward the arsenate species. In most upland soil systems, the chemistry of arsenic becomes the chemistry of arsenate (Carbonell et al., 1998; Cullen and Reimer, 1989; Fox and Doner, 2003; Moore et al., 1990). The estimated half-life of elemental arsenic in soils is about 65 years, although losses of 60% in 3 years and 67% in 7 years have been reported (Texas Commission on Environmental Quality, 2014a).

The surface soil at both sites was oxidative and aerobic. A portion of the solid phase in the surface soils at the two sites consisted of organic matter. Organic soils have a high water-holding capacity, and during heavy rainfall events can become completely saturated. Under conditions of excessive rainfall and poor drainage, oxidized forms are reduced as a result of the respiratory requirements of anaerobic bacteria (Manning and Goldberg, 1997; McGeehan and Naylor, 1994). The complete conversion of arsenate to arsenite in anoxic media can take about 18 days at 1 ppm (McGeehan and Naylor, 1994). The ratio of arsenite to arsenate equilibrates slowly between both oxidation states dependent on redox level of the soil. Sampling was conducted at both sites during both the rainy season and drier conditions to look at the variability in speciation. The lack of water retention at both sites corresponds with the resulting higher percentage of arsenate observed.

Most risk-based standards are based on physical, chemical and toxicological properties of arsenite. This approach, considered conservative, does not accurately describe the toxicity of arsenicals in upland soils. Sites historically contaminated with arsenical pesticides in upland soils will contain a greater concentration of arsenate and the risk to ecological receptors will be lower. Heavily weathered upland soils with low redox potential will concentrate arsenate. The present study demonstrated that arsenate represents 90% or more of total arsenic in the soil at the two historically contaminated sites. The arsenite species represented less than 10% at each site. Based on the Least Shrew, the weighted permissible concentrations of total arsenic were 24 mg/kg (NOAEL PCL) and 239 mg/kg (LOAEL PCL).

The original Least Shrew PCL for arsenic was 8.8 mg/kg which is 3 times less than the weighted NOAEL PCL. Regulatory limits are generally based on the more toxic form of a contaminant and as such are more conservative (100% arsenite). Additionally, regional background concentrations can range from 2.1-45 mg/kg. U.S. Environmental Protection Agency regional and national cleanup standards for arsenic in soil average 181 ppm and 190 ppm, respectively. The maximum concentrations at the two sites were 36.63 mg/kg and 30.5 mg/kg at sites one and two, respectively. The 95% upper confidence level for the two sites was 32 mg/kg which is above the NOAEL PCL but below the LOAEL PCL.

Arsenates are generally less toxic, less soluble and less mobile than the trivalent species and can impact the hazard quotient at a given site (Agency for Toxic Substances and Disease Registry, 2007; Bradham et al., 2013; Davidson et al., 1986). Arsenates are less mobile than arsenites due in part to their stronger adsorption to sediments. This adsorption process depends largely on total arsenic concentrations, sediment characteristics, dissolved oxygen and iron (Hughes et al., 2011; Barbafieri, 2000). An important mechanism of arsenic adsorption onto sediments is the interaction of arsenates with hydrous iron- and manganese oxides. It should also be noted that anions when present (particularly phosphate) effectively compete with arsenic for adsorption sites (Hughes et al., 2011).

Arsenic has not been shown to be an essential plant nutrient (Carbonell et al., 1998; Bagga and Peterson, 2001). The availability of arsenic for plant metabolism is mediated by the oxidation state. Arsenate has been reported to stimulate growth in maize, peas, wheat, potatoes, rye, soybean, cotton, rice, and tomato (Carbonell et al., 1998; Meharg and Hartley-Whitaker, 2002; Tassi et al., 2004; Williams et al., 2005). Arsenate competes with phosphate as a substrate for the phosphate uptake system in a wide variety of plant species (Tassi et al., 2004). The botanical phosphate carrier has a higher affinity for phosphate than arsenate and media with sufficient phosphate will suppress arsenate uptake in roots.

2.6 CONCLUSIONS

The data described above strongly indicate that when evaluating well drained upland soils, estimates of the risks should be based on the toxicity of arsenate. Higher arsenate concentration is an indicator of aerobic conditions in the soil. At the two test locations, arsenate was found to make up over 90% of the total arsenic contamination. This adjustment substantially affects site-specific risk assessments, ecological risk assessments and remediation design in oxidative, aerobic soils. The current study urges a shift in the strategy for assessment of arsenic risk in upland soils, moving away from a focus on arsenite to evaluate arsenate risk.

The uptake kinetics of arsenate in soils match pathways for phosphate uptake in plants. Site specific data on oxidative state, pH, organic carbon and arsenical speciation can enhance phytoremediation decisions. Understanding the valence state of arsenic in poorly drained wetland soils adds value to the decision making process by indicating that a specific remediation technology may not be effective. The arsenic ratio can impact plant selection and types of amendments needed to create or enhance an aerobic environment to facilitate the mass balance to arsenate.

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CHAPTER 3
PHYTOREMEDIATION MODEL DESIGN AND VALIDATION TO PREDICT UPTAKE AND TRANSLOCATION OF ARSENIC USING STELLA

3.1 ABSTRACT

Environmental contamination of sites throughout the world has increased since the industrial revolution. Different cleanup techniques have been developed, tested and implemented globally. Phytoremediation is a viable and cost effective technology and can be employed throughout the world. Concerns with measuring phytoremediation system performance have led to this technique being underutilized. In this study, a dynamic phytoremediation model based on uptake and translocation of contaminants from the soil was developed in the STELLA modeling environment. The model was tested and assessed using peer reviewed experimental data, to demonstrate its capability to mimic phytoremediation processes.

Phytoremediation requires an understanding of the uptake kinetics and transport of soil and water contaminants by plants to be successful. This study investigated the removal of arsenic from a contaminated soil by Poplar tree through the examinations of seasonal variations of xylem water potential, leaf water transpiration, and root water and arsenic uptake. The model for uptake and translocation of contaminants from a soil-plant ecosystem was modified and incorporated into the STELLA software package for the purpose of this study. The model was calibrated using a field pilot study at an active remediation site prior to projecting a ten year trend.

The implementation of the model in the phytoremediation system provides knowledge about: pollutant-media-plant interaction, pollutant concentration and flow rate through the plant. This information offers the opportunity to have quantitative parameters to determine which plant systems is adequate according to its performance in a specific scenario.

3.2 INTRODUCTION

Pollution of soil, surface water, and groundwater resources by contaminants such as arsenic (As) is an environmental concern. As is often present in the atmosphere, in soils and ground waters. Humans have contributed to As contamination in the environment mainly from the combustion of fossil fuels, mining, smelting of ores or the application of arsenical pesticides, herbicides and wood preservatives (Mandal and Suzuki, 2002). Metals and metalloids such as As are of specific interest to remediation professionals as they are not easily degraded and tend to bioaccumulate (Kramer,, 2005).

Since the early 1800's, industrial pollution has been increasingly impacting the food web. Heavy metals frequently found in contaminated sites can be transformed by oxidative states, microorganism interactions, and soil and groundwater composition into a more bioavailable compounds (Wood, 1974; Ridley, 1977). Exposure to different arsenic species can inflict a variety of threats to human health, including irreversible damage to the nervous system (Henry, 2000; Shafaghat, 2012). The global arsenic budget has increased 3.3 times in postindustrial times which can be ascribed to use as afore mentioned.

Currently, remediation of arsenic contaminated soils focuses mainly on removal and impoundment. There is a growing interest toward the use of the phytoremediation for arsenic removal from contaminated soils utilizing hyper accumulators. The mechanisms for the uptake and translocation of soil and groundwater contaminants by plants must be understood to successfully apply phytoremediation technologies.

Although phytoremediation has shown significant potential for applications, our understanding of the impacts of plant physiological, microbiological, hydrological, and environmental conditions upon its applications are still disjointed. Knowledge of these impacts is crucial to effective applications of the technology. Since the uptake and translocations of arsenic from a soil–plant system are complex processes, it would be difficult to learn by experimentation alone for a variety of plant species, soil physicochemical properties, climatic conditions, and soil arsenic bioavailability. Therefore, a need exists to develop a dynamic model for predicting uptake, translocation, accumulation, and transport of arsenic in the soil–plant system.

There is a practicable and environmental need to analyze contamination issues to develop standardized protocols. Currently, those analyses mainly consist in site contaminant characterization and construction of mathematical or graphical models, in which multivariate sequential probabilities can be exhibited and map the contaminant dispersion based on background information (Smith-Downey, 2010). These kinds of approaches have been implemented to determine the environmental hazard index linked to a specific site location map (Franco 2006).

In the past, several investigators have developed mathematical models to study the fate and transport of organic contaminants in plants (Burken and Schnoor, 1996; Ouyang, 2002) although studies have evaluaed modeling arsenic uptake and transport in the soil–plant system. The CTSPAC (Coupled Transport of Water, Solutes, and Heat in the Soil-Plant-Atmosphere Continuum) model, developed by Boersma et al. (1991), consists of coupling a soil sub-model to a plant sub-model. The soil sub-model has three time dependent equations for vertical simultaneous flow and transport of water, solutes, and heat through the vadose zone. The plant sub-model is based on compartmentalization of the plant into local regions of similar tissue structure and function.

A CTSPAC model can provide good insights into the phytoremediation of heavy metals, like arsenic. The CTSPAC model divides a plant into more than separate 32 compartments. This requires a significant number of input parameters related to transport, translocation, and accumulations in a plant. These input parameters can be difficult to obtain through the experimental measurements and at times must be estimated with uncertainties through theoretical calculations, calibrations, and validations. A need exists to develop a realistic and less complex model that can allow for a more efficient investigation of phytoremediation in the soil–plant system.

The goal of this study was to construct a simulation model for predicting the long term uptake and transport of arsenic by poplar tree, using the commercial available software package STELLA. STELLA is a modeling tool for building a dynamic modeling system by creating a pictorial diagram of a system and then assigning the appropriate values and mathematical functions to the system (Isee System, 2006). A brief overview of STELLA is given in the next section.

Our specific objectives of this study were to: (1) develop a dynamic phytoremediation model designed to predict uptake and transport of arsenic by plants based on water potential gradient; (2) calibrate the model using available experimental data; and (3) apply the model for predicting phytoremediation of arsenic by a poplar tree.

3.3 METHODOLOGY

3.3.1 Model Development

STELLA

The development of the phytoremediation model was performed using STELLA^{TM} (Strongly Typed Lips Like Language; system thinking software of Isee Systems). STELLA is a commercially available, dynamic software that implements pictographic modeling representation based upon four basic components: stocks, flows, connectors and converters. This pictographic interface is used to facilitate construction of dynamic system models. The key features of STELLA consist of the following four tools: (1) Stocks, which are the state variables for accumulations. They collect whatever flows into and out of them; (2) Flows, which are the exchange variables and control the arrival or the exchanges of information between the state variables; (3) Converters, which are the auxiliary variables. These variables can be represented by constant values or by values depending on other variables, curves or functions of various categories; and (4) Connectors, which are to connect among modeling features, variables, and elements.

STELLA offers a practical way to dynamically visualize and communicate how complex systems and ideas really work (Isee System, 2006). STELLA has been widely used in biological, ecological, and environmental sciences (Hannon and Ruth, 2001; Peterson and Richmond, 1996; Costanza et al., 2004; Aassine and El Jai, 2002). An elaborate description of STELLA package can be found in Isee System (2006).

Conceptual Model

In the subsurface, dissolved chemicals are known to be removed by the influence of the root systems of plants by any of three mechanisms:

1. Direct Transpiration (Uptake)
2. Root Sorption
3. Biodegradation

The transpiration factor (TF) is the quantitative affinity of a dissolved chemical to be taken up into the root system of a plant. The TF of a solute is the ratio of the concentration in transport and the concentration in the saturated zone. The value of TF varies from 0 to 1 and depends on the chemical properties of the compound (Schnoor 2002). The root concentration factor (RCF) is a parameter that is similar to the distribution coefficient used in modeling sorption to aquifer solids. The RCF is the ratio of concentration of bound to the root system vs the concentration in the saturated zone (Schnoor 2002). A value of zero for TF and RCF indicate that a solute will not be transpired or bound, respectively. Large values reflect a high affinity for transpiration or binding, respectively.

Mathematical models are utilized in environmental science to help to evaluate different scenarios and to make a decision based on all the available information. Human rational can promote errors and/or biases (Sterman, 1989), particularly in complex systems. This is the case when evaluating plant-soil interaction.

Within the past forty years, mathematical approaches have been used to illustrate the soil-plant interaction. These can be applied to modeling phytoremediation systems specific to long term evaluations. Various mathematical algorithms have been employed to phytoremediation process understanding. These models are mathematically intensive and very specialized. The System Dynamic Approach (SDA) has provided differential equation solution sets as defined by models for compartmentalization of the plant physiology (Ouyang 2007, Ouyang 2008).

The most important concerns about phytoremediation are: 1) bioavailability; 2) uptake rate by roots; 3) proportion of contaminant “fixed” within the roots; 4) rate of xylem loading/ translocation to shoots; and 5) cellular tolerance to toxic contaminants (U.S. Environmental Protection Agency, 2000; Sarma, 2011; Deuren, 2006). It is possible to have all of these compartments constructed using STELLA, considering the internal interactions of the contaminant according to the plants’ metabolism and uptake of water. The CTSPAC model described plant systems using over 40 variables which may not be available to accurately describe the environmental conditions at a specific site (Ouyang, 2007; Ouyang, 2008). These variables and their differences in the categorization may enhance the model’s complexity, but generally do not increase model accuracy.

Phytoremediation Model

The phytoremediation model for heavy metal cleanup was developed using an adaptation of the mathematical models presented by Sundberg et al. (2003) and Thomas et al. (2005), while the segmentation of the plant physiological parts follows the protocol described by Ouyang et al. (2007) and Ouyang (2002, 2008). Sundberg et al. (2003) established a set of five compartment Plant Kinetic Model (PKM), four of which mimic plant anatomy and physiology.

The flow interaction on the PKM is governed by gradient differences between the compartments. The present study but includes a threshold contaminant level to activate the flow rates between compartments which creates a time dependent flow between stocks. The phytoremediation model incorporated the pollutant saturation point and constant transfer rate, assumption, as recommended by Thomas et al. (2005), who designed a pure differential equation model considering assumptions related to pollutants saturation point, constant transfer rate, immediate transfer rate and bi-flux of pollutant. For modeling the phytoremediation process, three pairs of compartments representing the xylem and phloem in the root, stem and leaf, were considered to simulate the contaminant exchange between compartments, following the procedures described by Ouyang et al. (2007) and Ouyang (2002, 2008). The present phytoremediation model considers only the upward net flux of the pollutant and water, through the plant model structure to avoid conceptual, mathematical and validation complexities. Two main interactions are utilized in this phytoremediation model, underground (soil-plant) and above ground (plant uptake to the atmosphere) soil-plant-atmosphere interactions as represented in Figure 3.1.

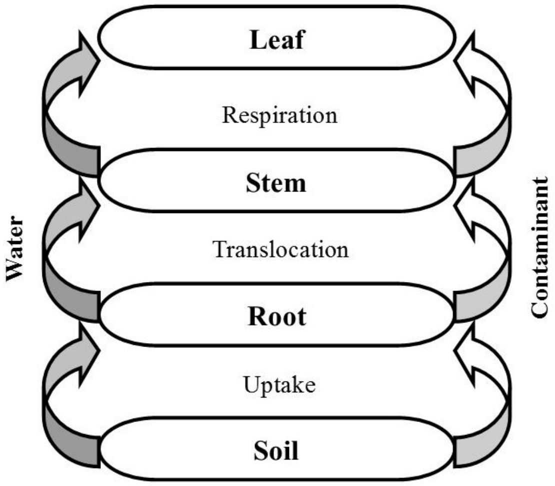

Figure 3.1: Basic schematic representation of plant physiology, which represents the phytoremediation process.

Model Construction

The phytoremediation model is the schematic representation shown in Figure 3.2, which follows different modeling approaches and assumptions about the functional structure of plant physiology, as discussed by Stern et al. (2003), Sundberg et al. (2003), Thomas et al. (2005), and Ouyang (2007, 2008). The phytoremediation model considers the upward net flow between the soil and plant compartment representations. The contaminant flow rate on each section of the model is dependent on the concentration difference between the plant structural representations. These assumptions were taken in order to harmonize the model with current literature. This method establishes an average contaminant concentration on each physiological part of the plant (Wang et al., 2010), and is consistent with the PKM (Sundberg et al., 2003).

The construction of the phytoremediation model takes into account the previous model approaches which implement system dynamics and plant physiological structure. A dynamic model for uptake and translocation of contaminants from a soil-plant ecosystem was previously developed using the STELLA modeling tool (Ouyang, 2007). However, simpler plant structure interaction is being incorporated as well as a plant growth factor and seasonal effects. The objective of this study was to modify and simplify previous models and to simulate the uptake and transport of arsenic by poplar trees.

A conceptual diagram representing the major mechanisms of uptake and transport composed of structural blocks and process is given in Figure 3.1. The model diagram was divided into four sectors representing soil, roots, stems, and leaves, respectively. Each block has the intent to mimic the contaminant concentration as a function of plant physiology and soil interaction.

The arrows indicate the net contaminant flow between blocks. Extraction section represents the root capability to remove the contaminant from soil. Translocation is the contaminant movement from the root to plant upper tissue (Lasat. 2000). In order to have a clear distinction, this process has been divided in two steps. Translocation represents the contaminant flow from root to stem, and respiration characterizes the contaminant flow from stem to leaf.

The development of the phytoremediation model performed using STELLA is based upon four basic components: stocks (level variables), flows (rates), connectors (relationship) and converters (auxiliary variables) (Ouyang, 2007; Ouyang, 2008). The plant is represented by three functional parts (root, stem, leaf) as stocks (level variables) interconnected, mimicking its anatomy and physiology, and two stocks represent abiotic factors (soil, atmosphere) of the environment (Figure 3.2). The transport of contaminant within the plant is balanced with a hydraulic model. A similar structural representation can be found in a different phytoremediation modeling approach (Sundberg. 2003;Thomas. 2005; Ouyang. 2008).

In order extend the applicability of the modeling approach another stock was added to represent the contaminant concentration released to the atmosphere. After the incorporation of the assumptions described in the research literature and the application of STELLA, the schematic representation of the phytoremediation model was developed. It is composed of ten stocks, nine flows, and auxiliary variables for both water and contaminant uptake as depicted in Figure 3.3. Stocks (level variables) represent structural reservoirs of the plant physiology and environment, while flows (rates) characterize the upward net soluble contaminant as a function of exchange between its compartments. The auxiliary variables are the parameters which govern the model behaviors categorized as: assumed, estimated and calibrated. Figure 3.4 shows the differential equation system, which governs the model behavior. Using standard mathematical notation, the model can be denoted by mathematical expressions (Table 3.1).

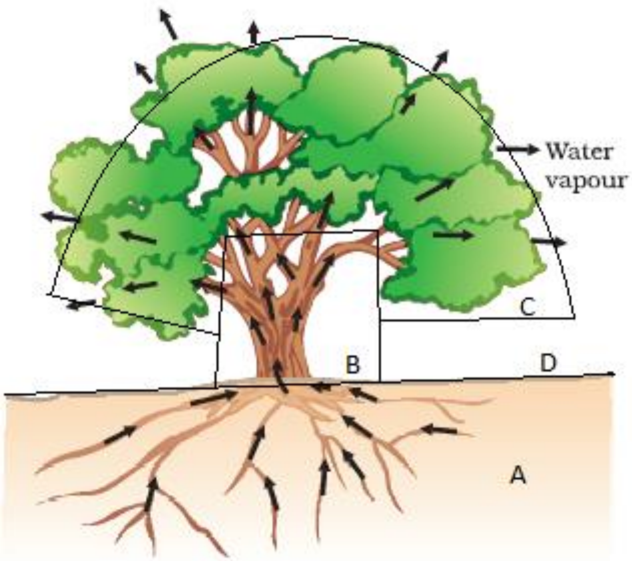

Figure 3.2: Structure diagram for the phytoremediation model. The compartments can be classified as above or below the ground. The (A) compartment represents the soil-plant interaction at the root zone, which is the below the ground section involving two stocks: soil and root. The above ground segment; are composed by three stocks: (B) stem, (C) leaf, and (D) atmosphere. Modified from figure 6.12, June 2010, Movement of water during transpiration in a tree. Posted in 10th Science CBSE Biology.

Table 3.1: Differential equation system which describes the phytoremediation model.

Model Section	Mathematical Representation
Contaminant	
Root	$F_{Ext} = \left(S_{Soil} * \left(\frac{S_{Soil}}{Init\_S_{Soil}}\right)^{Fraction}\right) * R_{Ext}$
Stem	$F_{Tran} = (S_{Root} - ThC_{Root}) * R_{Tran}$
Leaf	$F_{Inc} = (S_{Stem} - ThC_{Stem}) * R_{Inc}$
Volatilization	$F_{Vol} = \left(S_{Leaf} - ThC_{Leaf}\right) * R_{Vol}$
Water	
Root	$Q_R = \frac{2.64 * 10^{-3} e^{(62(\theta - \theta_1))}}{6.68 - ln(RD)}$
Stem	$Q_S = A_{Stem} * L_{Stem} * (\Psi_{Stem} - \Psi_{Root})$
Leaf	$Q_L = A_{Leaf} * L_{Leaf} * \left(\Psi_{Leaf} - \Psi_{Stem}\right)$
Volatilization	$Q_{WV} = A_{Leaf} * L_{Leaf} * (\Psi_{WV} - \Psi_{Stem})$

As shown in Table 3.1, a description of the contaminate pathway model function symbols are described by the following; The S_ function represented stocks, with their respective sub-index (Soil, Root, Stem, Leaf or Vol for atmosphere). The expression Init_S_{Soil}, corresponds to the initial contaminant concentration in the soil, which is implemented as a constant to calculate the bioavailability as time evolves. The ThC_ identifies the threshold contaminant concentration to initiate the movement through the system; R_ means the rates at which the contaminant moves once the threshold is attained. The neighbors' stocks is represented by F_. Each one of these functions has a sub-index, which identifies the interaction in the model (Ext = Extraction, Tran = Translocation, Inc = Incorporation, Vol = Volatilization).

A description of the water uptake pathway model function symbols are described by the following; The A_ function represents the plant mass according to their respective sub-index (Stem and Leaf). The function Θ represents the total water and water available for uptake by roots. The RD expression represents the root mass. The L_ corresponds to the conductivity of the plant tissue dependent on plant type. The $\Psi\_$ describes the hydraulic potential between compartments where the difference between compartments describes the potential for uptake from one compartment to the next. $Q\_$ represents the amount of water moved from the previous compartment which is the quantity of water available to transport to the next compartment and has a sub-index detailing the compartment (R = Root, S = Stem, L = Leaf, WV = Volatilization).

The model combines the structural diagram between environmental components with the schematic representation of the plant physiology. The model behavior will be governed by the fundamental assumption stated as follows:

1) Fluxes (rates) depend on the contaminant concentration of the previous stocks (level variables), which relate to section rates and threshold concentration. Section rates are calibration variables. Threshold concentration is an estimated variable, which value establishes the minimum concentration that previous stock has to achieve to allow the contaminant flow to the next stocks. Once threshold concentrations are achieved, the value should be maintained during the time frame modeled (Root threshold concentration, Stem threshold concentration, Leaf threshold concentration). This works as osmotic concentration levels, which is a phenomenon observed as a function of plant species and contamination, as reported for plant tissues (Jadia 2009,Sarma 2011,Yu 2001).
2) Once the threshold concentration is achieved the section flow rates are constant during the time frame modeled (Extraction rate, Translocation rate, Incorporation rate, Volatilization rate) around plant transport capacity. Ions in solution are moved through transporter and is characterized mainly by their transport capacity $_{(Vmax)}$ and binding affinity (Km) (Lasat, 2000).

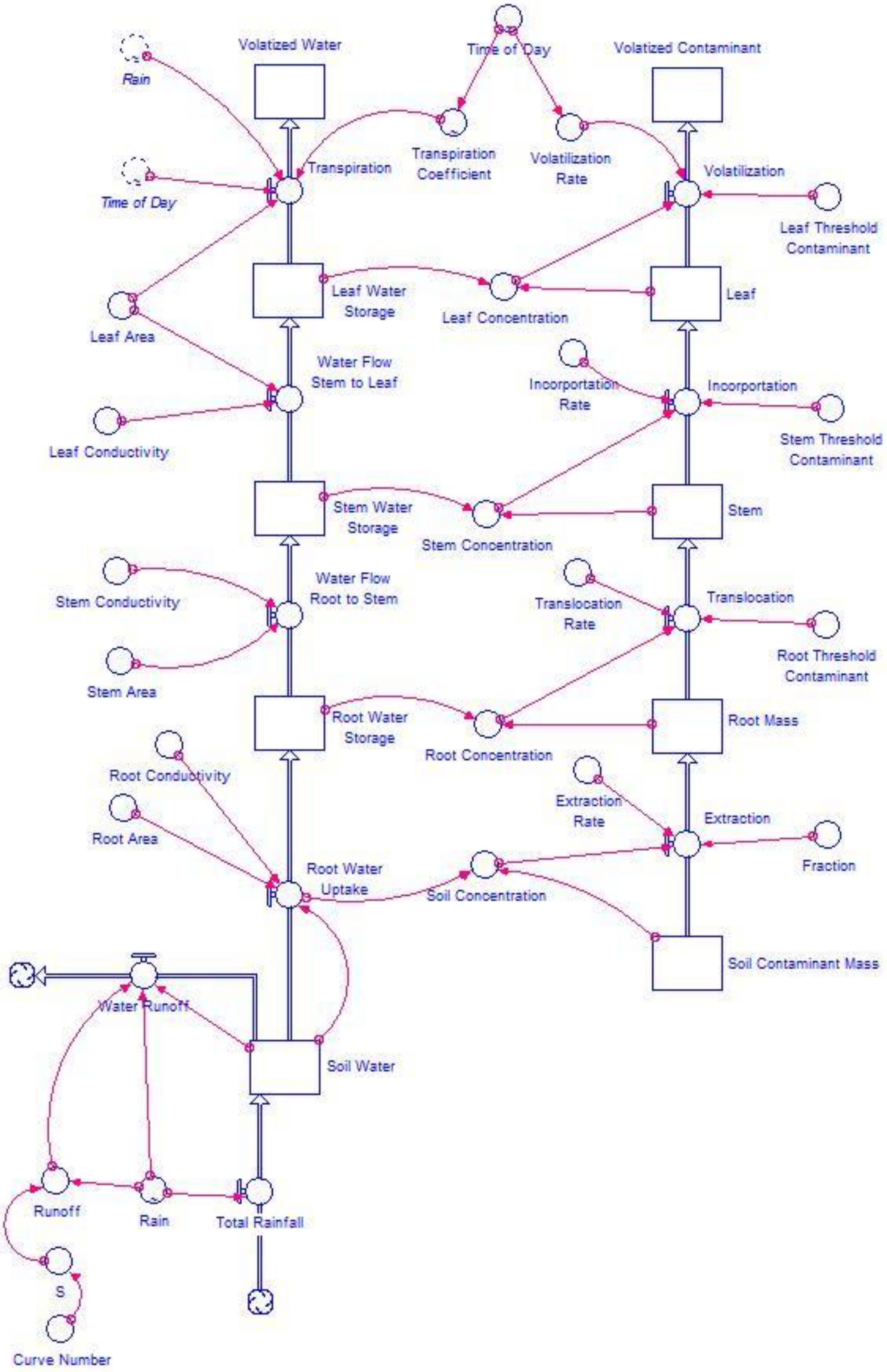

Figure 3.3: The Forrester Diagram schematic representation of the phytoremediation model.

```
Leaf(t) = Leaf(t - dt) + (Incorporation - Volatilization) * dt
INIT Leaf = 0
 INFLOWS:
   Incorporation = (Stem_Concentration-Stem_Threshold_Contaminant)*Incorporation__Rate
 OUTFLOWS:
   Volatilization = (Leaf_Concentration-Leaf_Threshold__Contaminant)*Volatilization_Rate
Leaf_Water__Storage(t) = Leaf_Water__Storage(t - dt) + (Water_Flow_Stem_to_Leaf - Transpiration) * dt
INIT Leaf_Water__Storage = 0
 INFLOWS:
   Water_Flow_Stem_to_Leaf = Leaf_Area*Leaf_Conductivity
 OUTFLOWS:
   Transpiration = If (Time_of_Day>0) then (Time_of_Day*Transpiration_Coefficient*Leaf_Area)-Rain
   else 0.0
Root_Mass(t) = Root_Mass(t - dt) + (Extraction - Translocation) * dt
INIT Root_Mass = 0
 INFLOWS:
   Extraction = Root_Water_Uptake*Extraction__Rate*Fraction
 OUTFLOWS:
   Translocation = (Root_Concentration-Root_Threshold_Contaminant)*Translocation_Rate
Root_Water_Storage(t) = Root_Water_Storage(t - dt) + (Root_Water_Uptake - Water_Flow__Root_to_Stem)
* dt
INIT Root_Water_Storage = 0
 INFLOWS:
   Root_Water_Uptake = Root_Area*Root_Conductivity*Water__Content
 OUTFLOWS:
   Water_Flow__Root_to_Stem = Stem_Area*Stem_Conductivity
Soil_Contaminant_Mass(t) = Soil_Contaminant_Mass(t - dt) + (- Extraction) * dt
INIT Soil_Contaminant_Mass = 300
 OUTFLOWS:
   Extraction = Root_Water_Uptake*Extraction__Rate*Fraction
Soil_Water(t) = Soil_Water(t - dt) + (Total_Rainfall - Root_Water_Uptake - Water_Runoff) * dt
INIT Soil_Water = 0
 INFLOWS:
   Total_Rainfall = Rain
 OUTFLOWS:
   Root_Water_Uptake = Root_Area*Root_Conductivity*Water__Content
   Water_Runoff = (Water__Content+Rain)-Runoff
Stem(t) = Stem(t - dt) + (Translocation - Incorporation) * dt
INIT Stem = 0
 INFLOWS:
   Translocation = (Root_Concentration-Root_Threshold_Contaminant)*Translocation_Rate
 OUTFLOWS:
   Incorporation = (Stem_Concentration-Stem_Threshold_Contaminant)*Incorporation__Rate
Stem_Water__Storage(t) = Stem_Water__Storage(t - dt) + (Water_Flow__Root_to_Stem -
Water_Flow_Stem_to_Leaf) * dt
INIT Stem_Water__Storage = 0
 INFLOWS:
   Water_Flow__Root_to_Stem = Stem_Area*Stem_Conductivity
 OUTFLOWS:
   Water_Flow_Stem_to_Leaf = Leaf_Area*Leaf_Conductivity
Volatized_Contaminant(t) = Volatized_Contaminant(t - dt) + (Volatilization) * dt
INIT Volatized_Contaminant = 0
 INFLOWS:
   Volatilization = (Leaf_Concentration-Leaf_Threshold__Contaminant)*Volatilization_Rate
Volatized_Water(t) = Volatized_Water(t - dt) + (Transpiration) * dt
INIT Volatized_Water = 0
 INFLOWS:
   Transpiration = If (Time_of_Day>0) then (Time_of_Day*Transpiration_Coefficient*Leaf_Area)-Rain
   else 0.0
```

Figure 3.4: The differential equation system of the phytoremediation process.

3) Initial level concentrations of all stocks except soil and soil water begins at zero to indicate that the plant is not contaminated.
4) The contaminated soil stock begins with the site specific or data specific concentration.
5) The soil water stock begins with enough water to not be a limiting factor in uptake to mirror site specific conditions
6) Contaminant bioavailability depends on the exponential ratio between the current and initial contaminant concentration in soil. This dependence is represented in the flow equation in the phytoremediation model soil section and is called Fraction. This function combines soil-plant interactions to include factors such as plant transporters and soil physical-chemical properties into one normalized function. The Km measures the transporter affinity for a specific ion, where high values represent low affinity. The contaminant bioavailability has complex interactions with soil pH, oxidation state, organic matter, conductivity and grain distribution. The pH and oxidation state affects the bioavailability of arsenic and modifies the cation exchange capacity (Violante, 2010).

3.3.2 Validation

Qualitative Validation

This phytoremediation model has been developed to mimic phytovolatilization because it is the most comprehensive process and includes all physiologic section of the plant. Plants that can hyperaccumulate arsenic have been studied extensively in the past 10 years, yet limited research has been performed on arsenic phytovolatilization (Rugh, 1996; Hussein, 2007; Bizily, 1999; Ruiz, 2003). The accumulation kinetics of various heavy metals were used to establish estimated threshold values for each physiological section of the plant (Bizily, 1999; Ruiz, 2003).

Sakakibara et al. (2007) showed a comprehensive phytovolatilization experiment for arsenic from neutralized acid mine drainage. The remediation and hyperaccumulation capability of *Pteris vittata* was evaluated during this study. The study focused on contaminant tissue concentration and volatilization over time. The volatilization data for the *P vittata* are shown in Figure 3.5, for arsenic. Volatilization is an important mechanism to avoid toxic effects of arsenic and varies as the arsenic concentration in soil or groundwater (Mirza, 2011).

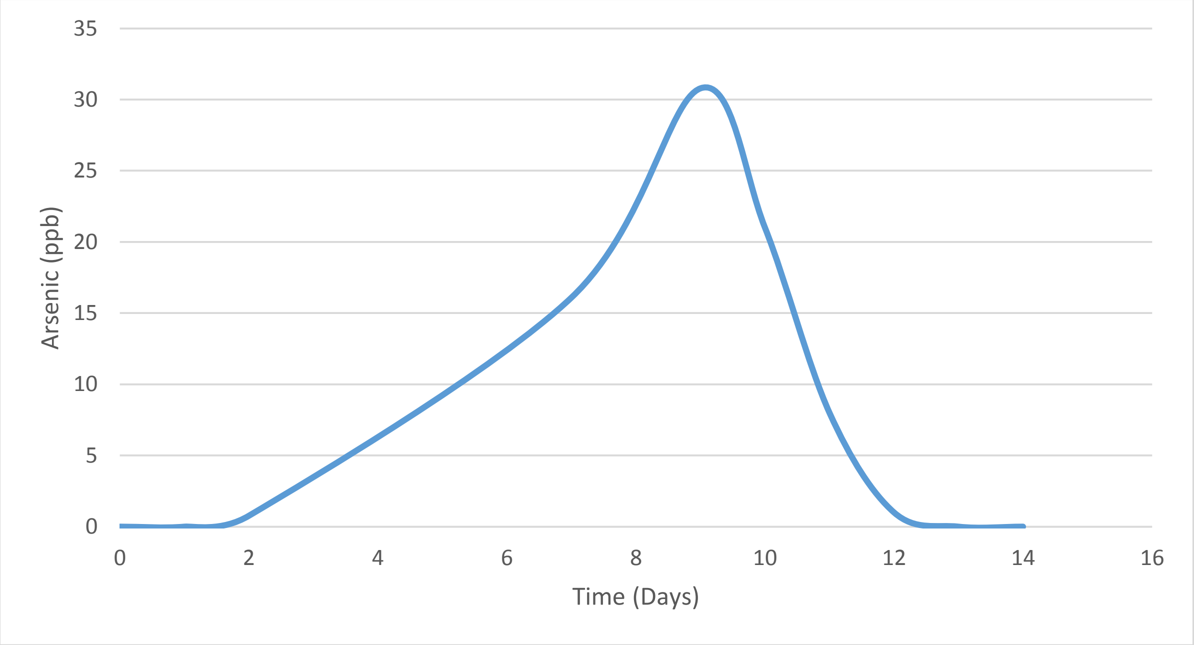

Figure 3.5: Volatilization data by *P. vittata* on contaminated soil with arsenic (adapted from Sakakibara 2007).

A sub model was constructed in order to analyze and compare the actual amount of arsenic released to the atmosphere verse modeled (Figure 3.6). In the Figure 3.7, the likeness between the predicted and the experimental data from Sakakibara et al. (2007) are depicted. This high similarity between the model and the experimental data validate: 1) the fundamental assumptions of the model; and 2) the value of the auxiliary variable in the base scenario which are reasonable and feasible (Table 3.2). Mirza et al., (2011) reported accumulation of arsenic in leaf tissue was a precursor to metabolic conversion and volatilization with *A.donax* L. volatilized an average 15.7% of arsenic uptake and is in accordance with Sakakibara et al., (2007).

The model has multiple auxiliary variables that have been categorized; four as estimated, four as calibrated and the remainder from literature. The categorization was performed according to the way in which their value was obtained, estimated for the value extracted from the literature and calibrated for the variables values modified to adjust model behaviors to the experimental data. The estimated parameters are supporting variables which values were approximated from experimental data. The estimated threshold concentrations impact the time step and stabilize the approximate distribution of arsenic to tissue based on literature. The variables are divided in three groups: threshold, rates and bioavailability constant (Fraction).

Table 3.2: Input parameter values for simulation

Parameter	Value	Reference
Contaminant Uptake		
Root threshold	0.5 ppm	Estimated
Stem threshold	0.004 ppm	Estimated
Leaf threshold	0.001 ppm	Estimated
Transpiration rate	0.001 ppm/d leaf	Estimated
Extraction rate	1.3×10^{-4} ppm/d soil	Calibrated
Translocation rate	7.25×10^{-5} ppm/d root	Calibrated
Respiration rate	3.55×10^{-4} ppm/d stem	Calibrated
Fraction	68	Calibrated
Water Uptake		
Curve number	81	Nearing et al.,1996
Rainfall	Time series measurements	Weather station
Transpiration coefficient	-1e-8*time*time+0.0002*time+0.032	Lee&Jose 2005
Time of day (diurnal factor)	1-5 (time variable)	Ouyang 2002
Root Conductance	0.02638	Boersma et al 1991
Stem Conductance	1.36132	Boersma et al 1991
Leaf Conductance	0.025043	Boersma et al 1991
Transpiration Conductance	0.1419	Boersma et al 1991

Model Calibration and Validation

In order to use the STELLA model to estimate the uptake kinetics of arsenic in a phytoremediation system, the input values of the parameters must be known and the model must be calibrated using a set of observed data. Model calibration is a process of adjusting input parameter values within a reasonable range to obtain the best fit between the observed and simulated results. The values of the parameters were obtained from theoretical calculation, published literature, or model calibrations. To reduce the uncertainties of the model predictions, two types of input parameters were used for model calibration. The calibration was accomplished by adjusting the rate and conductance coefficients to match kinetic rates observed in the test data.

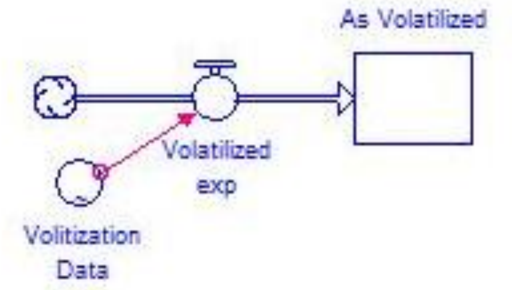

Figure 3.6: Schematic representation of Stock (level variables) and flow model to obtain the cumulative volatilized arsenic using experimental data.

The model was calibrated using data from experimental data reported by Sakakibara et al. (2007). These authors studied the phytoremediation of arsenic by phytoextraction through phytovolatilization. In the greenhouse experiment, arsenic contaminated soil was collected from a deposit site of neutralized acid mine drainage in Japan. The soil concentration of arsenic was 6,540 mg/kg-dry weight. The volatilized arsenic concentration data was selected to perform the quantitative analysis because of the environmental relevance and availability of data.

The percent of difference between experimental data and model for each analysis did not exceed 0.9%. Figure 3.7 shows a regression fit analysis, demonstrating a strong correlation

(99.4%). The slope of the regression line differed in 0.9% in comparison with the theoretical one. These values represent reasonably good correlations between the model predictions and the experimental measurements.

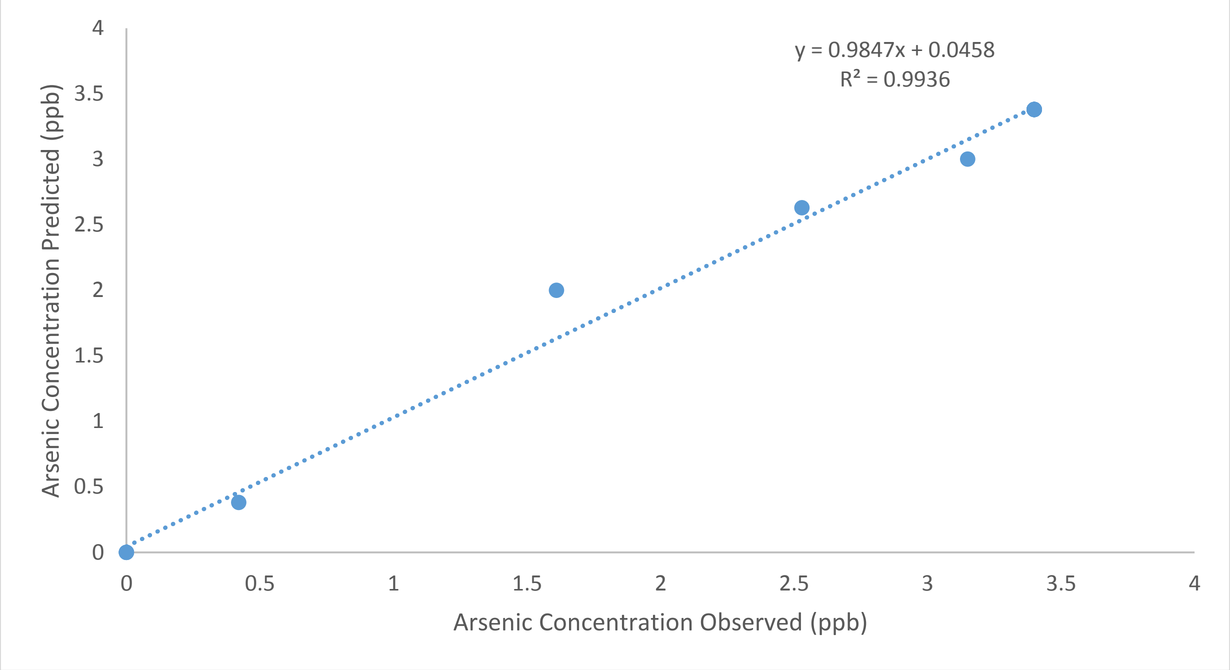

Figure 3.7: Regression fit analysis between experimental data (Sakakibara, 2007) and modeled prediction for cumulative arsenic concentration in ppb.

3.4 RESULTS

A simulation scenario was performed to investigate the dynamic uptake, transport and translocation of arsenic and water by a poplar tree. The poplar tree was divided into root, stem, and leaf compartments with the calculated growth factors. The growth volumes were extrapolated from literature sources and onsite data from active phytoremediation plots. Growth rate was established by a height of 2 meters and 2.2 centimeters diameter per year. The max growth potential was set at 14.5 meters, which is the average height of a mature poplar. Volume of mass of the tree was divided between compartments based on 18% leaf, 63% stem and 19% root (Johansson and Hjelm, 2012). The stem compartment is the total volume of trunk and associated limbs and branches.

The bioavailability of arsenic was represented in the soil section of the model by the Fraction calibration variable. This value represents the percentage of the contaminant unavailable for the plant uptake and removal per time step. The variable was constructed as an exponential dependence of the ratio of contaminant concentration in soil divided by the initial contaminant concentration in soil. The calibrated value for this scenario is 68, which mean that only the 32% of the arsenic is accessible for the removal at each time step. The concentration of the metal that is retained on each plants physiological section is represented in the value of the threshold variables. The contaminant flow through the phytoremediation system is characterized by the rate variables.

The ranking in ascending order of the threshold according to the contaminant concentration is: leaf < stem < root and rates is: translocation < extraction < respiration. The volatilization rate was excluded because it was calculated based on seasonality and a function of daily average temperature. The root has the higher value according to the threshold but its corresponding rate (extraction) was not. This magnitude relationship needs to be carefully analyzed because it can be a determining factor to the phytoremediation process.

3.4.1 Water Uptake, Transport and Transpiration

Rates of water uptake from roots to atmosphere is a factor of water potential and is directly comparable to water flow rates. Water flow rates vary in plant systems vary based on seasonality. Changes in average temperature and dormancy changes the water potentials which directly effects water uptake rates. The rate of water uptake by roots was significantly decreased from November to March due to decreased water potential gradient between soil and roots during dormancy of the poplars. Starting in April (spring) through October (fall), this rate increased dramatically and reached its maximal values modified by temperature variations (Figure 3.8). This occurs due to the high water potential gradients in soil to atmosphere during fall and summer.

The rate of transpiration for the simulated period for one year illustrates the seasonal average changes. The rate of leaf water transpiration was minimal during the winter due to an estimated dormancy and limited water need. The dramatic increase in the rate during the spring and summer cycle is due to ending dormancy and the beginning of the next growth cycle. Although the maximum rates of water uptake by the different compartments were varied, the averaged rates for all of them were similar. This rate keeps the amount of water flow into and out of the plant compartments balanced.

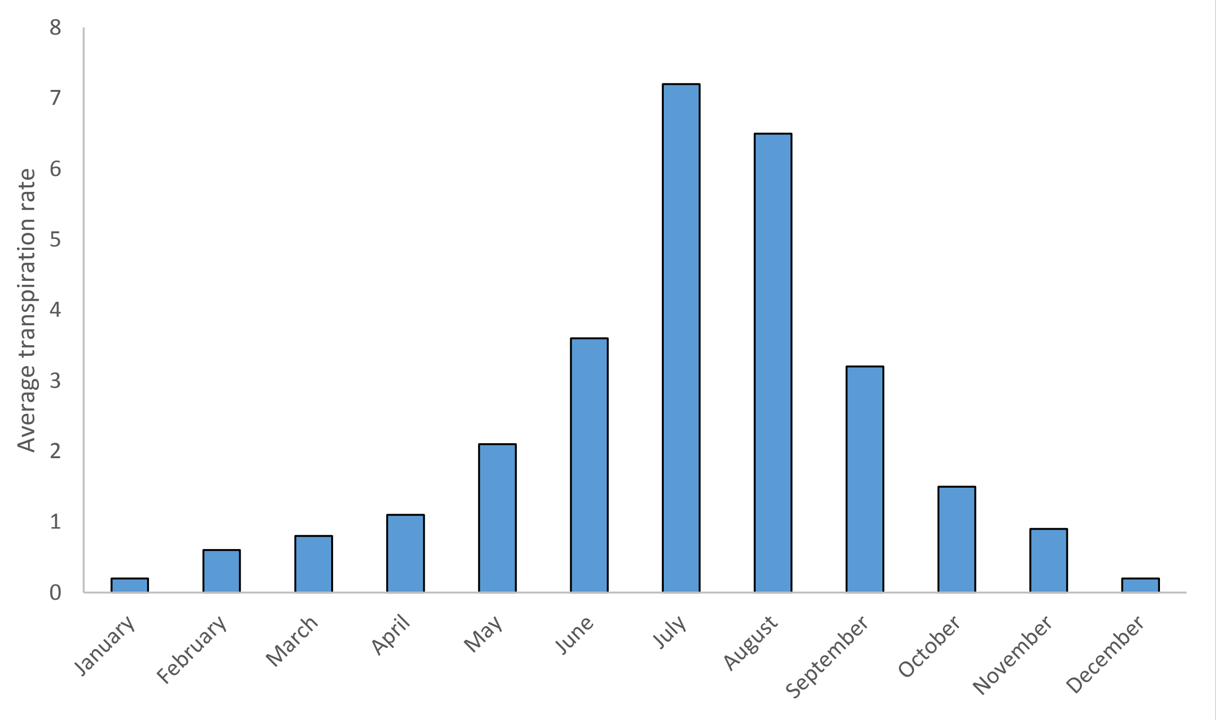

Figure 3.8: Average transpiration rates for each month for the one year modeling period 2012

3.4.2 Arsenic Uptake, Translocation, and Transpiration

The simulation started with the initial arsenic concentrations of 1000 ppm in the soil and 0 ppm in the plant. Arsenic uptake by roots was connected to root water uptake within the model because uptake of contaminant is a function of the dissolved portion of the contaminant. Arsenic uptake was decreased during the dormant season as a function of decreased water uptake in the plant and increased to maximal levels during the growing season. The rate of arsenic transport increased from the beginning of the growing season and reached equilibrium within the 14 days. The time to reach equilibrium was short do to the rapid growth associated with poplar.

The simulated accumulation of arsenic mass in roots, stems, and leaves increased from 0 mg at the beginning of the simulation to 66.8, 52.2, and 44.0 mg at the end of the simulation, respectively. This equates to 41% of arsenic in the roots, 32% in stem, and 27% in leaves in 365 days. The accumulation pattern is similar to previously reported patterns. The arsenic entered the roots and transported from the roots upward through the plant to the leaves with some transpired into the atmosphere. Results suggest that phytoremediation efficiency of soil contaminants depends not only on the plant species but also on the ratio of plant to soil volume.

A contaminant mass balance estimation was conducted using an initial arsenic mass of 1000 mg in the soil. The results of the one year (365 day) simulation resulted in 84.5%, 2.3%, 6.4%, and 4.7% of arsenic, respectively, resided in the soil, roots, stems and leaves. At a steady state rate of 15% per year uptake, the level of As in the soil will drop below 25% of the original concentration in approximately 9 years (Figure 3.9). Transpiration into the atmosphere from leaves was calculated at 2.1%. The lower transpiration rate is important as it becomes the limiting stem decreasing uptake of arsenic over time. The respiration rate becomes the rate limiting step in the mass balance of the system. This implication is useful when applying phytoremediation technique to remove contaminants from contaminated soils.

Pilot Study

The initial site sampling for the pilot study was conducted in June 2012 and consisted of 48 discrete samples collected from surface soils down to 2 meters. Analytical analyses for arsenic resulted in a 95% upper confidence level of 35.5 ppm (ranged from 5.6 to 709 ppm). Ten sample locations were selected from the 48 to sample on a quarterly basis for arsenic removal. The analytical analysis for the ten quarterly locations for arsenic resulted in a 95% UCL (upper confidence limit) of 41.8 ppm (1.64 to 192.54 ppm) (Table 3.3).

The pilot study was planted with poplar trees which were identified for potential adaptability to the site conditions. After installation of the pilot study, stabilized groundwater was used to irrigate the system. This water source was used during the first year of growth to establish the trees after the stress of transporting to and planting at the site. The quarterly pilot study results were plotted against the modeled extraction results using the initial concentration of 41.8 ppm which is equal to the 95% UCL for the ten quarterly sampling locations (Figure 3.10).

Table 3.3: Initial arsenic results for the pilot study in ppm. Quarterly locations are marked *

Sample	Arsenic	Sample	Arsenic	Sample	Arsenic
1	0.23	18	0.75	33*	26.10
2	81.87	19	2.52	34	2.98
3	1.33	20	6.17	35	0.95
4*	9.31	21	0.88	36*	9.32
5	0.91	22*	5.25	37	17.41
6	1.50	23	18.75	38	0.97
7	9.98	24	113.70	39	407.97
8	0.57	25	1.40	40	225.14
9	1.93	26	1.09	41	0.57
10	5.32	27	0.87	42	0.10
11	0.11	28*	10.74	43	0.85
12	11.09	29*	1.64	44*	2.29
13*	192.54	30*	9.76	45	0.13
14	4.91	31	82.60	46	0.20
15	12.08	32	709.00	47	0.83
16	0.13	33*	11.81	48	0.78
			95% UCL	Total	35.5
				Quarterly	41.8

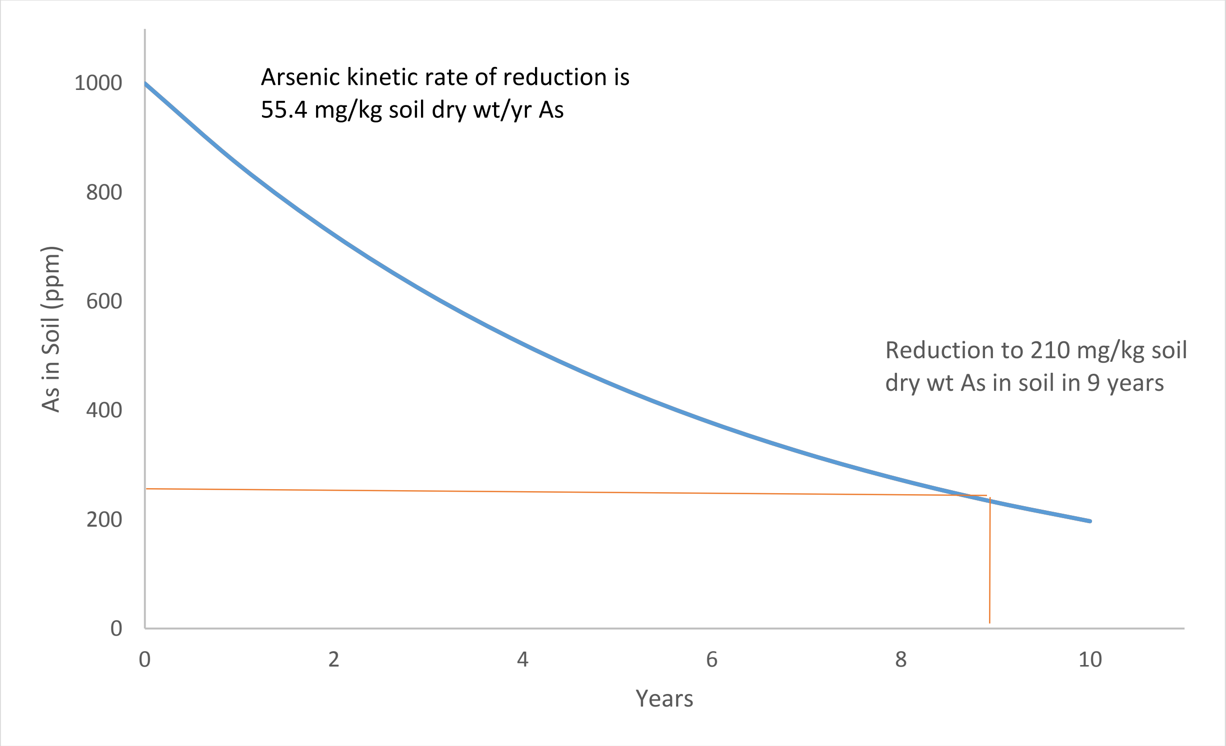

Figure 3.9: Graph of nominal 15% removal of As in soil showing 25% reduction in 9 Years

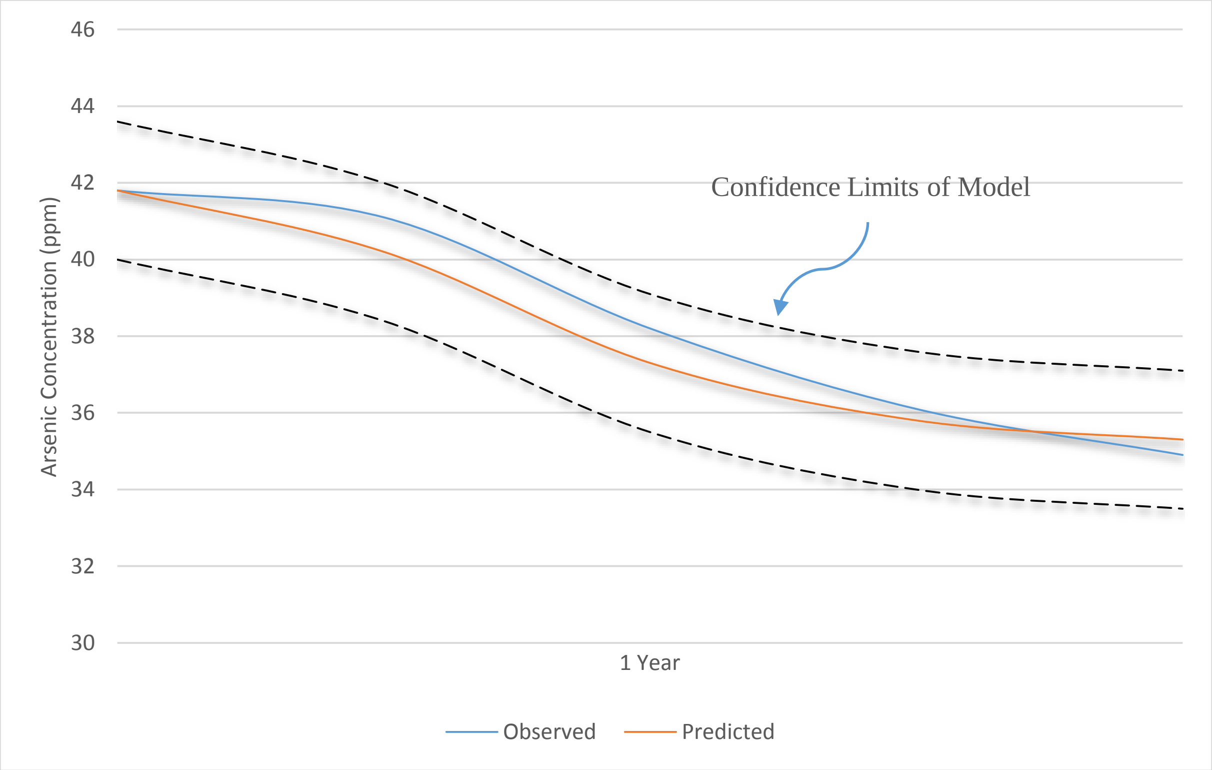

Figure 3.10: Graph of the comparison of cumulative arsenic removal from observed data versus predicted.

3.5 DISCUSSION

In this study, a phytoremediation model for uptake and translocation of contaminants and water was developed in STELLA. The model includes seasonal variations and growth which effect the water uptake potential. The model was tested against experimental data from published sources and active phytoremediation systems. The model was calibrate using this data and good agreement was obtained between the predictions and the measurements.

Phytoremediation implementation has not occurred to a significant level because of the lack of knowledge about the processes and availability of predictive tools. The phytoremediation model is capable of providing useful information to assess the performance of this approach. As an example, the interaction between the contaminant, soil and root can be summarized and modeled using the variables of fraction and extraction rate. Those interactions have been identified as a limiting factors in previous studies (Lasat, 2000; FRTRa, 2006). The selection of plant type or species given different scenarios is also a concern (U.S. Environmental Protection Agency, 2000; Pezzarossa et al., 2011). General concerns about implementation of phytoremediation are related to answering the following questions:

1. How will the plant respond to contaminant concentrations and environmental factors?
2. Which is the best plant type based on remedial goals?
3. What are the limitations of the system and time required to achieve goals?

These questions can be answered with the phytoremediation model calibrated to site conditions.

The bioavailability factor represented in the soil section of the model is governed by the Fraction calibration variable. The Fraction variable was correlated to the concentration of arsenate found in the experimental soil data. This value takes into account that arsenate is more bioavailable than arsenite. Soils contaminated with arsenic that are aerobic will favor arsenate over arsenite, as illustrated previously. Arsenate can follow the same metabolic pathway as phosphate and has been shown in other studies to increase plant growth. Given the current model, this factor was not evaluate due to increasing complexity.

The uptake rate (R_) function from one compartment to the next is dependent on the plant species selected. Based on the equations in table 3.1, the R_ function is directly proportional to contaminant movement. The uptake rates at each level will differ between groups, species and sub-species. The design of the model allows for the evaluation of different plants by changing the uptake rates to match published or experimental data available. Uptake rates may only be available for the total plant, but the compartment R_ factor can be estimated to match pilot data to evaluate the plant. The model specifically looks at the uptake rates for arsenic, but has the capacity to review additional contaminant classes by changing bioavailability and the R_ function. The uptake rates can also be calibrated to match observed contaminant removal if data on the specific plant does not exist. There are over 350,000 different species of plants, most of which have never been evaluated for application to phytoremediation (www.theplantlist.com, 2016).

Phytovolatilization is a favorable endpoint for contaminant uptake in a plant system. The modeled system considers uptake and volatilization of arsenic from the plant system based on previously reported studies. The volatilization is one way in which the plant system limits the overall contaminant concentration in tissues to limit toxicity. Although this is a favorable path, it is not necessary for the model to mimic uptake. Without the volatilization component of the model, contaminate uptake will continue as the growth function increases plant tissue. Uptake will continue until the tissue components reach a maximum level based on previous analysis of toxicity in the subject plant.

The concentration of arsenate in soils can be utilized to design a phytoremediation system focused on uptake kinetics of phosphate. Proper installation of phytoremediation systems can increase available oxygen in the soil to change the redox potential. As arsenate is removed from the soil by uptake through the plant, remaining arsenite will be oxidized to arsenate and taken up by the plant system. The phytoremediation model has the ability to reproduce the experimental results of experiment data with an excellent degree of accuracy and statistical significance as demonstrated by the analysis. The differential equations system summarizes the interaction between soil and plant, bioavailability, flows rates of both water and contaminant and concentration. These factors are some of the most influential concerns about phytoremediation that tackles the fully commercially implementation (U.S. Environmental Protection Agency, 2000; Sarma, 2011; Deuren, 2006).

Phytoremediation is considered a long term system that can take many years to lower contaminant concentrations to an acceptable level. The utilization of trees in these systems must consider that they will grow significantly during the operation of the system and uptake kinetics will change over time. Growth is of specific concern if hydraulic capture is a necessary component of the system. Many installations use average values of water uptake for mature trees when evaluating a systems efficacy or calculating the number of trees needed to effect the contaminant plume. Evaluating a system design based on mature growth will underestimate the ability of the system to achieve capture. The phytoremediation model increases system understanding leading to better decision making and calibration to specific site situations. STELLA’s graphical flow diagram presents the system in a transparent manner that provides for understanding to regulators about system considerations.

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CHAPTER 4
SIMULATING GROWTH, RAINFALL, AND SEASONAL TEMPERATURES ASSOCIATED WITH PHYTOREMEDIATION STUDY USING STELLA

4.1 INTRODUCTION

The remediation goals of each site may be different. For some sites, the remedial goal is determined by a contaminate concentration downstream of the source, and a remediation approach is needed to avoid groundwater movement to a critical receptor site. In other situations, the remedial goal could be removing or sequestering the solute mass from the source. Finally, some remediation goals would be decreasing groundwater flow to the point of hydraulic capture. The objective of the phytoremediation system at the subject site was broken down into the following phases:

- Hydraulic capture of ground water
- Contaminant mass removal over time

This study adds modular components to enhance useful data of the STELLA model in addressing several issues pertaining to the design and evaluation of a phytoremediation system with respect to the ability of the system to achieve the stated goals. The previous model description was enhanced with modules to create a more accurate depiction of the natural system. The modules included functions for Growth, Seasons, and Rainfall. Each of these components require significant mathematical computation in addition to the basic phytoremediation model

Computational tools are needed to predict the effect of deep rooted poplars to provide a large degree of solute mass uptake, despite variation in water use rates by systems. Modeling clearly has applications at phytoremediation sites for evaluating and designing a remediation system with respect to factors such as tree planting density, plant mass of the phytoremediation system, contaminant source, ground water flow and seasonal effects.

4.2 MODEL DESCRIPTION

Mass uptake of contaminants as a function of water use over extended time frames is not explicitly addressed in most models. Given that mass uptake is a function of the mass of the plant system, biological factors and seasonal variation, modules were created to run independently within the model. The independent modules were run first to calibrate to known data and then in time series to evaluate the effects on the modeled system.

4.2.1 Plant Growth Module

The plants installed in a phytoremediation system will continue to grow over the lifetime of the system. Models previously developed evaluate the system with plant mass in steady state. The plant growth module simulates sigmoidal growth, where height is assumed to asymptotically behave as a concave power function of time and is derived from the following equation

$$h(t) = \left(\frac{R\lambda K_R^{\lambda-1}}{m1}\right)^{1/\lambda} t^{1/\lambda} \text{ , when } t \gg 1$$

where

$$\lambda = 1 + m2(1 - m1).$$

With $0 < m1 < m2$, where t is the time step, R is the maximal growth rate, K_R is the horizontal maximum parameter, and m1 and m2 are shape parameters (Bontemps 2010). The numerical restrictions on m1 and m2 requires λ to be greater than 1. The equation for a generic one-dimensional model of plant growth is based on a "continuous medium" assumption of mass conservation and of the proportionality of the flux $\partial K_R/\partial x$ at the boundary to the value of K_R; and an assumption of no deficiencies in nutrients retarding growth (Zeide, 1993, 2004). Growth data was obtained from a site specific single year pilot study and literature sources on poplar growth dimensions (Woollons, et.al 1990).

4.2.2 Daily Rainfall Module

Rainfall data can be described by a gamma distribution (Stern, 1984; Katz, 1998; Wilks, 1999; Rosenberg et al., 2004). The reason for this is due to the equation being a representation involving only two parameters (Wilks, 1999). An extended model is explained for situations when the probability of a zero daily total is non-zero. The daily rainfall totals for the site will be modelled as non-negative random variables. For each day *t* of the year there is a chance that no rain will fall and so it is necessary to consider a model that allows positive probability for a zero total. To begin we divide the data into two groups; zero records and nonzero records. The probability of a zero total on day *t* is estimated by

$$p_0 = \frac{k}{n}$$

Where we use $k = k[t]$ to denote the number of zero rainfall records and n to denote the total number of records (Wilks, 1999; Rosenberg et al., 2004). The gamma distribution is used to model the strictly positive component of the daily rainfall. The gamma distribution is defined on $(0,\infty)$ by the density function

$$p[\alpha,\beta](x) = \frac{x^{\alpha-1}e^{-x/\beta}}{\beta^{\alpha}\Gamma(\alpha)}$$

where $\alpha > 0$ and $\beta > 0$ are parameters (Harris, 1998). The parameters $\alpha = \alpha\ [t]$ and $\beta = \beta\ [t]$ for daily *t* will be determined from the observed non-zero records by the method of maximum daily likelihood (Guenni, 1996). The general distribution of rainfall on the interval $(0,\infty)$ for day *t* can now be modelled with a cumulative distribution function. Let $x_a = x_a[t]$ and $x_g = x_g[t]$ be the arithmetic and geometric means of the observed non-zero values and $x_i = x_i[t]$ for day t in which case the maximum likelihood equations can be written in the form

$$\psi(\alpha) - \log_e(\alpha) + \log_e\left(\frac{x_a}{x_g}\right) = 0$$

where $\alpha\beta = x_a$ and $\psi(\alpha) \triangleq \frac{\Gamma\prime(\alpha)}{\Gamma(\alpha)}$ for each $\alpha > 0$ (Lehmann 1983).

Daily rainfall totals are based on the non-negative random variables from a mixed distribution. Simply, the zero rain day is based on the probability of a random number being less than or equal to zero based on known records for the site. The non-zero outcome is based on the random number being greater than the probability derived from a gamma distribution based on α and β parameters (Guenni, 1996).

4.2.3 Seasonal Variability Module

Seasonal variation can be modeled based on soil temperature which affects root water uptake. In the model, root water uptake plays a key role in the simulation. Heat is generally used in solute or water transport mathematical modeling (Bristow et al. 1986). Soil temperature has a major effect on hydraulic conductance of water into the plant. Seasonal variations affect the soil temperature and is a good measure for change in the phytoremediation model. A lowering of soil temperature to 5 to 35 ^{0}C strongly decreases water uptake (Kramer and Boyer 1995). A rise in soil temperature from 14 – 26 ^{0}C can increase water uptake by 30% (Hurd and Graves 1985).

The changes in root water uptake was model as follows:

$$n(z,t) = T(z,t) * R(z,t)$$

where $n(z,t)$= normalized function describing the relationship between soil temperature and root water uptake; $T(z,t)$= soil temperature profile distribution; and $R(z,t)$ = changes of root water uptake considering soil temperature (Yoshida and Eguchi, 1989).

4.3 RESULTS

The addition of growth, rainfall, and temperature had a significant effect on the uptake, transport and translocation of arsenic and water within the poplar tree. Previous models approach these ideas singularly or utilize a steady state set of parameters over a shorter period. The time step used in the model was 3650 days (10 years) after phytoremediation starts. This time series allows for maximal growth over time. The separate but connected modular components can be evaluated for use with the phytoremediation model without impacting the basic model structure.

Plant Growth

The graph of the modeled results in Figure 4.1 correlate with the expected growth pattern of the subject species which is a sigmoid growth curve with a horizontal parabolic branch. The numerical simulations of the model were based on the parameters of the poplar trees and pilot study generated averages. The branching would indicate that at or about maximal height the average speed of growth of the tree decreases. At some point the speed of growth becomes negligible with limited or no impact on the modeled results. The model indicates that the maximum rate of growth for poplars at 2.6 meters per year when the poplar is 4 meters tall. The growth trajectory for the poplar compared to two other species (pine and willow) are illustrated in Figure 4.1. The graph shows that within this simulation, both the pine and willow would have different growth potentials and rates based on the data.

The actual average growth of the poplar in the study site is similar in magnitude to the projected growth (Table 4.1). The observed poplar growth data at the study site was compared to the modeled data in Figure 4.2. The time scale of the observed data is comparable to the modeled data for the given time period. This is a good indication that the growth function is scaled to match the initial growth rates of the poplar trees. Continued evaluation over time will increase the validity of the growth function according to site data. The module is flexible enough to allow for new site data to be added and run based on current tree growth evaluations. Since the calculation is based on maximum tree height, if the trees toped or pruned for site reasons, the model can be evaluated under the new conditions.

Table 4.1: Average growth of poplar study site

Time	Diameter (mm)	Height (m)
Initial	41.4	2
Yr1	50.8	4.5
Yr2	68.6	5.6
Yr3	86.4	6.7

The total growth curve depicted in Figure 4.2 illustrates the change in rate of early growth vs late growth. Given that mass of the tree is a function of growth the module output becomes the input for root, stem and leaf mass based on the total growth of the tree. The plant mass ratio for each compartment, as previously noted, based on 18% leaf, 63% stem and 19% root (Johansson and Hjelm, 2012). The previous model design began with a static volume of mass and the static values were replaced with a linear growth model without change and caped at 15 meters. The sigmoidal growth module more accurately depicts the natural growth of the poplar trees as growth rate changes over time and tissue volume. The maximum growth rate of the willow and pine were 1.25 and 0.5 meters per year, respectively. The pine does not show a sigmoidal variation most like due to the stable growth rate and maximum height of 30 meters. The maximum height of the willow was similar to the poplar yet the maximum growth rate was significantly lower. Lower growth rate and height would indicate a lower overall mass for the plant system. The growth rate of the pine was lower and will create less mass for the uptake equation.

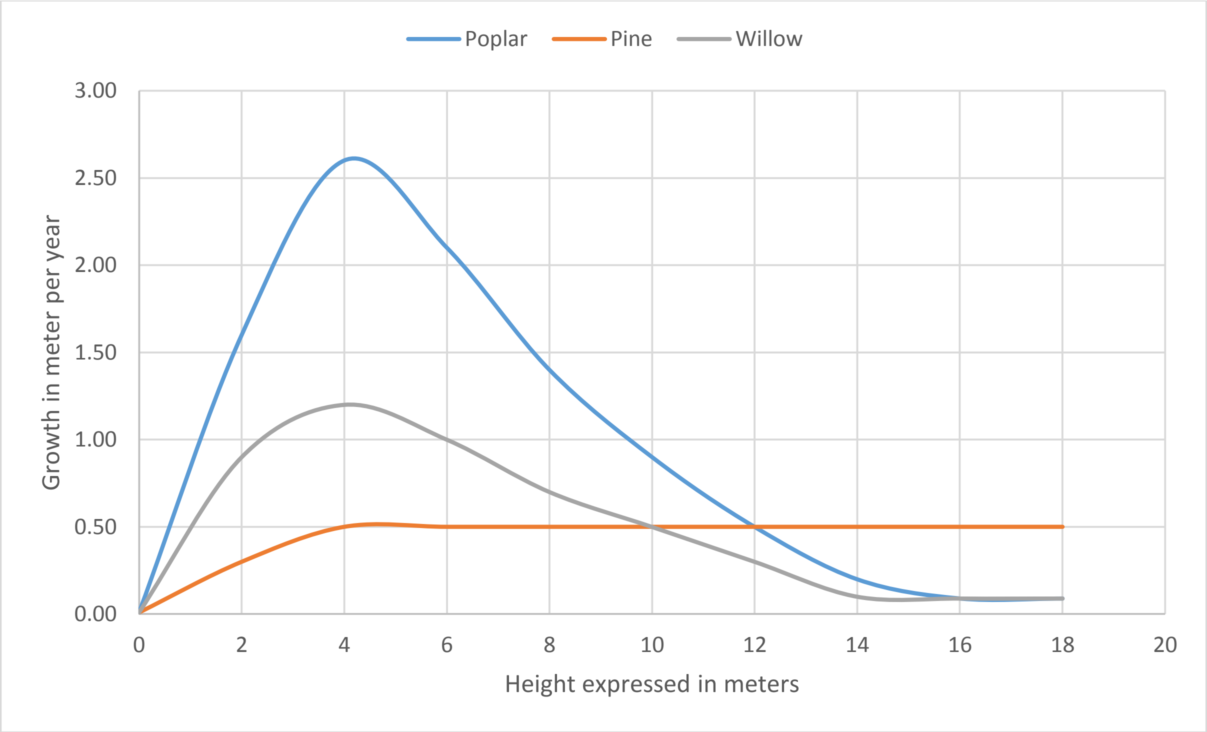

Figure 4.1: Graph of the estimated sigmoidal growth equations depicting growth per year as a function of maximum height.

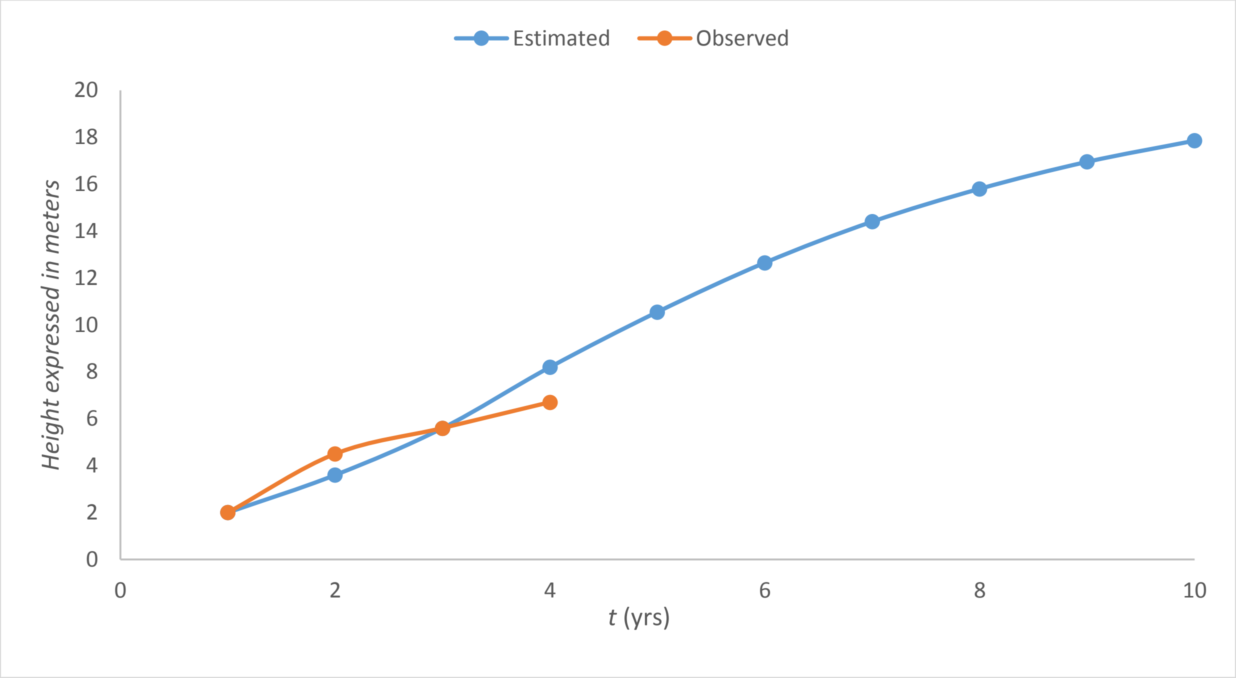

Figure 4.2: Graph of the estimated sigmoidal growth depicting maximum growth over time step and observed growth based on field measurements.

Rainfall

The maximum water uptake rate decreases to near zero during rainfall events. During times of rainfall, the stomata close and the hydraulic potential becomes nearly zero. The model in chapter 3 utilizes times series measurements with a ten year repeating pattern. The objective within this module was to utilize a synthetic rainfall model to estimate daily rainfall occurrences verses monthly averages. The maximum likelihood to find parameters was used for both the probability of a zero outcome and the gamma distribution that best matches the observed probability density for the strictly positive outcomes. The performance of the module was assessed by comparing the average of each characteristic from the synthetic generation with the observed historical data.

Climate data was obtained from the golden gate weather services. Table 2 indicates that the winter months have the highest levels of rainfall and the highest levels of variability. Months with the highest level of rainfall tend to also have the highest level of variability. This is consistent with rainfall data from other locations. Table 4.2 lists the parameter estimates for α and β using maximum likelihood.

Table 4.2: Monthly means and standard deviations for site #1.

	Mean (mm)	Standard Deviation
January	114.90	85.68
February	94.15	69.15
March	77.83	54.08
April	38.08	38.42
May	15.44	19.92
June	4.06	8.70
July	0.45	1.65
August	0.93	2.77
September	6.52	13.75
October	26.06	29.52
November	66.17	57.02
December	108.83	81.69
Annual	553.43	191.26

Table 4.3: Parameter estimates for monthly rainfall records at site #1.

	α	β
January	1.84	62.84
February	1.48	64.05
March	1.64	47.48
April	1.11	35.09
May	0.81	21.49
June	0.61	10.03
July	0.85	1.49
August	0.69	3.26
September	0.71	14.34
October	0.83	34.14
November	1.24	57.79
December	1.81	60.82

The synthetic rainfall generated by the gamma distribution based on the two parameter estimates suggest that there is a reasonable independence. To generate the sequence of rainfall, we generate a sequence of independent random numbers uniformly distributed on the unit interval [0,1], and then solve the probability distribution equation

$$F[p_0, \alpha, \beta][t](x) = r[t]$$

to find the corresponding rainfall denoted by $x=x[t]$. If $r[t] < p_0[t]$ then $x[t]=0$ (Dick and Bowden 1973). The parameters are defined by the maximum likelihood estimates from the observed monthly data. Figure 4.3 and 4.4 shows a histogram of the observed monthly totals versus the generated monthly totals using the 2-parameter gamma distribution for January and September. The two histograms were used to evaluate the distribution of data between wet versus dry months.

For each month, a large number of daily rainfall totals are generated and summed. The daily rainfall totals that best match the monthly total is selected as the synthetic daily realization. Figure 4.5 and 4.6 illustrate the generation of two different daily realizations, which match the monthly totals for January (176 mm) and September (3 mm). Although the daily-estimated data is quite different, the monthly totals are the same. This methodology for generating daily rainfall totals preserves the daily statistics and matches the monthly totals. Any sequence of daily totals that match a pre-determined monthly total are equally likely. Thus we can select any of these estimations as a possible sequence for the modeled month. In this way, we ensure that the long term statistics are preserved at both time scales.

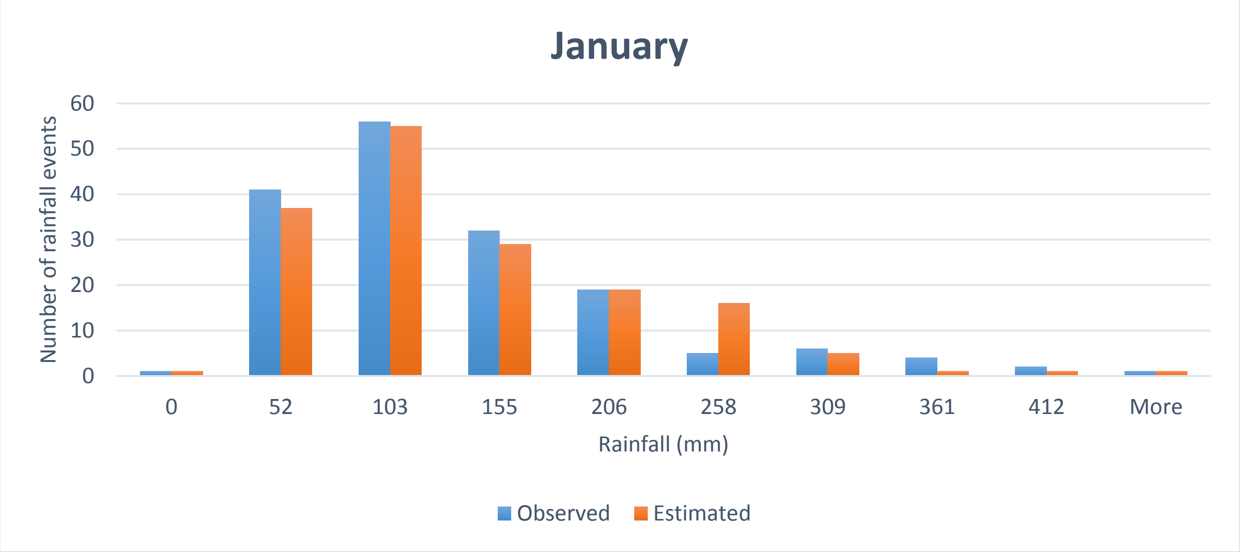

Figure 4.3: Histogram of observed vs estimated monthly rainfall totals for January.

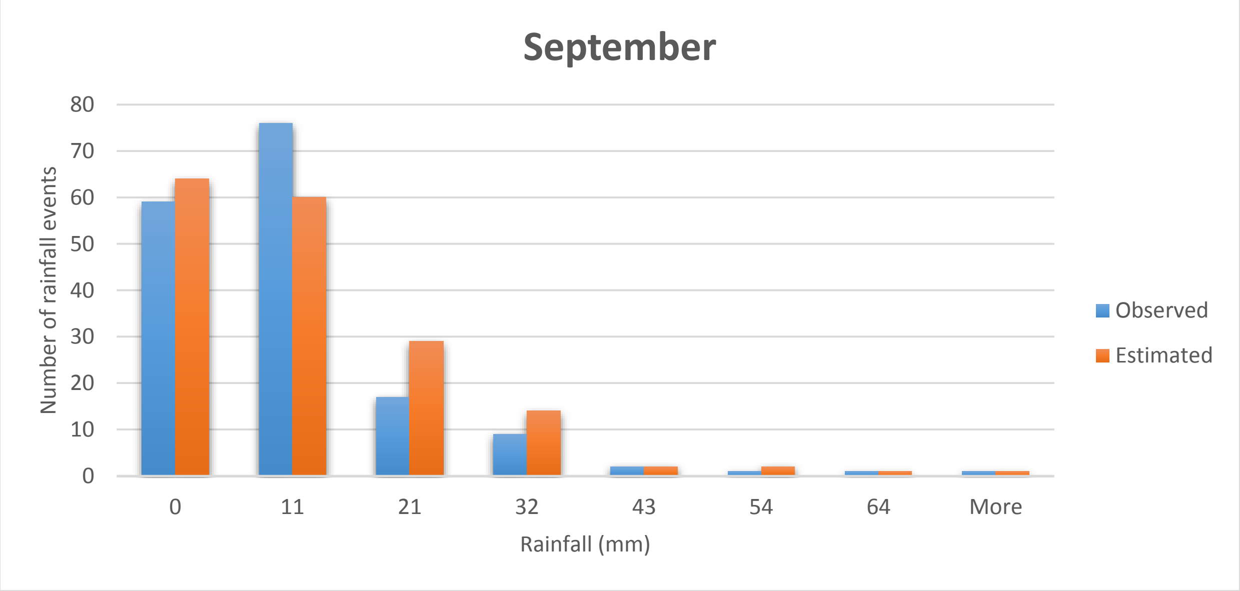

Figure 4.4: Histogram of observed vs estimated monthly rainfall totals for September

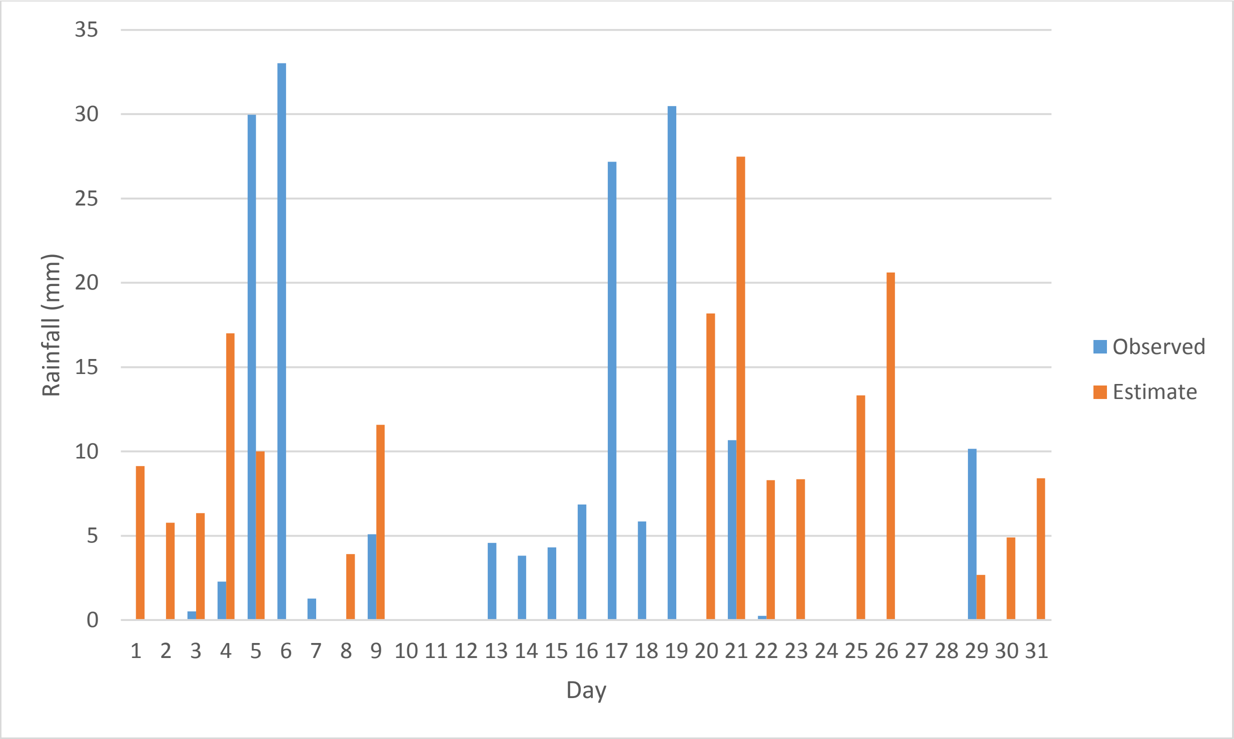

Figure 4.5: Generated daily estimates compared to actual daily data for January 2015

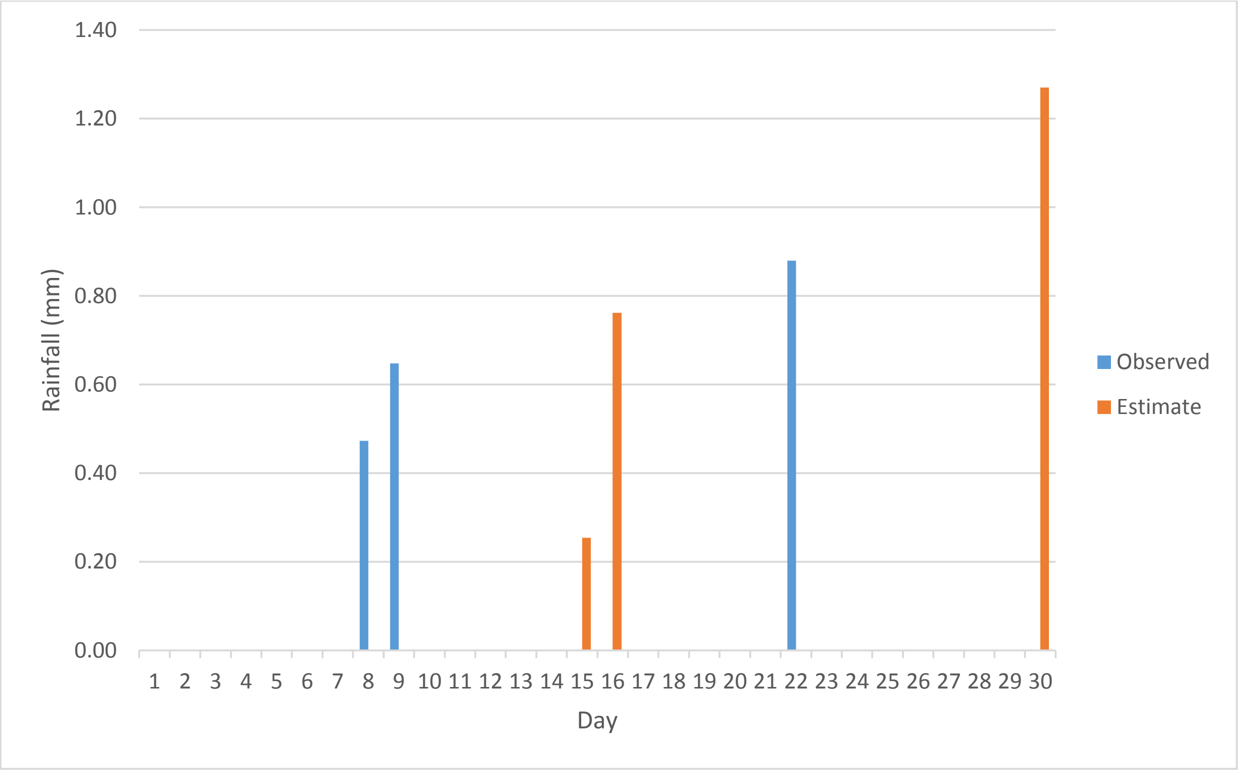

Figure 4.6: Generated daily estimates compared to actual daily data for September 2015

Seasonal Variability

The relationship between soil temperature and root water uptake was taken from literature. Root water uptake for poplars was evaluated and estimated based on literature values and data collected from a one year pilot study. Root water uptake rate changed logarithmically when considering soil temperature. The function between temperature and water uptake was fitted using a logarithmic regression of the data model effect (Figure 4.7). The fitted formula was used to describe the root water uptake for soil temperature ranging from 8 to 36^{0}C, which was mainly in the range of annual soil temperature.

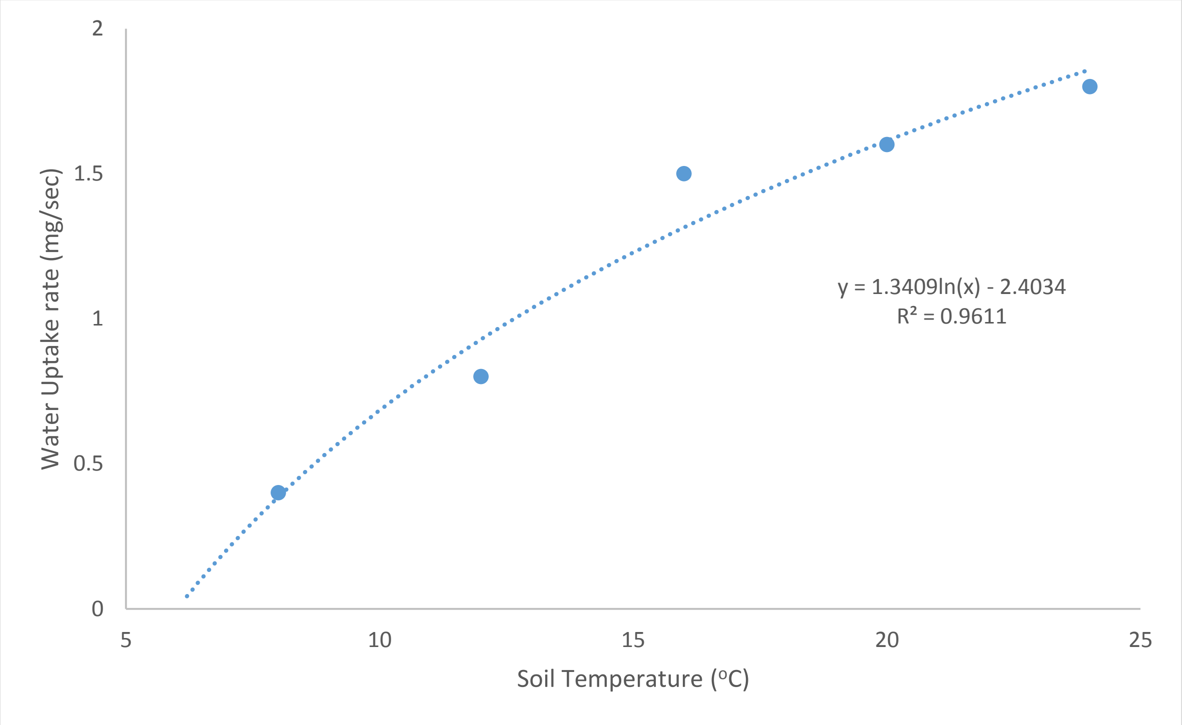

Figure 4.7. Relationship between root water uptake rate and temperature estimated for poplar.

4.3.1 Effects on Water Uptake

Rates of water uptake from roots to atmosphere is a factor of water potential and is directly affected by rainfall, growth and seasonal temperatures. Changes in temperature effect water potential, which directly effects water uptake rates. The rate of water uptake by roots was significantly decreased from November to March due to decreased water potential gradient between soil and roots which was a direct result of decreases in temperature and increases in rainfall. Starting in April (spring) through October (fall), this rate increased dramatically and reached its maximal values modified by temperature variations. This occurs due to the high water potential gradients in soil to atmosphere during fall and summer.

The increase in rate of transpiration for the simulated period of 10 years is directly proportional to the rate of growth of plant mass. The rate of leaf water transpiration was minimal during the winter due to a decrease in temperature and increase in rainfall limiting water need. This simulates the dormancy period for the poplars. The dramatic increase in the rate during the spring and summer cycle is due to favorable conditions and the beginning of the next growth cycle. Although the maximum rates of water uptake by the different compartments were varied, the averaged rates for all of were similar.

Plant mass in each compartment directly effects water uptake as plant mass and water potential are directly correlated with total water uptake. As either changes, the maximum uptake of the plant system changes. The growth module has an input of initial plant mass and estimates, based on growth rate, the increase mass over time. The total plant growth is then subdivided into percent to each compartment. The model then calculates the total water potential between compartments based on the increase in plant mass as previously described.

Over the ten year modeled run, the total annual water potential increased within the plant as growth increased. Given variation in rainfall and temperature, which directly effects water potential, the annual totals for ten years was illustrated to minimize the monthly variation from these factors. The combination of growth and hydraulic potential based on temperature has a direct effect on total water uptake. The effect of rainfall and temperature variation becomes more pronounced after the tree has reached maximum growth. There is a combined effect when the temperature variation limited the effect of growth on the total water uptake potential.

4.4 DISCUSSION

In this study, the phytoremediation model for uptake and translocation of contaminants was enhanced using independent modules in STELLA. The modules include Growth, Rainfall, and Season. The feasibility of the modules were tested against the experimental measurements prior to their application. A good agreement was obtained between the estimates and the observed. Simulation scenarios were chosen to demonstrate the uptake and translocation of arsenic by a deep rooted poplar tree for a maximum simulation period of 10 years. Simulations showed that the modules are directly related to the total water uptake in the poplar, which is the driving factor in solute uptake.

The average water uptake rates of the system generally increased over time based on growth and seasonal variations. Rainfall also decreased the overall uptake of water and contaminant but was muted somewhat by the timing of the wet season versus overall temperature. The climate in the area is dry during the warm season with minimal rainfall and high temperatures and wet during the cold (dormant) season. The overall effect was to minimize the impact of the rainfall on total water uptake. The model simulation period was set at 10 years and correlates to the maximum growth of the poplar.

The independent modules can be run concurrent with as well as separated from the main phytoremediation model. This allows for the addition of new data to the modules to be tested and validated without effecting the overall model. This modular component can be a valuable tool for gaining insights into the mechanisms controlling uptake and translocation within system and can be used to suggest alterations to the system in order to keep both water and solute uptake at expected levels. This information could be useful in management of the phytoremediation process, assisting managers in determining the optimum time frame for poplar replacement. The accumulation of As in plant tissue can become an issue when the tree is distressed. Although the model was not calibrated specifically to final plant tissue As concentration, samples can be taken during the pilot study to estimate the level fixed in tissue. Recognizing that uptake and translocation is a function of both plant and environmental conditions and that those conditions are dynamic will help environmental managers make decisions that will positively impact the efficacy of the system.

The growth portion of the model starts the system with lower plant mass than the averages given for daily uptake of water. As the tree grows, the average daily uptake changes with growth and can surpass the standard daily averages currently used in design assumptions. The growth module has the flexibility to change plant species and assess plant mass changes based on different growth dynamics. The percent mass between compartments is based on the tree species and will differ based on the different species and plant classes. Growth is directly proportional to overall plant mass and water uptake. The changes in the plant growth dynamics will change the rates of contaminant and water uptake. The model is designed with flexible input variables and allows for the evaluation of other plants.

The growth module can run with different species data for growth rates and maximum height. The output of the model gives a total tree mass at each time step that is input into the water uptake side at each stage. The equation at each stage has a root, stem or leaf mass component that is taken from the total estimated mass over time. The total is subdivided based on the plant species and is directly proportional in the water uptake equation for each tissue section. The rate of growth vary with different species as well as the percent of mass in root, stem and leaf (Table 4.3).

Total plant mass is directly related to the capacity of the plant to transmit water. The plant matrix transports contaminant mass in solution as a function of water uptake. The plant growth rate and maximum height can indicate how quickly the plant can increase mass and it ability to remove contaminates from the media. The percent mass ratio is also an indicator of where the concentration of contaminants should be the highest based on available mass. The total uptake of water and solute can be evaluated based on plant species as a function growth as a selection criteria for the best species to evaluate within a pilot study.

Table 4.4: Percent mass ratio between compartments, max height and growth rate based on species.

Species	Root	Leaf	Stem	Height (m)	Growth Rate (m/yr)
Pine	20	9	71	30	0.5
Spruce	20	12	68	18	1
Fir	25	17	58	21	0.6
Yellow Pine	31	5	64	35	0.36
Hemlock	24	5	71	21	0.6
Hard Wood (average)	32	4	64	18	0.27
Alder	33	4	63	39	2
Birch	28	5	67	18	0.8
Willow	15	12	73	6	1
Aspen	29	3	68	15	2

(Modified from Hakkila, 1991)

The percent mass of stem is significantly greater in comparison to the other plant tissues. The percentage indicates that the stem would have the greatest capacity to store or hold contaminants without adverse effect to the plant as a whole. This also illustrates that as part of the final remedial solution the end of life of the system should consider stem tissue concentration for disposal of dead trees or if complete removal is part of the design. Leaves have the least mass of all the tissues and as such may concentrate contaminants quicker and require periodic removal during leaf drop. The total transpiration rate is limited by the mass of the leaf compartment. The lower mass percent of leaf will be a limiting factor of the maximum rate of both water and contaminant volatilization.

The model can also use a combination of growth and seasonal changes to predict chances of seasonal extremes that can lead to decreases in water uptake irrespective of the current level of growth. The seasonal changes effect the daily average uptake and can be used to ensure that breakthrough does not occur if hydraulic control is the goal. A more in-depth understanding of hydraulic conductivity in the groundwater system would be needed to understand dormancy effects on the system.

The phytoremediation model requires an understanding of the local environmental, including soil, water, rainfall, and seasonality. To be able to apply the model to a specific site, a minimum of information is needed to generate results. A hierarchical decision tree of model input considerations is illustrated in figure 4.8. The decision tree is a logical path of the informational concerns that must be addressed and incorporated into the model for phytoremediation system analysis. The application of the model is dependent on the level of data available and the identification of data gaps. The model evaluation can lead to an understanding of what data gaps exist and direct future decisions on data collection as part of the pilot study. The collection of data from the pilot study can then be focused on the data gaps identified by the decision path and the modeled outputs.

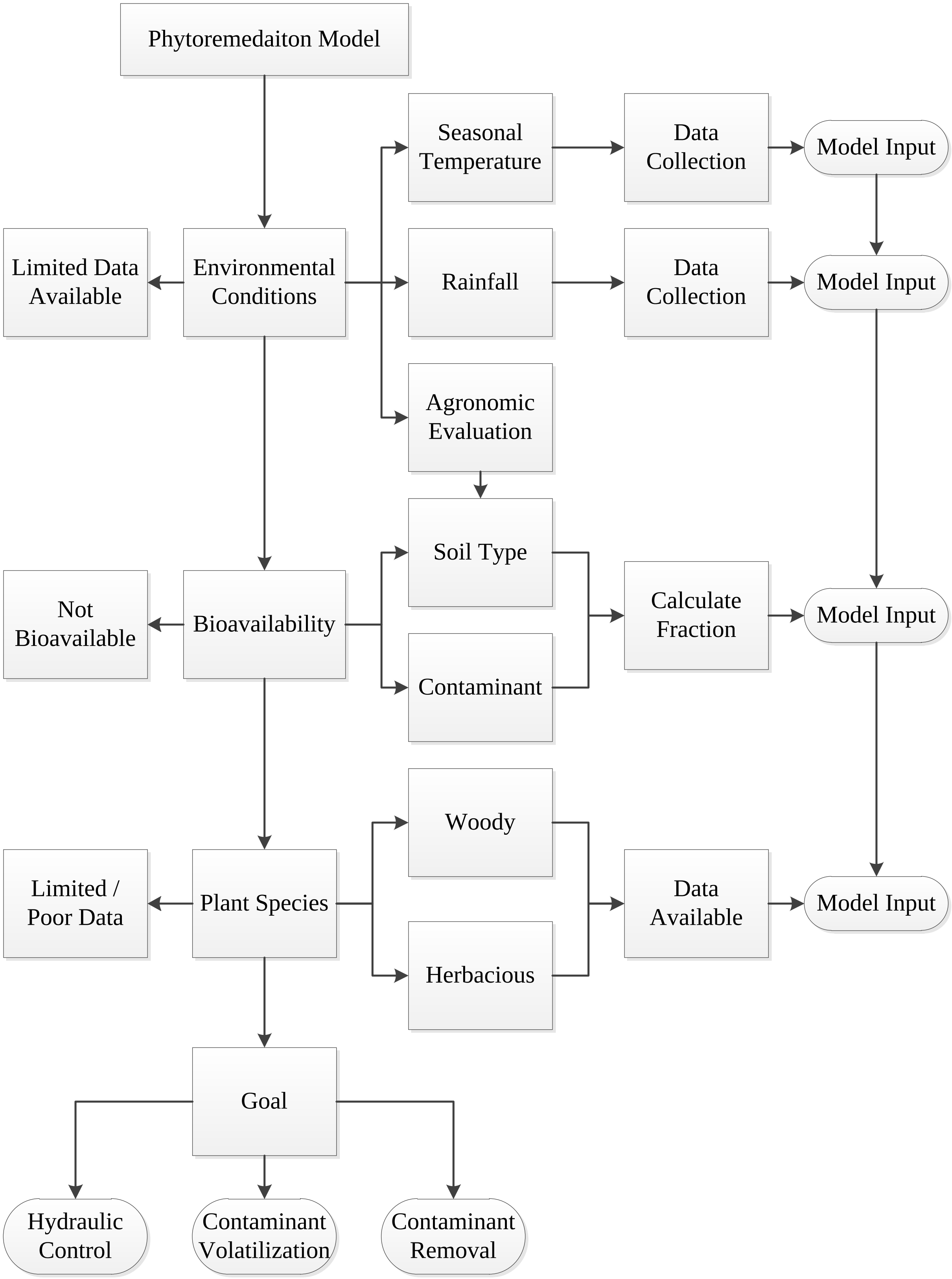

Figure 4.8: Hierarchical decision tree of model input considerations

Model strengths include its ability to: (1) provide information and insights concerning time dependent behavior of the system like growth, season changes, and rainfall over the course the remediation; (2) tie together information and empirical data from many different sources, providing a comprehensive view of the system; (3) provide information on seasonal changes that may impact the system and allow managers to plan; (4) flexibility allows for different input variables based contaminants, soil type, bioavailability, plant species, and different environmental parameters; and (5) can be utilized as a decision tool to evaluate different plant species within the same site for pilot study selections.

Model limitations include: (1) assumptions that cannot be tested by conventional means; (2) estimated parameter values contain a level of uncertainty; (3) requires information on plant species that may not be currently available; (5) requires knowledge of contaminant to estimate bioavailability to the plant; and (5) arid site conditions may affect the models ability to predict uptake. As more information is gathered, this model can be further refined and/or modified, and should continue to serve as a useful tool for gaining insights that may increase the viability of the phytoremediation process. Pilot studies conducted to evaluate multiple species and their effectiveness to achieve site goals can be enhance by baseline modeling assumptions. The model can be used as a guide to choose the best options for a pilot study and increase the efficiency of the decision process. The model can also be used as a guide to the types of data gaps that need to be closed to predict the long-term performance of the system. The tissue concentration estimation in each stock is a predictor of possible future tissue toxicity when capacity is reached. Phytoremediation may take longer than traditional methods to reach final cleanup levels, but site specific modeling data will allow engineers to evaluate the proposed system and estimate the time to completion of goals.

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CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

Many sites throughout the world are contaminated with arsenical compounds from mining, pesticides (Woolson et al., 1977), industrial manufacturing and through natural transformation of arsenic in soils (Adriano, 2001; World Health Organization, 2001; Singh 2011). Arsenic is a naturally occurring element that ubiquitously exists in both organic and inorganic form in the environment. Arsenic contamination is an issue of concern worldwide and it is a considerable risk factor in various countries.

Arsenic is toxic, affecting essentially all human organs, and has been associated with certain cancers including skin and lung through reactive oxidative species. Inorganic arsenic can be separated in to two forms arsenate and arsenite. Arsenate is less toxic and less mobile in the environment than arsenite, but each conveys significant health threats to animals and humans. Wetland or seasonally watered soils can become anoxic and reduce arsenate to arsenite increasing environmental threat. The results of the initial risk based study strongly indicate that when evaluating well drained upland soils, estimates of the risks should be based on the toxicity of arsenate.

In well drained soils the arsenate form is the predominant form found. This understanding affects site-specific risk assessments, ecological risk assessments and remediation design in oxidative, aerobic soils. Current information urges a shift in the strategy for assessment of arsenical risks in upland soils, moving away from a focus on arsenite. Arsenate can be reduced to arsenite during flooded conditions in upland soils. The flooding of upland soils from intense rain events cover the ground with oxygen rich waters which decreases the speed conversion of arsenate to arsenite. Another characteristic of arsenate is its resemblance to phosphate, which is noted in the periodic table by arsenic and phosphorus occur in the same group (column).

The uptake kinetics of arsenate in soils match pathways for phosphate uptake in plants. This preset pathway increases the likelihood of plants being able to uptake and respire arsenate. Site specific data on oxidative state, pH, organic carbon and arsenical speciation can enhance phytoremediation decisions. Understanding the valence state of arsenic in poorly drained wetland soils adds value to the decision making process by indicating that a specific remediation technology may not be effective. The arsenic ratio can impact plant selection and types of amendments needed to create or enhance an aerobic environment to facilitate the mass balance to arsenate.

Phytoremediation has been shown to be an effective alternative to remove contaminants from soil, sediments, and groundwater with relatively inexpensive operation and maintenance costs (Salt et al., 1998; Dietz and Schnoor, 2001; Pilon-Smits, 2005; Gerhardt et al., 2009). Removal of arsenic occurs because plants are able to uptake, metabolize and store arsenic in plant tissues. Several mathematical models have been developed to describe contaminant uptake as a function of chemical compounds involved, plant species used and environmental conditions at the subject site. The modeling for natural processes are dynamic and depend on time dependent environmental conditions like rainfall, growth, and seasons.

In order to describe the arsenic uptake kinetics, a dynamic systems model was developed to simulate phytoremediation. This was done using the STELLA modeling environment. The choice of modeling tool was because STELLA uses a graphical user interface that is both easily understood and creates a visual conceptual systems model. The visual aspect allows for stakeholders, regulators and scientists to understand the general logic of the model and the functional aspects. This wider understandability of the model will lead to efficient critical decision making. A general groundwater solute transport with phytoremediation model was developed to study fate and movement of arsenic through a poplar tree. The model consisted of two components: one for uptake of groundwater and one for contaminant uptake.

This study demonstrates the usefulness of numerical groundwater modeling in addressing several issues pertaining to the design or evaluation of a phytoremediation system which depends on trees. The engineered system of deep-rooted poplars trees (or similar species) was predicted to provide a large degree of hydraulic control and direct uptake or translocation of contaminants, despite seasonal variation in water use rates. The evapotranspiration was periodically increased and decreased by simulating seasonal changes in plant consumption. Modeling clearly has application at phytoremediation sites for evaluating ~~or~~ and designing a containment system with respect to factors such as tree planting density, seasonal effects, residence time of groundwater within the active microbial rhizosphere, prediction of downgradient distance where the contaminant concentration reaches a point of compliance (POC), and future modifications to the system design to reduce the contaminate mass-flux.

The enhanced modular model presented in Chapter 4 extended the capabilities of plant uptake simulation to include three different modules that can be evaluated, tested and updated independent of the model. The model was used to investigate several site specific parameters for phytoremediation including growth, seasonal temperature and rainfall and their effects on water and contaminant uptake. In general, modeling researches on phytoremediation helped to determine the various mechanisms involved in movement of soil constituents in presence of plants. This model could also be utilized in design to predict the feasibility of using trees/phytoremediation for controlling or remediation contaminated soils and groundwater. Phytoremediation is economically competitive and results are impressive to regulators and user communities. Enhanced biodegradation in presence of plants occurs in this process but was not demonstrated in this study because the focus of new model was plant uptake. The root zone supports a eutrophic environment by exuding sloughed root masses and rhizodeposits that provide carbon and energy to diverse microbial consortia indigenous to soil.

The benefits of phytoremediation in comparison with traditional cleanup techniques are numerous, yet U.S. Environmental Protection Agency has concerns with regard to the best plant species for a particular contaminant and the time required for cleanup (U.S. Environmental Protection Agency, 2000; Chaney et al., 2007). Several mathematical approaches have been implemented to understand the soil-plant interaction (including phytoremediation) during the last forty years (Benbi and Nieder, 2003). Besides the system dynamic approach, it has been found that the theoretical point of view provides the differential equation solution set, defined by models for compartmentalization of the plant and a variety of other approaches to understand the phytoremediation phenomena in a comprehensive way (Robinson et al., 2003; Trapp, 2004; Thomas et al., 2005; Japenga et al., 2007; Qu et al., 2010). These models are mathematically intensive and very specialized. These implementations have considerable complexity, having 30 to 40 variables per model or more. Those variables have to be: calibrated, estimated and assumed. The phytoremediation model is a classical plant physiology structure, providing an understandable and comprehensive tool; representing the plant as a pipeline structure coupled with contaminant uptake dependent on the water uptake side of the model. The final phytoremediation model contains modular components that can be run independent or turned off depending on the need for added complexity.

One of the biggest concerns about phytoremediation approach is plant selection (U.S. Environmental Protection Agency, 2000; Pezzarossa et al., 2011). Using the phytoremediation model as a plant performance evaluation tool for a specific scenario an objective selection could be performed. The uptake kinetics of differing species of plants could be used to calibrate variables that reproduce the experimental data behaviors either created or from literature. The model can generate data that can be used to estimate the long term effects of a specific plant species performance with respect to historic site conditions and contaminant. Most phytoremediation systems are evaluated based on a pilot study to evaluate best species with respect to site conditions and contaminant. A good agreement between the pilot study and the phytoremediation model can establish the model significance or correlation between observed and estimated data.

In the present work, the phytoremediation model has been shown to be a useful assessment tool for the evaluation of site characteristics and plant dynamics. The implementation of the model can evaluate different contaminants and concentrations, plant types (trees, hyper accumulators, etc.) and phytoremediation processes. The phytoremediation model can be implemented as a standardized tool for phytoremediation systems performance evaluation. The performance dynamics can be updated with updated data on growth, weather patterns, site specific uptake kinetics and environmental changes. Environmental management of phytoremediation needs continuous assessment tools based on a total quality management approach. Different phytoremediation systems can be implemented through the statistical correlations between data sets from literature and pilot studies.

The metal bioavailability has been mirrored successfully by model, determining its dependence of contaminant concentration. The Fraction auxiliary variable, which summarizes the bioavailability of the contaminant to the root soil is the exponent factor of the contaminant dependence. This variable synthesizes the soil's physical and chemical factors, such as: pH, organic matter, carbonates, electrical conductivity and grain distribution, which govern the contaminant bioavailability. As the Fraction variable increases the contaminant has less mobility.

The threshold values for each physiological section established in the model can address the drawback portion of the contaminant kept in the plant section (root, stem, leaf). The final concentration of contaminant by physiological section are consistent with the typical experiment of contaminant concentration accumulated (Jadia and Fulekar, 2009; Sarma, 2011). The modeled contaminant accumulation within the plant sections can be used to compare with previous knowledge about contaminant tolerance within the plant. The modeled results obtained by the phytoremediation model can indicate if the tree or plant species can survive during the phytoremediation process and for how long. The phytoremediation model has the capability to appraise the rates according to the physiological process: extraction (soil to root), translocation (root to stem), respiration (stem to leaf) and volatilization (leaf to atmosphere).

The uptake rate of water and contaminant can vary in different plant species. The model was designed to use estimated, calibrated and observed uptake kinetic data to account for variability due to species and to evaluate the usability of different plants in a phytoremediation system. Growth dynamics differ by species, climate, and conditions and directly impacts the uptake rate of the solute. The growth module within the model allows for independent calibration to the growth dynamics of a plant to match understood patterns. The model divides total plant mass derived from the module by percent root, stem and leaf which can be matched to estimated or published data to equal expectations in the field.

Contaminant uptake was considered as a function of water uptake from roots to atmosphere and is directly comparable to water potential. Water flow rates vary in plant systems based on seasonality. Changes in average temperature and dormancy changes the water potentials which directly effects water uptake rates. The model was able to predict the effects of seasonal variation and growth on the water and contaminant transport through the plant system. The additions of the modular components for rainfall, growth and seasonal change in temperatures allow the model to be tuned to the specific environmental factors at a given site. The model can be run at steady state given averages for each component or a set rate value. This allows the flexibility to create scenarios for singular events or to project over extended periods given enough historical data. The modules can be enhanced with different constants, data, or equations as understanding within a system expands. This greater understanding of the system allows managers to enhance the phytoremediation project to achieve required goals.

Modeling allows the analysis of different scenarios, and determines and ponders the most relevant criteria to assess system performance (Fisher, 2007); these features are highly desirable for the environmental decision making process. This was demonstrated with the model, which has the capability to mimic phytoremediation processes and water uptake. Also, the fundamental assumptions of the model structure which theorize the plant physiological behaviors as a system composed with stock (level variable) and flows (rate) was validated, concurring with findings reported by Sakakibara et al. (2007) and Mirza et al. (2011).

Phytovolatilization of contaminants metabolized by the plant is advantageous to the continued function of the system. Contaminant will continue to increase with time when they are not volatilized as the endpoint. This path it is not necessary for the model to mimic uptake given the increase of plant mass over time due to growth. When the plant system reaches maximum growth potential, the uptake of contaminant will outpace the growth rate and cause plant toxicity. The volatilization is one way in which the plant system limits the overall contaminant concentration in tissues to limit toxicity.

The typical experimental setup approach found on metal phytoremediation fields determined that the physiological system has a time lag of the order of days, according to contaminant concentration processed (Jadia and Fulekar, 2009; Sarma, 2011). This effect has been observed in different bioremediation systems and has been explained as a resilience adaptation time of the organism in a new environment with a toxic substance. This behavior is also observed in the phytovolatilization arsenic data (Sakakibara et al., 2007; Mirza et al., 2011) and was mimicked successfully by phytoremediation model. The model also provides the opportunity to analyze the flow rates of different phytoremediation systems. This kind of analysis provides environmental managers more information to enhance the decision making process.

Plant selection can be one of the most challenging subjects when designing a phytoremediation system. The model can be modified to use different species of plants based on available water and contaminant uptake rates. When comprehensive data is not available for a plant species being evaluated, estimates can be made based on available literature and pilot studies. The evaluation of growth and uptake potential using the model can aid in choosing the most appropriate species given site location and remedial goals. Not all plants are created equal. The model can illustrate the possibility of using a particular species given site specific and contaminant specific condition.

5.1 CONCLUDING REMARKS

Arsenic speciation in soil can provide insightful information associated with risk assessment, fate and transport, and chemical equilibria within the substrate. Risk based remedial goals are set using data from arsenite studies and few evaluations of risk utilize current studies of arsenate toxicity. In oxygen rich, upland soils the predominant form of arsenic was found to be arsenate and the risk assessment illustrated this understanding. Proper risk assessment of site contaminants is necessary to establish a site specific remedial goal that is protective of sensitive species. This ecological risk assessment of arsenic is dependent on the continual study of the toxicity of arsenate and arsenite and their prevalent forms in the environment. Of the two, arsenate is the less toxic and mobile in the soil yet it has a higher bioavailability then arsenite. Arsenate is a phosphate analogue and shares the same uptake pathway which increases its bioavailability and as such is readily taken up by plant roots.

The phytoremediation model was constructed to estimate the ability of the plant system to remove arsenic from soil and groundwater. It has been validated qualitatively, quantitatively and proven statistically to have the capability mimic the behavior of phytoremediation data. The model is robust enough to explain the uptake kinetics of both water and contaminant in a dynamic system. The model has the capability to explain more than 95% of the experimental data values, proving the robustness of the model's schematic structure (Forrester diagram) and the validity of the established assumptions.

The schematic representation of the model facilitated the comprehensive understanding of the phytoremediation process. The model can be used as a teaching learning tool for regulatory entities, to explain the system behavior, filling the gap of the decision making process, evaluating different possible settings. The modular components allow for an understanding of the inputs into the system and the probability of different scenarios. This approach will provide a common ground of knowledge for stakeholders. The model has the capability to make comparisons between: contaminant, contaminant concentration, plant types, seasonality and phytoremediation processes. Assessing this information, environmental managers can better understand the system's behaviors and can make more informed decisions to recommend to the regulatory agencies or select the best approach to attend the environmental issue.

The accurate assessment of risk at a site is required to establish remedial goals. The risk assessment of arsenic should consider that the predominant toxic forms are inorganic arsenate and arsenite. The speciation of arsenic at a site is determined by the redox potential of the soil. Arsenate is the predominant form of arsenic in well drained upland soils. This fact can drive the characterization of risk to target species at a site and well as indicated applicable remedial solutions. Phytoremediation may be favored in areas where arsenate is the main contaminant due to the similarities to phosphate.

5.1.1 Limitations of the Study

When a computational model is being developed, modelers need to solve issues related to scales, determinism, parameterization and validation. The phytoremediation model is a deterministic model with stochastic functional modules. The model relies on the availability of data on plant species, general uptake kinetics, contaminants of concern, soil type, and seasonality. Data with these parameters can be found in published technical sources or pilot studies and used to validate model for a site, contaminant or species.

5.1.2 Recommendations for Future Research

1- Model improvements

    a. Create modules for probabilistic evaluations.
    b. Create modular units that contain plant species specific data.
    c. Decrease complexity of water uptake in the plant system.

2- Simulate natural attenuation of contaminant.

4- Simulate the biodegradation rhizosphere effect.

5- Development of arsenate/arsenite uptake kinetics and the shift in soil due to removal of arsenate.

6- There is potential for conducting more statistical analysis and/or regression for the results of studied cases to come up with empirical relationships between the phytoremediation system design parameters and the site remediation goals which can be easily used as a decision supporting tool.

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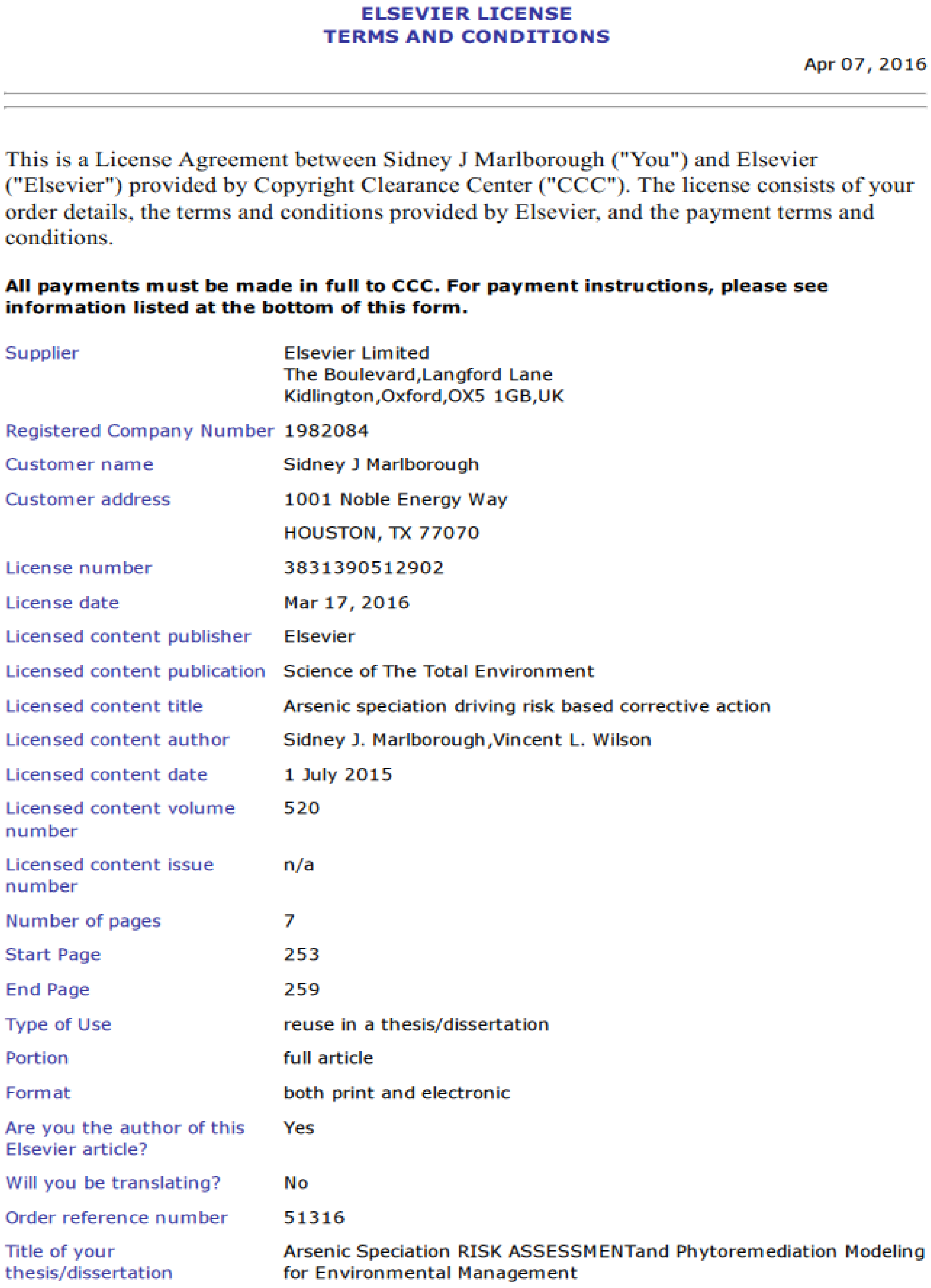

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VITA

Sidney Joseph Marlborough III, was born on October 4 in the day of bell bottoms in a taxi crossing the Greater New Orleans Bridge, and life has been an uphill climb since. He graduated eighth grade from Holy Name of Mary in Old Algiers on the west bank. He then went on to San Diego for the next four years and finished high school at Orange Glen High School in Escondido, California. His freshman year of college was completed at Louisiana State University in 1992. After the grueling years of studying, working and dragon slaying, he finally graduated in 1998 with a Bachelor of Science in Environmental Management Systems. Being a gluten for punishment, he then entered a master's program under Doctor Vince Wilson and graduated in 2004. Dr. Wilson believing that I had not been punished enough, entreated me to join the hallowed ranks and started a doctoral program in Environmental Science.

Finally, after 25 years of college, he shall be free of the chains to go off into the world as a newly minted doctor. Free at last free at last. He is joined in this effort by his amazingly hot wife and three munchkins. As all good things must come to an end, so too does this chapter in the life. Of course we may all see each other again in Space Balls 2 the search for more money. There is a great restaurant at the end of the Universe, See You there.