MODELING HEAVY METALS UPTAKE BY PLANTS: A CASE STUDY OF PHYTOREMEDIATION FROM SOUTHERN TURKEY

by

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A CASE STUDY OF PHYTOREMEDIATION FROM SOUTHERN TURKEY

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ABSTRACT

MODELING HEAVY METALS UPTAKE BY PLANTS: A CASE STUDY OF PHYTOREMEDIATION FROM SOUTHERN TURKEY

Removal of heavy metals from the soil by phytoremediation has been a subject of interest in recent years due to the difficulties of removing heavy metals with conventional methods. Modeling is considered as a promising tool to understand the mechanisms of contaminant uptake by plants since it is the cheapest and the most time efficient way to predict the removal efficiency of the contaminant from the soil.The aim of this thesis is to model the uptake of heavy metals (Cu, Pb, Zn) by Sorghum and Sunflower. The model data were obtained from soil in Kilis, which was planted in 2011 and 2012. Modeling of heavy metal uptake was conducted using the GoldSim contaminant transport module. This mass transport model is a mathematical representation of an actual system, which can be used to simulate and hence predict the fate and transport of heavy metals within a coupled environmental system comprising both soil and plant.Model results are in good agreement with observed data. Kd, partition coefficient heavy metals between soil water and soil solid values for Cu, Zn, and Pb are found to be 3.47, 3.05, and 2.42 respectively. Results suggest that the uptake rate of Sunflower was higher than that of Sorghum. Partition coefficient is found to be the most effective parameter, followed by transpiration rate and plant mass in determining the residue heavy metal soil concentration.

ÖZET

AĞIR METALLERİN BİTKİLERLE ALIMININ MODELLEMESİ: GÜNEY TÜRKİYE'DEN BİR FİTOREMEDİASYON ÇALIŞMASI

Toprakta ağır metallerin fitoremediasyon ile uzaklaştırılması, ağır metallerin konvansiyonel yöntemlerle çıkarılmasının zorluğu nedeniyle son yıllarda ilgi konusu olmuştur. Modelleme kirleticilerin bitkilerle alım mekanizmasını anlamak için uygun bir araçtır. Çünkü bu, topraktan kirletici giderimini tahmin etmenin en uygun ve zaman kazandırıcı yoludur.Bu tezin amacı; ağır metallerin (Cu, Pb, Zn), Darı ve Ayçiçeği ile alımının modellenmesidir. Model verileri 2011 ve 2012 yıllarında ekim yapılan Kilis toprağından alınmıştır. Modelleme için GoldSim kirletici transfer modülü kullanılmıştır. Bu kütle transfer modeli, toprak ve bitkideki kütlenin nihai durumunu simüle etmek ve dolayısıyla tahmin etmek için kullanılabilen gerçek bir sistemin matematiksel bir temsilidir.Model sonuçları, gözlem verileriyle uyum içerisindedir. Kd değeri Cu, Zn ve Pb için sırasıyla 3.47, 3.05 ve 2.42 bulunmuştur. Sonuçlar gösteriyor ki Ayçiçeği'nin kirletici alım oranı Darı'nınkinden daha yüksektir. Toprakta kalan ağır metal konsantrasyonunu belirlerken en etkili parametreler ağır metallerin toprak-su dağılımı Kd, takiben bitkilerin terleme miktarı ve biyokütlesidir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS/ABBREVIATIONS

Symbol	**Explanation**	**Unit**
Cu	Copper	
Kd	Soil-water Partition Coefficient	L/kg
Kow	Partition Coefficient of a Substance between n-octanol and Water	
Pb	Lead	
Tc	Transpiration Stream	L/kg_{dry}
Zn	Zinc	
Q	Water Flux	L/d

Abbreviation	**Explanation**
Ave	Average
AMF	Arbuscular Mycorrhizal Fungi
BCF	Bioconcentration Factor
C	Concentration
DNA	Deoxyribonucleic Acid
Dw	Dry Weight
M	Mass
NS	Nash and Sutcliffe
PGPMs	Plant Growth Promoting Microorganisms
RCF	Root Concentration Factor
ROV	Ratio of Variation
TSCF	Transpiration Stream Concentration Factor

1. INTRODUCTION

Heavy metal pollution in the soil is one of the most severe global environmental issues which can result from mining, smelting and metal treatment operations, automobile emissions and spillage of industrial wastes. Heavy metals are a threat to human and animal health due to their long-term persistence in the environment; they also cause extreme damages to ecosystems i.e. soil quality degradation, crop yield reduction, and poor quality of agricultural products. Heavy metals accumulate in the tissues of animals or human beings and increase up the food chain, in a process called biomagnification. Due to mutagenic properties of heavy metals, this may result in DNA damage and cancer-causing impacts (Knasmuller et al., 1998). Contamination of soil by heavy metals affects about 235 million hectares of arable land worldwide (Bermudez et al., 2012).

Phytoremediation is a relatively new technology and is accepted as an economical and environmentally friendly method of utilizing plants to extract or inactivate contaminants from the soil. The generic term ‘Phytoremediation’ comprises of the Greek prefix phyto (plant) appended to the Latin root remedium meaning (Cunningham et al., 1996). This technology involves the utilization of plants to improve soil and/or water quality by inactivating or translocating pollutants in the different plant organs without having negative effects on soil biological activity, structure and fertility (Ebbs et al., 1997; Salt et al., 1995). Phytoremediation can be an alternative to disruptive cleanup technologies, such as dig and haul, pump and treat that can drastically change the chemical and physical properties of the soil (Palmroth et al., 2002).

1.1. Aim of the Study

The aim of this research is to develop a process-based, mathematical contaminant transport model for the uptake of heavy metals (Zn, Pb, Cu) by Sorghum and Sunflower, using field data obtained from Kilis, Southern Turkey. Phytoextraction of heavy metals is simulated using GoldSim’s contaminant transport module. This study also aims to determine the most significant parameters affecting the heavy metal uptake process by plants.

2. THEORETICAL BACKGROUND

2.1. General Aspects of Phytoremediation

Living organisms require trace amounts of some heavy metals; however, any excess amount of these metals may have detrimental effects on the organisms (Berti W.R. and Jacobs L.W., 1996). Heavy metals commonly found at contaminated sites are Lead (Pb), Iron (Fe), Aluminium (Al), Chromium (Cr), Arsenic (As), Zinc (Zn), Cadmium (Cd), Copper (Cu), Mercury (Hg) and Nickel (Ni) (Subhashini and Swamy, 2013). Major health risks to humans associated with heavy metal contamination include cardiovascular disease, chronic anemia, cognitive impairment (Iqbal, 2012), cancer, damage to kidneys (Wuana and Okieimen, 2011), nervous system, brain (Järup, 2003), skin, teeth, and bones (Luo et al., 2012).

Phytoremediation is both a natural process and a promising remediation strategy that has been gaining attention, especially in recent years due to its cost-effectiveness (Hechmi et al. 2015). Phytoremediation can be described as the direct use of green plants and their associate microorganisms, to stabilize or reduce contamination in soils, sludges, sediments, surface and groundwaters (EPA, 2015).

In a phytoremediation process, a living plant acts as a solar-driven pump, which can extract and concentrate specific heavy metals from the environment (Raskin et al., 1997). This remediation strategy retains for the biological properties and physical structure of the soil. The technique is environmentally friendly, inexpensive, aesthetically pleasing and also offers the opportunity of bio-recovery of the heavy metals (Yang et al., 2002).

Use of plants and related microorganisms for phytoremediation is to immobilize (phytostabilization), to remove (phytoextraction), to evaporate (phytoevaporation), or to degrade (phytodegradation, rhizodegradation) contaminants from the soil and water environment (Cunningham et al. 1995; Jabeen et al. 2009; Reevers and Baker 2007; Wei et al. 2008). Phytoremediation of soil is a cheap, socially acceptable, also eco-friendly technique for cleanup of the contaminated land (Padmavathiamma and Li 2007; Grobelak et al. 2010; Wu et al. 2010).

Plants that have the capability to grow on polluted soils and to accumulate many heavy metals into the aerial parts without suffering phytotoxic effects are termed as ‘hyper-accumulator’ plants (Rascio and Navari-Izzo, 2011).

Phytoextraction (also referred to as phytoaccumulation, phytoabsorption and phytosequestration), as depicted in Figure 2.1., is the uptake of contaminants from soil or water by plant roots and their displacement and accumulation in aboveground biomass i.e., leafs, shoots (Ghosh and Singh, 2005; Kotrba et al., 2009; Garbisu and Alkorta, 2003).

The term ‘phytoexcretion’ to describe the idea of using plants as biological pumps has been introduced to indicate a novel phytoremediation process for lands degraded with heavy metals. Technological developments bring new potential for the collection of excreted metals before they return to the soil. Furthermore, a major problem of managing the disposal of contaminated plant parts can be eliminated (Manousaki et al., Kadukova et al., 2008).

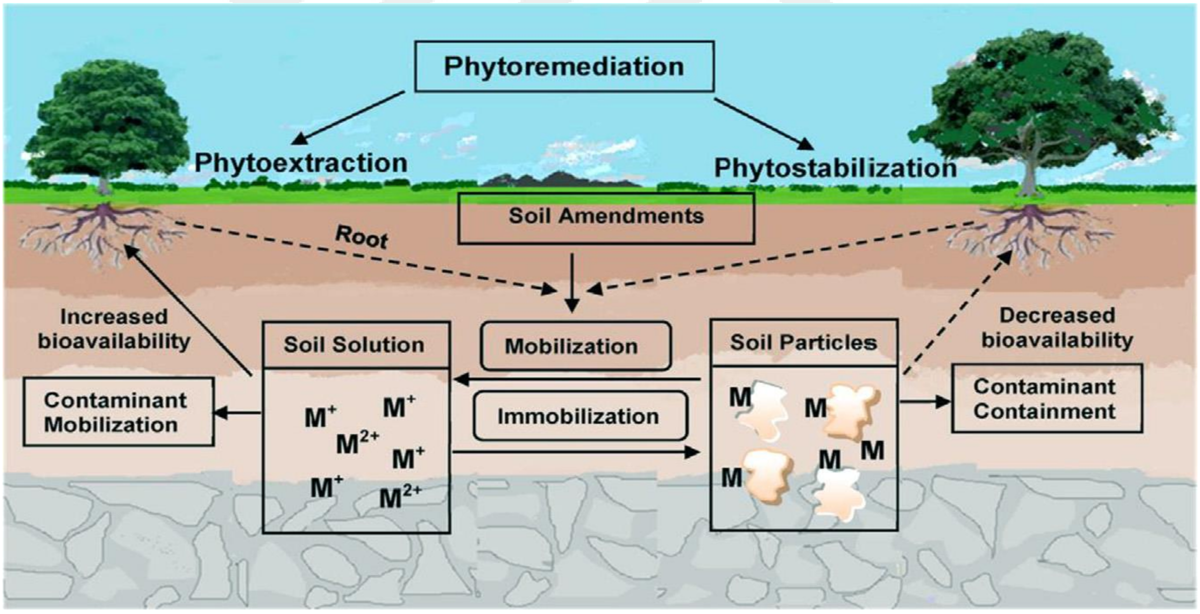

Figure 2.1. A schematized representation of the relationship between immobilization, bioavailability and phytoremediation of toxic heavy metals (Bolan et al., 2014a).

2.2. Microbial Assisted Phytoremediation

Successful phytoremediation requires a rapid growing plant which has high biomass, as well as the bioavailability of heavy metals in soils. Plant roots are not able to easily absorb most heavy metals, therefore root-associated microbes may contribute to mobilize metal ions via their enzymatic activities and increase the bioavailable fraction of heavy metals (Li et al., 2009).

Microbes can facilitate phytoremediation in different ways, which are shown in Figure 2.2. These are accelerating plant growth, increasing phytoextraction, decreasing phytostabilization, as well as enhancing metal translocation from soil to root (bioaccumulation) or from root to shoot tissues (translocation) (Ma et al., 2011a, 2013; Rajkumar et al., 2012).

The composition of the microbial community at the soil-root interface can significantly assist the establishment of plants on heavy metal–contaminated soils by mediating nutrient mineralization and uptake. Microbes may reduce the toxicity of metals or increase their bioavailability, and thus, have some potential to improve phytoextraction efficiency. The effects of heavy metals on the plant and microbe interactions are complex and may be affected by various factors, such as the concentrations in chemical properties of the metals (Egamberdieva et al., 2016).

There is a symbiotic relationship between mycorrhizal fungi and plants. Two benefits of the symbiotic relationship are of particular importance for the plant: an improved nutrient uptake, especially of phosphorus, and an improved ability to acquire water for growth.The widely accepted mechanism for the increased drought resistance often found for mycorrhizal plants, which have considerably smaller diameters of fungal hyphae compared to the roots of plants, enabling an improved access to water even in the smallest soil pores to the benefit of the host plant. Indeed, research by Khalvati et al. (2011) demonstrated a significant increase in water uptake in plant the rhizosphere through the mycorrhizal contribution in comparison to plants without mycorrhizae.

Root exudates and microorganisms are important components of rhizosphere ecology and play important roles in changing the bioavailability of metals and nutrients; they can thus be explored to improve microbe-assisted phytoremediation. Plant root exudates are useful nutrient and energy sources for soil microorganisms (Ying Ma et al., 2016). On the other hand, microorganisms enhance the resistance of plants to adverse environmental stresses such as drought, salts, heavy metals, and nutrient deficiency (Egamberdieva et al., 2015). Moreover, the inoculation of plants with metal resistant, root-associated beneficial microbes is an efficient bioremediation process for the degradation of contaminants, potential metal bioaccumulation, and promoting plant growth (Srivastava et al., 2013).

Some beneficial bacteria and fungi, acting as plant growth promoting microorganisms (PGPMs), may reduce metal phytotoxicity and solubilize of mineral nutrients (nitrogen, phosphate, potassium, iron, etc.), produce plant growth promoting substances and discharge of specific enzymes. PGPM can also change metal bioavailability in soil through various mechanisms such as acidification, precipitation, chelation, complexation, and redox reactions (Ying Ma et al., 2016). Using plant growth promoting microorganisms (PGPMs) rather than chemical amendments may have some advantages in phytoremediation, because the microbial metabolites produced in the rhizosphere are biodegradable and less toxic (Rajkumar et.al., 2012). A schematized representation of the plant-microbe-metal interactions and their mechanisms are illustrated in Figure 2.2.

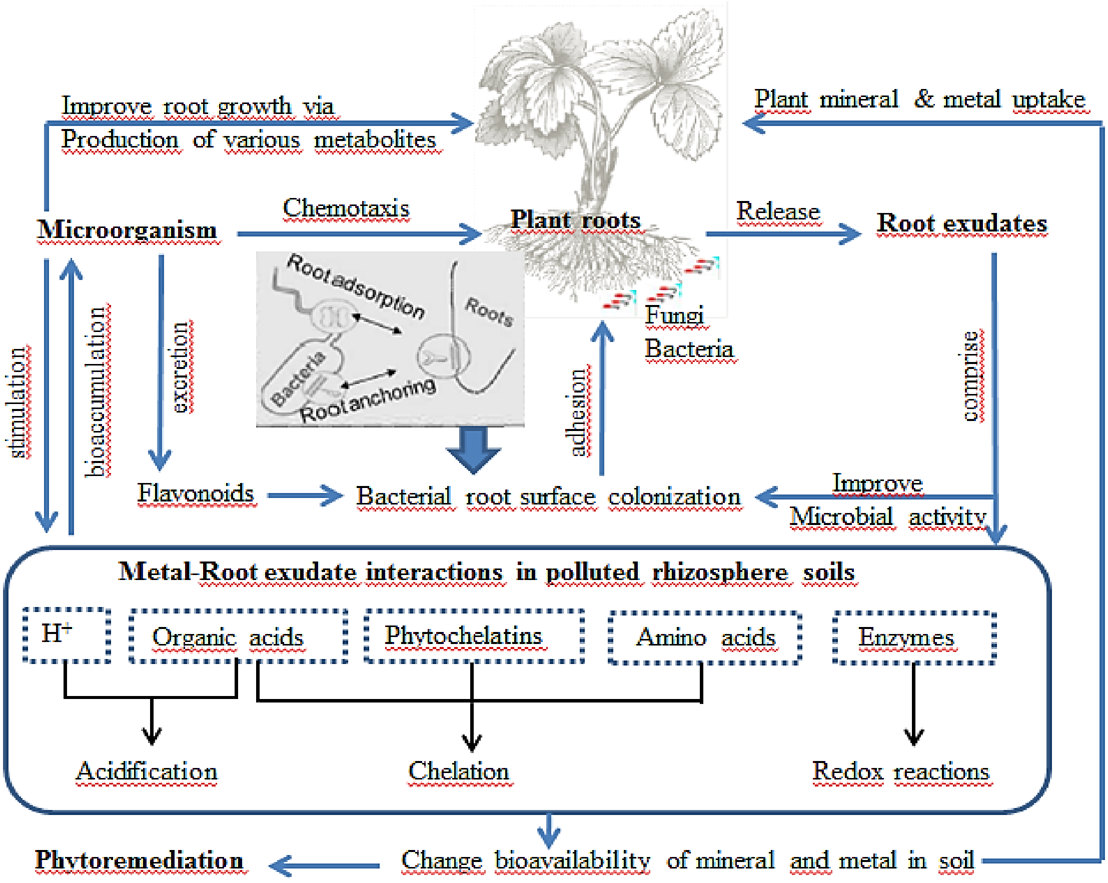

Figure 2.2. A schematized representation of the plant-microbe-metal interactions mechanisms, redrawn from (Ying Ma et al., 2016).

Metal-resistant beneficial microbes, bacteria and Arbuscular mycorrhizal fungi (AMF), are used as bioinoculants to increase metabolic functions and membrane permeability of root cells, and thus to enhance the establishment, growth and development of remediating plants in metal contaminated soils (Ying Ma et al., 2016). AMF alleviate drought stress in their host plants via the direct uptake and transfer of water and nutrients through the fungal hyphae to the host plants.

Quantifying the contribution of the hyphae to root water uptake confirms that there is the transport of water by the hyphae under drought conditions. Higher hyphal density in the root compartment indicates a larger amount of water uptake by the hyphae that may occur in the root compartment. In a comparison of barley plants with and without AMF under drought conditions, growth of the shoots and roots significantly improved ($p < 0.05$) by AMF, with the shoot and root dry weights of the AM plants being 50% and 17% higher, respectively, compared to those of the non-AMF plants (Khalvati et al., 2005).

Proper selection of functional microbes to match plants used for phytoremediation is the key to optimizing microbe-assisted phytoremediation efficiency in mining-contaminated soils. Microbe–plant systems should be selected properly for phytoremediation of contaminated soils. In determining the optimal combination of plants, microbes, and chemicals for heavy metal decontamination a more comprehensive understanding of the combination among these three factors should be considered for rational remediation of mining contaminated soils (Du et al., 2016).

2.3. Models and Processes of Phytoremediation

2.3.1. Modeling of Phytoremediation

Models can be used to identify the governing mechanisms of a particular remediation method, to determine critical variables affecting the remediation efficiency, and subsequently to provide valuable information for field implementation.

Simulation models can assist in predicting the fate of contaminants in soil which can guide users in the collection of relevant data, while minimizing the acquisition of irrelevant data in field applications. They also provide predictive results, which may help to quantify factors within the remediation plan, such as duration, monitoring schedule, expected results, and follow-up measures (Kijune Sung, 2000).

Modeling approaches of entire plant metabolism are really rare due to the complex interaction of factor; consisting of physicochemical properties of the xenobiotic, physiological and biochemical processes within the plant, and the environmental components influencing plant processes (Giersch, 2000; Satchivi et al., 2000a, 2000b, 2001). Because the phytoextraction and translocation of heavy metals from soils into plants are very different, for a variety of plant species and also the soil physicochemical processes, climatic conditions, and soil arsenic bioavailability solely by experimentation, it is quite hard to quantify. Therefore, developing a physically-based mathematical model for predicting dynamic uptake, translocation, accumulation, and transport of heavy metals in the soil-plant system is a needed. In the past decade, mathematical models have been used to study the fate and transport of organic pollutants in plants (Burken and Schnoor, 1996; Ouyang, 2002; Trapp and McFarlane, 1995).

The uptake of solutes by roots is an active process that depends on the plant demand and the soil supply and which has widely been described by plant physiologists. The uptake rate can be simulated via mathematical models that are generally described using Michaelis-Menten kinetics (Mullins et al. 1986; Nedunuri et al. 1998; Seuntjens et al. 2004). For example, Rengel (1993) examined assorted nutrient and contaminant uptake models and classified them as either empirical or mechanistic. While the mechanistic models simulate the solute uptake by roots mathematically using some uptake kinetics, empirical models simply relate the soil solute concentration with its presence in the plant biomass for a certain soil-plant system. Assuming steady state moisture and solute conditions, most of the possible mechanistic models predict the transport of plant nutrients (Claassen et al. 1986; Hoffland et al. 1990; Van Rees et al. 1990).

A review of the literature indicates that not many rhizosphere models deal with heavy metal contaminant uptake by plant roots (Rao and Mathur 1994; Vogeler et al. 2000; Mathur 2004; Verma et al. 2006). Amongst these models, the metal uptake model of Vogeler et al. (2000) oversimplifies the uptake practice by assuming metal (copper) uptake to be a passive process. In in some of the other models, the metal uptake mechanism is assumed to be an active process; nevertheless, these models disregard the time-dependent root biomass and root density distribution function by taking the soil control volume instead of the root biomass volume. Consequently, an oversimplified extraction term is adopted in most of the heavy metal uptake models (Shashi et al. 2009).

Chemical, physical and biological processes (such as diffusion, adsorption, absorption, the growth of a plant, transpiration rate, etc.) in the soil, the soil rhizosphere and in the plant itself carry out transport of trace metals from the soil to the plant (Baltrėnaitė and Butkus, 2007). Mathematical modeling is designed to perform tasks in different areas utilizing the systems of a conjectural analysis. Modeling depends on the pattern and primary analysis of existing mathematical models, composition and analysis of digital algorithms, use of natural observations and experimental findings, in addition, receiving an analysis about finding of the processes. Working with models, but not with the real object itself, permits us to perform an examination of phytoremediation characteristics and behaviour in different possible circumstances inexpensively and sufficiently rapidly (advantages of the theory). Meanwhile, simulations allow us to perform a detailed, deep and sufficiently full examination of the phenomena under study, which cannot always be attained for with the assistance simply theoretical methods (Baltrėnas et al., 2006).

A number of mathematical models have been developed to describe contaminant uptake as a function of interrelated chemical compounds, plant species utilized and environmental conditions at various remediation sites. These models are generally physically-based and depend on mass balance equations that represent transport of the contaminant from the soil to the roots, and its subsequent accumulation in the plant organs. Such bioaccumulation models mainly concentrate on the transport, accumulation and chemical reactions within the plant (Paterson et al. 1994; Trapp and; Matthies 1995; Burken and Schnoor 1997; Undeman et al. 2009). Nowadays, the focus has shifted towards certain uptake models to couple soil moisture and root dynamics, which take into account contaminant advection, dispersion, adsorption-desorption and reactions in the unsaturated zone (Brennan and Shelley 1999; Vogeler et al. 2001; Ouyang 2002; Mathur 2004; Verma et al. 2006).

2.3.2. Uptake Processes via Phytoremediation

There are several uptake pathways, which are shown in Figure 2.3. The main pathway is the root’s passive and active uptakes, particulate deposition and direct contact between plant tissues and soil (Collins et al., 2006).

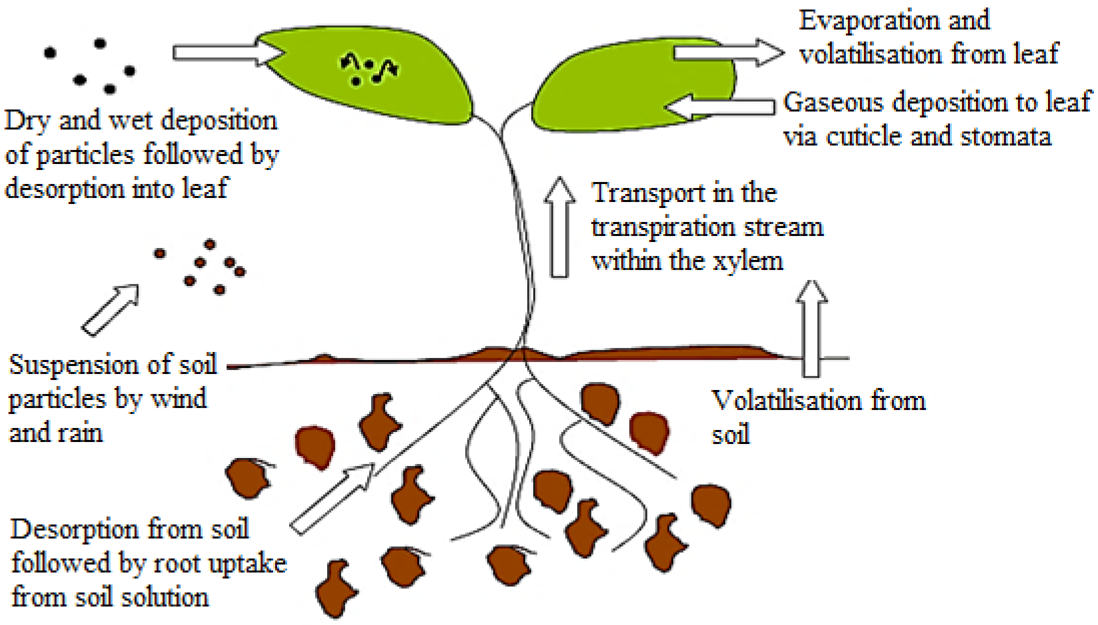

Figure 2.3. Uptake pathways of chemicals into plants (Collins et al., 2006).

In general, most plants have the three main parts: Roots, stems, and leaves. The role of the root is to anchor the plant in the soil and take up water and water soluble substances from the soil. The role of stems is to transport the water and soluble molecules upwards into the plant during the natural transpiration cycle, and leaves are responsible for taking up sunlight and CO_2 to make photosynthesis. Water evaporates when the plant takes up carbon dioxide from atmosphere (Trapp, 2013).

For estimating uptake of contaminants into plants some partitioning mechanisms that may occur between the soil, water and plant are summarized below.

Phase equilibrium is the endpoint of diffusion, and is achieved when the scope of the contaminant in the root tissue is equal to the scope of the contaminant in the aqueous solution (Lewis, 1907). The chemical concentration ratio between root and concentration found in an external solution in phase equilibrium is called the root concentration factor, RCF (L/kg) (Shone and Wood, 1974).

$$RCF = \frac{\text{Concentration in root (mg/g)}}{\text{Concentration in solution (mg/mL)}} \qquad (2.1)$$

Another partition coefficient is the equilibrium partition coefficient of a substance between n-octanol and water, which is given by Kow. Briggs et al. (1982) carried out an experimental study with the Barley roots and derived the following empirical relationship between RCF and Kow formula:

$$RCF = 0.82 + 0.03Kow^{0.77} \qquad (2.2)$$

The ratio of contaminant concentration in a plant to contaminant concentration in the surrounding medium is named the bioconcentration factor, BCF (Trapp, 2013). Measurements of concentrations in plant tissues and concentrations in soil yield a BCF, which is defined as:

$$BCF = \frac{\text{Concentration in plant (mg/g)}}{\text{Concentration in soil (mg/g)}} \qquad (2.3)$$

An empirical regression by Travis and Arms (1998) is given as:

$$logBCF = -0.578xlogKow + 1.588 \qquad (2.4)$$

Water and contaminant are transported upward from the root into other plant parts through the xylem by mass flow, resulting from a pressure gradient. This driving force is created during transpiration, where water is drawn in through the root system to replace evaporative losses from stomata within the leaves (McFarlane, 1995). Translocation of contaminants from roots into stems in the xylem is often described by the transpiration stream concentration factor, TSCF (Russell and Shorrocks, 1959):

$$TSCF = \frac{\text{Concentration in xylem sap (mg/mL)}}{\text{Concentration in solution (mg/mL)}} \qquad (2.5)$$

The most recent TSCF-estimation equation is a sigmoid curve developed by Dettenmaier et al.(2009):

$$TSCF = \frac{11}{11 + 2.6^{logKow}} \qquad (2.6)$$

2.4. Generic Phytoremediation Models

There are a number of predictive models for plant uptake of contaminants. Some of which are summarized in the following section.

2.4.1. Standard Uptake Model

Standard uptake models generally have flux-based solutions, simply assuming water flows from soil to the leaves or fruits. Every molecule in the water is transported unless it is adsorbed in soil, roots, stem or it is degraded or it evaporates. The standard model assumes purely physical fluxes and partitioning, not taking into account enzymatic reactions or active transport.

The standard model consists of four differential equations for fluxes, partitioning and exchange with soil and air: (i) steady state, (ii) dynamic, (iii) crop-specific, (iv) coupled soil-plant-air. Among these coupled linear three differential equations are listed below, and a schematized representation is provided in Figure 2.4 (Trapp, 1995).

A system of coupled linear differential equations;

$$\frac{dC_R}{dt} = C_W \times Q/M - C_R/K_{RW} \times Q/M - k \times C_R \qquad (2.7)$$

$$\frac{dC_L}{dt} = \frac{Q}{M_L \times K_{RW}} \times C_R + \frac{A_L \times g}{M_L} \times C_A - \frac{A_L \times g \times 1000Lm^{-3}}{K_{LA} \times M_L} \times C_L - k_L \times C_L \qquad (2.8)$$

$$\frac{dC_F}{dt} = \frac{Q_F}{M_F \times K_{RW}} \times C_R + \frac{A_F \times g}{M_F} \times C_A - \frac{A_F \times g \times 1000Lm^{-3}}{K_{FA} \times M_F} \times C_F - k_F \times C_F \qquad (2.9)$$

where; Index R is root, W is water, L is soil, F is fruit and A is air. C is the contaminant concentration (mg/kg), Q is the water flux (L/d), M is the plant mass (kg), K is the partition coefficient (L/kg or kg/kg), A is the area (m^2), g is the conductance (m/d), k is the growth degradation rate (1/d).

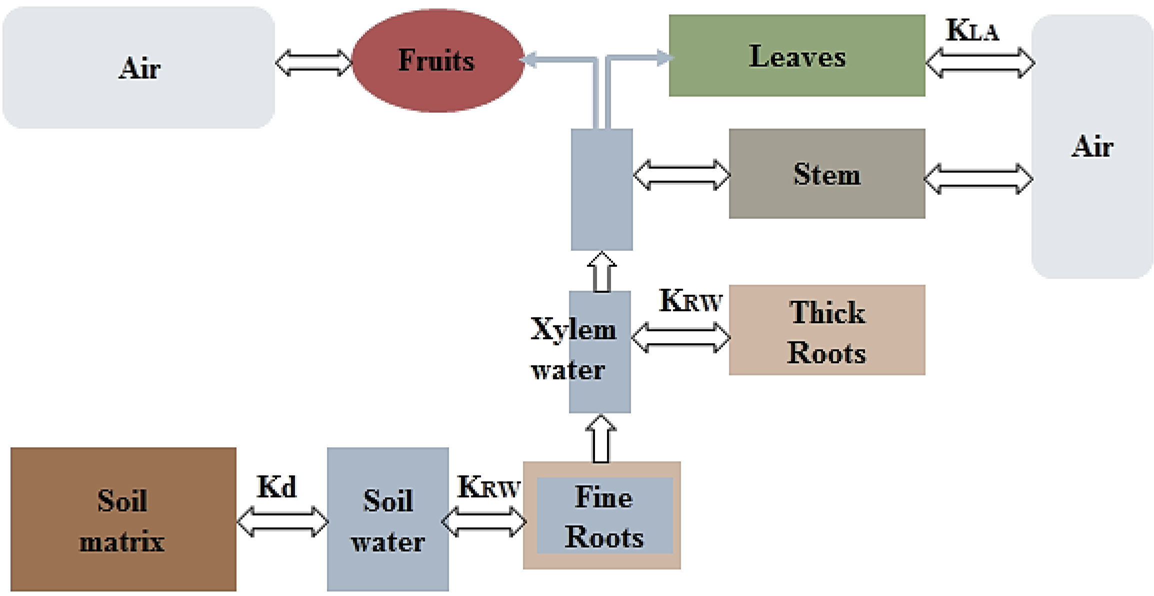

Figure 2.4. Schematic representation of Standard Plant Uptake Model (Trapp, 1995).

2.4.2. Mechanistic Partition-Limited Model

A partition-limited model for the passive root uptake of contaminants from soil is related to the chemical concentration in the soil and in the plant composition.The upper equilibrium limit for the level of the contaminant in a plant compared to that in soil, against which the actual equilibrium at the time of analysis could then be estimated.

Uptake occurs when the chemical is dissolved in water, carried into the plant during transpiration, and partitions from the water to plant tissue in contact with the solution. The concentration in the plant is estimated from the contaminant concentration in the pore water (which is assumed to be equal to the concentration in the transpiration stream) via the plant organic matter to water partition coefficient (Chiou et al., 2001). The mass of chemical per unit mass of plant can be calculated as shown in the equation below.

$$C_{pt} = \alpha_{pt}\left(\frac{C_{som}}{K_{som}}\right)\left[f_{pom}K_{pom} + f_{pw}\right] \qquad (2.10)$$

where $\quad f_{pom} + f_{pw} = 1$ and $f_{pom}K_{pom} = \sum f^{i}_{pom}\,K^{i}_{pom}, \qquad i = 1,2,3 \ldots n$

where; C_{pt} is the calculated mass of chemical per unit mass of plant (µg/kg FW plant), α_{pt} is the quasi-equilibrium factor, which describes the approach to equilibrium of any absorbed contaminant in the plant (or in a part of it) with respect to the same chemical in the external water phase, C_{som} is the soil organic matter normalised chemical concentration (µg/kg DW soil), K_{som} is the chemical partition coefficient between soil organic matter and water, fpom is the total weight fraction of the organic matter in the plant (g/g), K_{pom} is the chemical partition coefficient between plant organic matter and water, and f_{pw} is the weight fraction of water in the plant (g/g).

2.4.3. Dynamic Uptake Model

Dynamic models provide the temporal and spatial distribution of soil moisture. The dynamic models are based on the solution of the Richards'equation, which is developed by the combination of Darcy's law and the continuity equation (Richards, 1931). Plants are dynamic biological systems and often the contaminant pattern is non-steady. Therefore, dynamic simulations are superior to steady-state considerations, although steady-state simulations are simple and have relatively less data requirements (Rein et al. 2011).Three different types of dynamic contaminant input patterns are shown below:

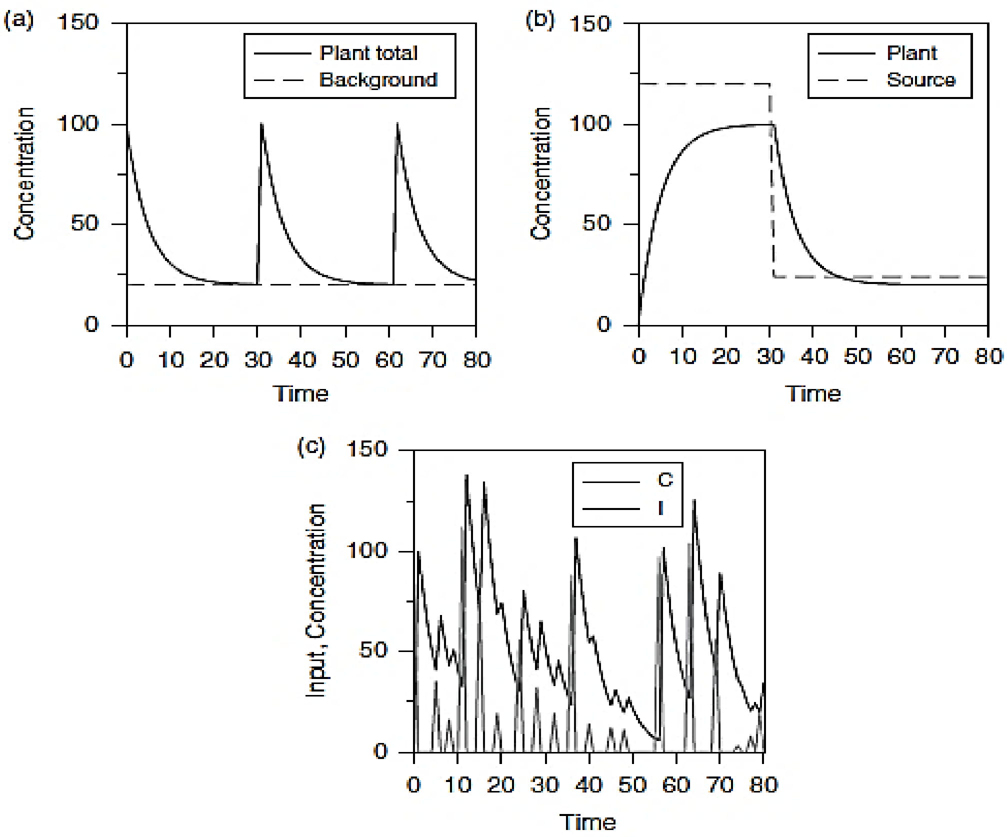

Figure 2.5. Different input functions and their consequence for the resulting concentration time course (Rein et al., 2011).

Repeated pulse input plus constant background;

i. Input from a quasi-constant external source (changing at t=30 units);
ii. Irregular, variable input function I and resulting concentration C.

Plant uptake models are developed according to logistic plant growth and transpiration are shown in the curve below:

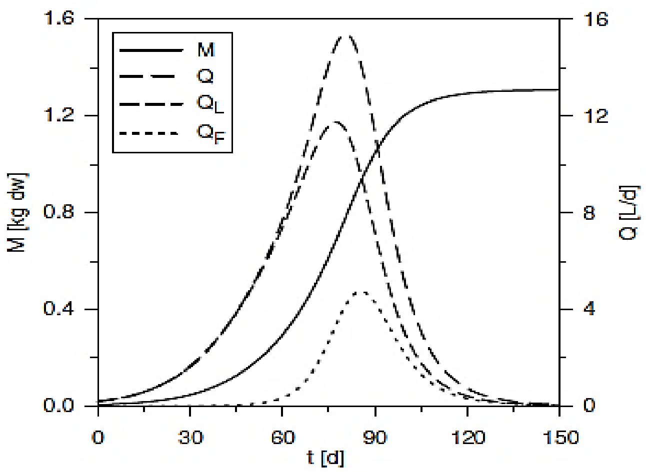

Figure 2.6. Simulated growth and transpiration of summer wheat (Rein et al. 2011).

where; M is total plant mass (dry weight, dw), Q is transpiration in roots and stem, Q_L is transpiration in leaves, Q_F is transpiration plus phloem flux to fruits.

The mass balance equations used for the different plant compartments are shown in Table 2.1.

Table 2.1. Mass balance differential equations for the change of compound mass m in root, stem, leaves and fruits (indices R, St, L and F) with time t (Trapp et al., 1998).

Plant Parts	**Differential Equations**
$Root$	$\frac{dm_R}{dt} = Q \times K_{WS} \times C_S - \frac{Q}{K_{RW}} \times C_R - k_{R,deg} \times m_R$ (2.11)
$Root$	$\frac{dm_{R,diff}}{dt} = 1000 \times A_R P_R \times K_{WS} C_s - 1000 \frac{A_R P_R}{K_{RW}} C_R$ (2.12)
$Stem$	$\frac{dm_{St}}{dt} = \frac{Q}{K_{RW}} C_R - \frac{Q}{K_{StW}} C_{St} + \frac{A_{St} P_{St}}{K_{AW}} C_A \times (1 - f_p) + A_{St} v_{dep} C_A \times f_p - 1000 \frac{A_{St} P_{St}}{K_{StW}} C_{St} - k_{St,deg}\, m_{St}$ (2.13)
$Leaf$	$\frac{dm_L}{dt} = \frac{Q_L}{K_{StW}} C_{St} + \frac{A_L P_L}{K_{AW}} C_A \times (1 - f_p) + A_L v_{dep} C_A \times f_p - 1000 \frac{A_L P_L}{K_{LW}} C_L - k_{L,deg}\, m_L$ (2.14)
$Fruit$	$\frac{dm_F}{dt} = \frac{Q_F}{K_{StW}} C_{St} + \frac{A_F P_F}{K_{AW}} C_A \times (1 - f_p) + A_F v_{dep} C_A \times f_p - 1000 \frac{A_F P_F}{K_{FW}} C_F - k_{F,deg}\, m_F$ (2.15)

where; C is the concentration of contaminant (mg/kg) in the plant compartments, in soil (CS) and in air (CA, mg/m^3), Q is transpiration (L/d), A is surface area (m^2), P is permeability (m/d), K_{AW} is the air-water partition coefficient (L/L), K_{WS} is the partition coefficient between water and soil (kg/L), K_{iw} is the partition coefficients (L/kg) between plant compartment i and water, $k_{i,deg}$ is the first-order degradation rate constant (1/d) in plant compartment i, f_P is the fraction of particles, and v_{dep} is the particle deposition velocity (m/d). Equation (2.11) describes root uptake due to advection only and Equation (6b) shows diffusion only. Equation (2.12) $dm_{R,diff}$/dt: mass balance describing solely diffusion into/out of the roots.

3. METHODOLOGY

In this study, a dynamic simulation model (GoldSim, 2018), is used to model heavy metal uptake by plants. The model is based on the mathematical representation of plant uptake of heavy metal residues in a soil solution. The simulation depends on adjustable parameters of both the plant, such as the plant mass, growth and transpiration, and the soil, such as pH and water content.

The model algorithms depend on the physics of the soil moisture flow, and the plant's water uptake mechanisms. Following the determination of the moisture content of the saturated soil, the water uptake and contaminant transport, by the plant are simulated.

The standard model, adopted here, assumes that the plant is a single compartment consisting of stem, leaf and fruit. Since plant roots will remain in the soil following harvesting, they are considered to be part of the soil. The physical transport processes in the model include advection, diffusion, and partitioning. Water uptake and transpiration are coupled processes related to the water use efficiency of the plant. Figure 3.1 provides a schematized representation of the transport processes included in the model. Kd is the heavy metals partition coefficient between moisture and soil, RCF is root concentration factor.

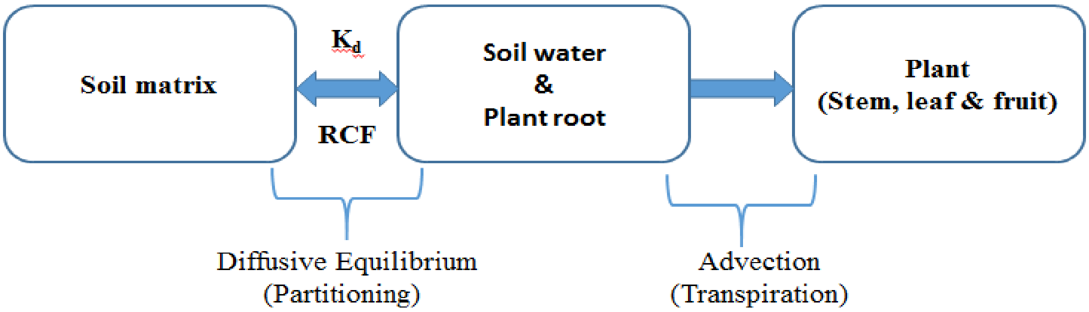

Figure 3.1. Principle of the standard model (Trapp, 2013).

The model simulation diagram produced using GoldSim, which includes the modeled processes and their interactions with each other are demostrated in Figure 3.2.

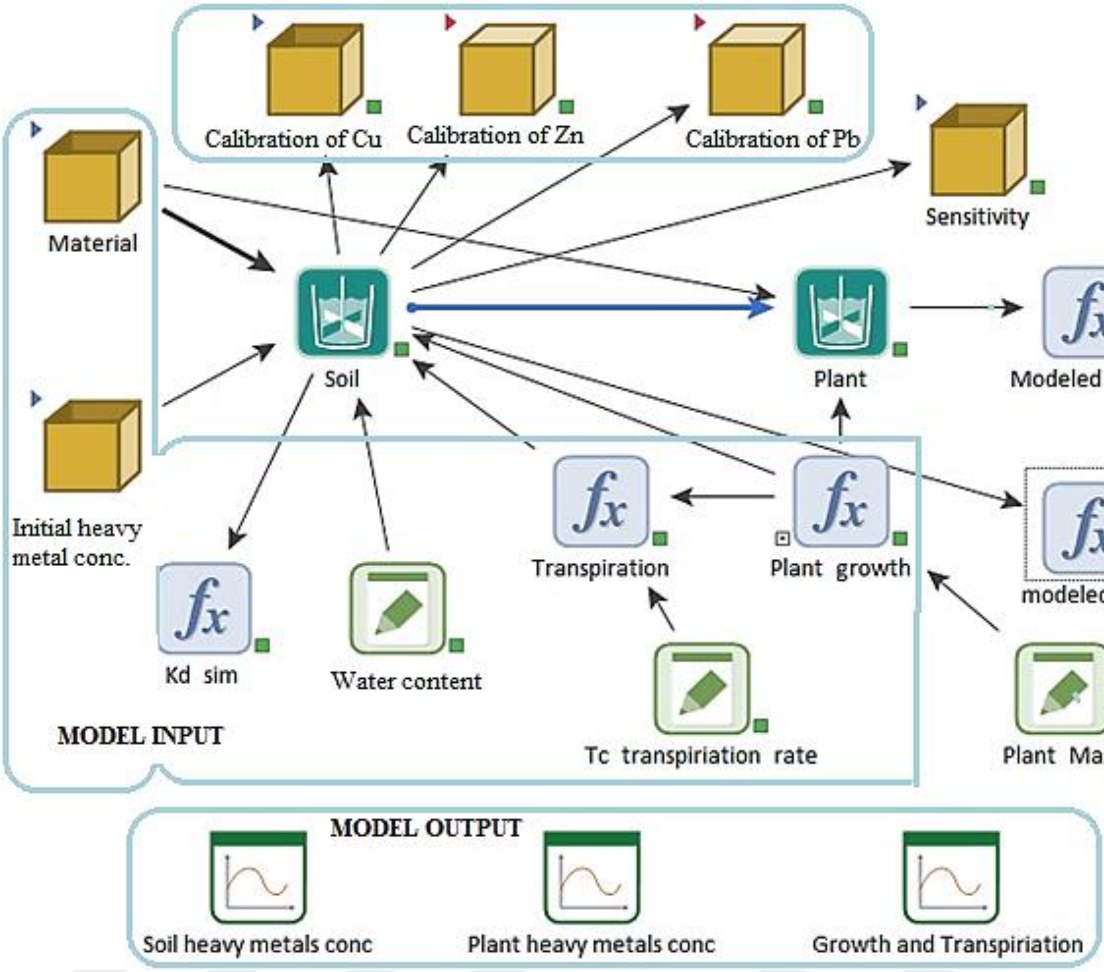

Figure 3.2. The model simulation diagram.

3.1. Site Description

The target area approximately 2000 ha for organic agriculture is located in the Gaziantep region of Turkey, around the town of Kilis. Kilis is a very old and traditional Turkish town with 4000 years of history. The town of Kilis is located in the southern part of the Taurus Mountains, west of the Euphrates River to the north of Syria. Kilis is around 60 to 80 km away from the sea. The average winter and summer temperatures range between 4-7 0 C and 25- 43 0C, respectively.

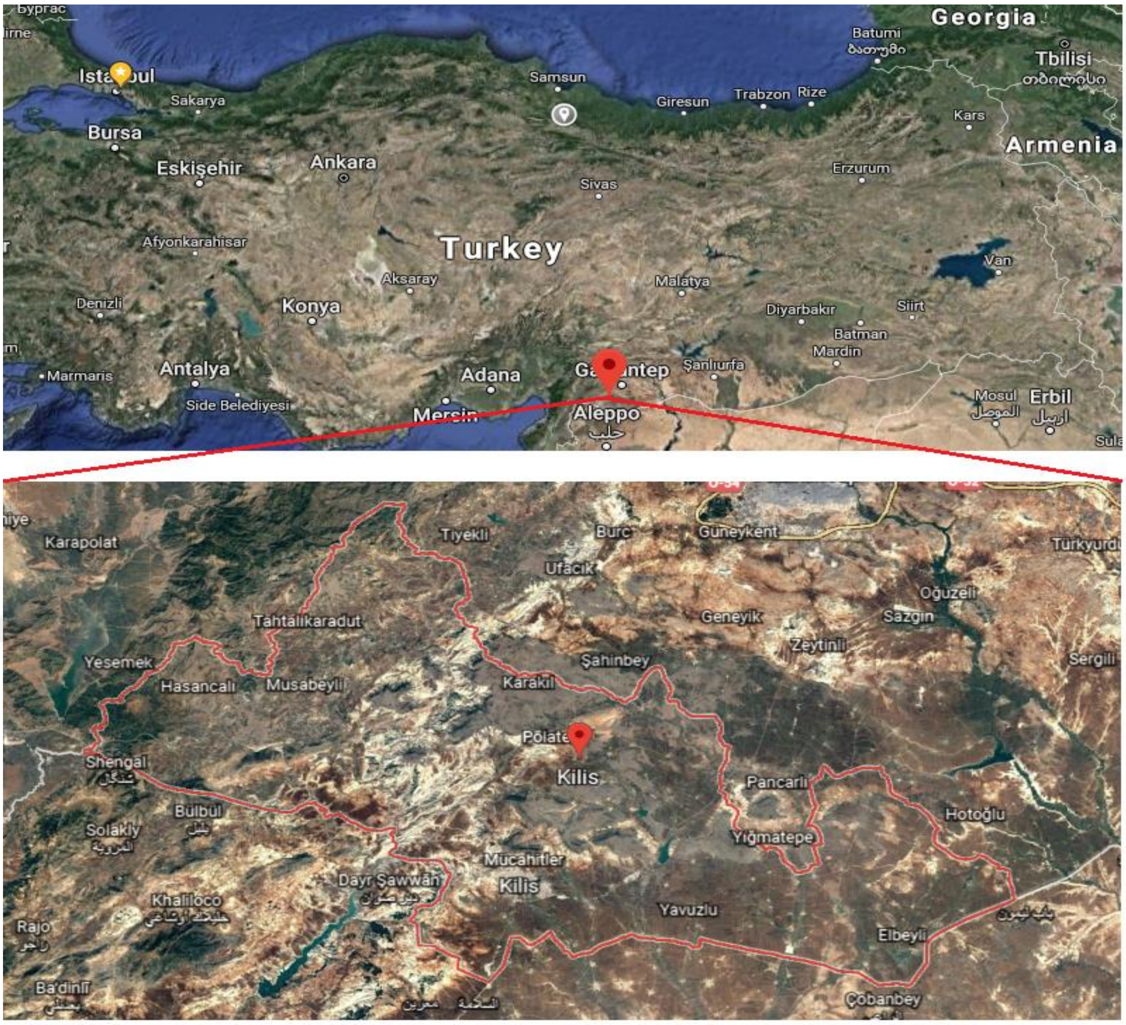

Figure 3.3. The location map of Kilis.

In the area, there are four mining facilities and five electric power plants currently in operation. During coal burning for electricity production, fly ash (0.001-0.1 mm particles) is the main by-product that comprises about 30% of the initial mass of ash. Fly ash can escape in the form of atmospheric emissions. Its exact chemical composition depends on the source of carbon, but fly ash generally contains elements that are important for plant nutrition, i.e., Ca, Fe, Mg, K, Si, B, Cu, Mn, Mo and Zn. Potentially toxic elements contained in fly ash are As, Se, Cd, Pb, Ni, Co and Cr. Fly ash also contains partially oxidized organic compounds, most of which are carcinogenic.

For the phytoextraction of heavy metals (Cu, Zn and Pb) from the soil, sunflower and sorghum are grown on the area of the town of Kilis. Soil sampling was carried out and collected from a depth of 0-35 cm from the target field (Khalvati, 2011). Sampling sites are illustrated in Figure 3.4.

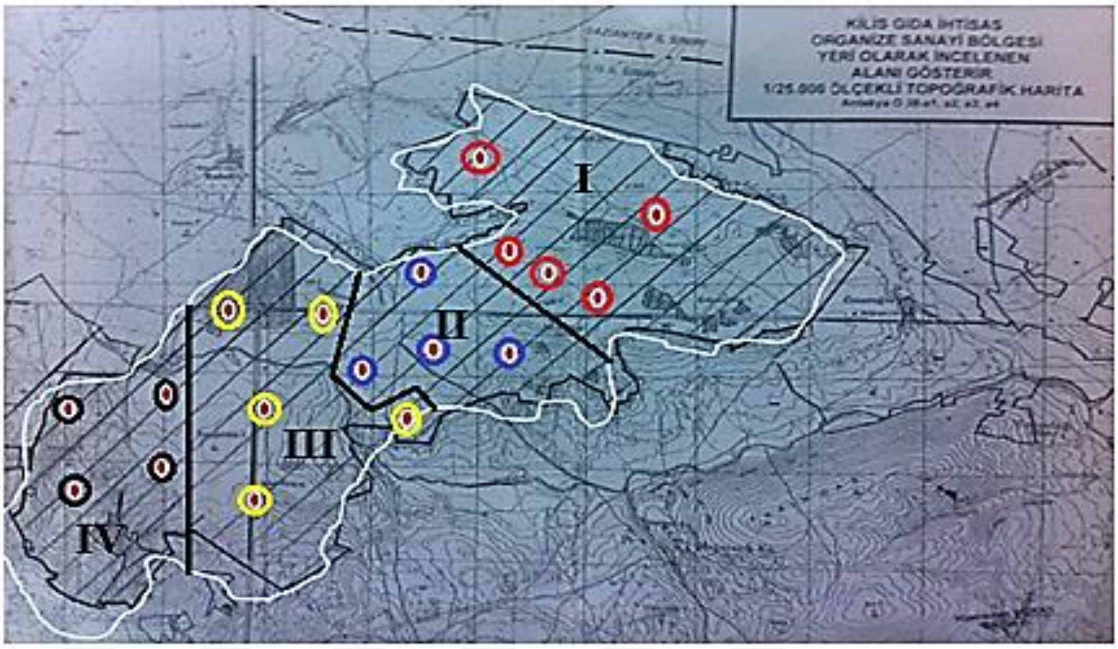

Figure 3.4. Map showing soil sampling stations and cultivated areas. Cultivation areas; I: Sorghum -Winter, II: Sorghum - Summer, III: Sunflower - Summer, IV: Sunflower - Winter).

3.2. Data Requirements

Data required for any modeling exercise fall into two main categories: (i) Calibration data, which are required to set the initial parameter values; and (ii) validation data required to assess how well the model outputs represent observed conditions. In this study, calibration was done using the summer data obtained from the field in 2011 and 2012 summer, and model validation is carried out with the winter data of 2011 and 2012. Heavy metal (Cu, Zn, Pb) concentrations, temperature and soil water content obtained from the field studies are provided in Table 3.1.

Table 3.1. Kilis soil field data from (Khalvati, 2011).

Cu		**ppm**					**^{0}C**	**% water content**				
2009	**Sample**	Cu I	Cu II	Cu III	Cu IV	**Cu ave**	T ave	**WC ave**	WC I	WC II	WC III	WC IV
	Summer	102	110	201	118	**133**	11	**11**	12	10	11	10
	Winter	103	113	277	109	**151**	6	**20**	23	17	18	22
2010	Summer	105	111	232	114	**141**	12	**12**	13	11	12	10
	Winter	100	118	216	120	**139**	4	**22**	22	21	20	26
2011	**Planting**											
Summer	Sorghum	98	99	180	100	**119**	12	**14**	15	14	12	16
	Sunflower	90	100	175	98	**116**	16	**12**	13	11	12	10

Table 3.1 continued.

Winter	Sorghum	100	101	228	110	**135**	7	**17**	16	15	17	20
	Sunflower	96	101	199	119	**129**	7	**15**	12	11	16	19
2012	**Planting**											
Summer	Sorghum	79	88	156	69	**98**	15	**13**	14	13	10	15
	Sunflower	76	78	161	66	**95**	15	**12**	11	12	13	11
Winter	Sorghum	78	77	209	100	**116**	12	**16**	15	14	13	22
	Sunflower	71	66	189	98	**106**	14	**16**	13	12	17	20

Zn		**ppm**					**^{0}C**	**% water content**				
2009	**Sample**	Zn I	Zn II	Zn III	Zn IV	**Zn ave**	T ave	**WC avg**	WC I	WC II	WC III	W IV
	Summer	221	234	412	231	**275**	11	**20**	23	17	18	22
	Winter	230	245	450	247	**293**	6	**20**	23	17	18	22
2010	Summer	222	241	414	233	**278**	12	**22**	22	21	20	26
	Winter	234	245	422	241	**286**	4	**22**	22	21	20	26
2011	**Planting**											
Summer	Sorghum	210	222	401	200	**258**	12	**14**	15	14	12	16
	Sunflower	190	200	339	211	**235**	16	**12**	13	11	12	10
Winter	Sorghum	200	213	330	210	**238**	7	**17**	16	15	17	20
	Sunflower	177	167	301	211	**214**	7	**15**	12	11	16	19
2012	**Planting**											
Summer	Sorghum	155	166	351	154	**207**	15	**13**	14	13	10	15
	Sunflower	134	150	221	190	**174**	15	**12**	11	12	13	11
Winter	Sorghum	122	200	301	174	**199**	12	**16**	15	14	13	22
	Sunflower	120	132	222	150	**156**	14	**16**	13	12	17	20

Pb		**ppm**					**^{0}C**	**% water content**				
2009	**Sample**	Pb I	Pb II	Pb III	Pb IV	**Pb ave**	T ave	**WC ave**	WC I	WC II	WC III	WC 4
	Summer	20	18	12	19	**17,3**	11	**20**	23	17	18	22
	Winter	15	16	11	20	**15,5**	12	**22**	22	21	20	26
2010	Summer	22	19	12	17	**17,5**	12	**22**	22	21	20	26
	Winter	16	16	10	21	**15,8**	4	**22**	22	21	20	26
2011	**Planting**											
Summer	Sorghum	19	18	11	18	**16,5**	12	**14**	15	14	12	16
	Sunflower	14	16	10	19	**14,8**	16	**12**	13	11	12	10
Winter	Sorghum	16	18	10	17	**15,3**	7	**17**	16	15	17	20
	Sunflower	13	13	10	16	**13**	7	**15**	12	11	16	19
2012	**Planting**											
Summer	Sorghum	11	14	10	15	**12,5**	15	**13**	14	13	10	15
	Sunflower	11	10	9	11	**10,3**	15	**12**	11	12	13	11
Winter	Sorghum	11	12	10	11	**11**	12	**16**	15	14	13	22
	Sunflower	10	11	9	10	**10**	14	**16**	13	12	17	20

Here, heavy metal uptake of plants was modeled using GoldSim's contaminant transport module, which consists of multiple components (soil and plant), each requiring input data for the model set up. Soil and plant data obtained from the field study and literature are shown in Table 3.2.

Table 3.2. Input data set for the calculation of plant uptake (normalised to 1 m^2 of soil).

Parameter	Symbol	Value	Unit	Source
Soil				
Soil wet density	q_{wet}	1.75	kg/L	USDA NRCS, 2014
Soil water content	Θ_{soil}	0.15	%	Table 3.1
Soil dry density ($q_{wet} - \Theta_{soil}$)	q_{dry}	1.60	kg/L	USDA NRCS, 2014
Mass of soil	M_s	1000	kg	Modeled soil mass
Plant (Sorghum)				
Plant dry density	q_{plant}	1	kg/L	Estimated
Transpiration stream	Tc	310	L/kg_{dry}	Murdy et al., 1994
Water content of plant	Θ_{plant}	0.70	m^3/kg	Carmelo et al., 2016
1^{st} order growth rate	k	0.19	1/day	Bilga, 2012
Mass of seeds	M_0	0.005	Kg/m^2	Estimated
Mass of root	M_{root}	0.36	Kg_{dry}/m^2	Amanullah, 2013
Mass of plants(max)dry	M_{max}	1.6	Kg_{dry}/m^2	Carmelo et al., 2016
Growth - ripening period	t	90	day	Murdy et al., 1994
Plant (Sunflower)				
Plant dry density	q_{plant}	1	kg/L	Estimated
Transpiration stream	Tc	577	L/kg_{dry}	Putnam et al., 1990
Water content of plant	Θ_{plant}	0.85	m^3/kg	Putnam et al., 1990
1^{st} order growth rate	k	0.12	1/day	Allen et al., 1998
Mass of seeds	M_0	0.005	Kg/m^2	Estimated
Mass of root	M_{root}	0.27	Kg_{dry}/m^2	Fang, 2017
Mass of plants(max)dry	M_{max}	1.16	Kg/m^2	Viorel et al., 2014
Growth - ripening period	t	120	day	Allen et al., 1998

3.3. Modeling Contaminant Transport

Phytoextraction of heavy metals was simulated using GoldSim's contaminant transport module. This module consists of two compartments/cells. The cell is a transport pathway element that is mathematically equivalent to a finite difference node. First cell (soil) is a mixture of soil, heavy metals, plant root and water. Second cell (plant) is a mixture of plant, heavy metals and water. Dissolved heavy metals in water move from the first cell to the second cell via advective flux, which occurs as the transpiration of plants during the growth period.

This simulation model integrates a soil water flow and contaminant transport model. The soil and the plant modules are solved via unidirectional data flow, from the soil to the plant. Plant biomass growth is calculated simply by multiplying the root water uptake rate via a transpiration related growth coefficient. Schematic representation of the modeling steps included in the heavy metal uptake process by plants is illustrated in Figure 3.5.

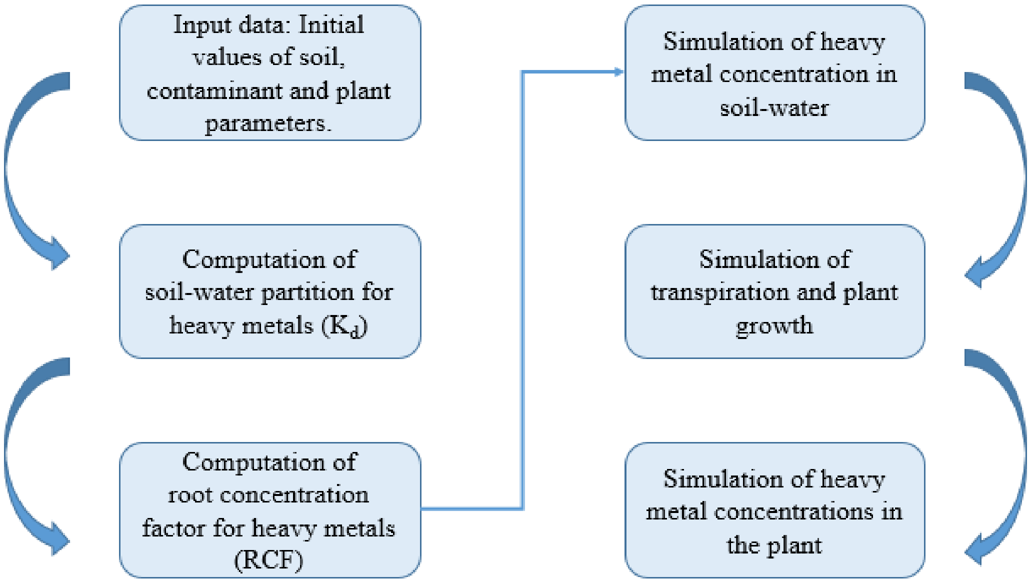

Figure 3.5. Plant uptake modeling procedure.

3.3.1. Computation of a Compartment /Cell Pathway

In the model, there are two cells. The first cell represents the soil, and the second one is for the plant. Cell is a transport pathway element that is mathematically equivalent to a finite difference node. Cell pathways are intended to represent discrete, well-mixed environmental compartments or ’mixing cells’ within the environmental system that is being simulated.

When multiple Cells are linked together via advective and diffusive mechanisms, the behaviour of the Cell network is mathematically described using a coupled system of differential equations. GoldSim numerically solves the coupled system of equations to compute the contaminant mass present in each Cell (and the mass fluxes between Cells) as a function of time.

Within a Cell, all species mass is assumed to be instantaneously and completely mixed and equilibrated within the Cell's media.

3.3.2. Advective Flux

For an advective mass flux link from Cell i to Cell j, the flux of species s, f_s, is computed as follows (modified from Barten, 1996):

$$f_{s,i\rightarrow j} = c_{ims}\,Tc \tag{3.1}$$

where Tc is the rate of advection (of the medium) for the mass flux link (L/T for fluid mass flux links, and M/T for solid mass flux links), c_{ims} is the total dissolved, sorbed or precipitated concentration of species s in medium m within Cell i [M/L if m is a fluid; M/M if m is a solid].

3.3.3. Partitioning Coefficient (Kd)

One of the most significant processes of the model presented here is adsorption to solids since the residue concentration of the heavy metals in soil water is directly related to the uptake of heavy metals into plants. This relationship is determined by a parameter known as partitioning coefficient (Kd), which is the distribution of the contaminant between soil and pore water (Equation 3.2.).

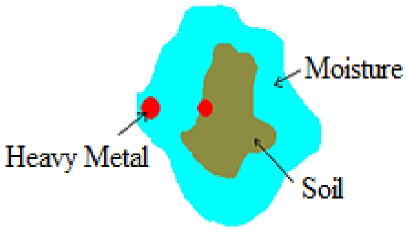

Figure 3.6. Heavy metal partitioning representation between moisture and soil.

$$Kd = \frac{\text{Concentration sorbed on soil (mg/kg)}}{\text{Concentration in solution (mg/l)}} \tag{3.2}$$

The partitioning of metals to solid particles can be influenced by a number of environmental and physicochemical parameters, such as soil dissolved organic carbon content, redox conditions, temperature, and pH of the soil. Therefore, under different conditions heavy metals have a broad range of Kd values, which are given in Table 3.3

Table 3.3. Kd parameter with heavy metals specific values from the literature. (Baltrenaite and Butkus, 2007).

Parameter, units	**Heavy Metals**		
	Cu	**Pb**	**Zn**
Molar mass, g.mol	63.5	207.2	65.3
Log Kd for soil, L/kg	0.1-3.6	0.7-5.0	-1.0-5.0

3.3.4. Root Concentration Factor (RCF)

The uptake of a contaminant by the roots occurs both with the advection (transpiration stream), and diffusion processes. There is a loss upward from the root as the water moves inside the plant (Larsen et al., 2005).

Plants' roots become a residue in the soil after harvesting; therefore, in this study, roots are considered part of the soil. RCF is used to determine the heavy metal concentration in plants' roots. Equilibrium between concentration in roots C_R (mg/g), and water C_W (mg/mL) is given with the following formula:

$$\mathrm{RCF} = \frac{\text{Concentration in root (mg/g)}}{\text{Concentration in solution (mg/mL)}} \qquad (3.3)$$

However, in this study an empirical relationship between RCF and octanol-water partition coefficient (Kow) is used for the determination of RCF (Briggs et al., 1982). This relationship is expressed by Equation 3.4. Kow values of different heavy metal types obtained from the literature (Baltrenaite and Butkus, 2007), and the RCFs calculated based on Equation 3.4 are also outlined in Table 3.4.

$$RCF = 0.82 + 0.03Kow^{0.77} \qquad (3.4)$$

Table 3.4. Calculated root concentration factors based on Kow parameters.

Parameter, Units	**Heavy Metals**		
	Cu	**Pb**	**Zn**
Kow	200	40	110
RCF, L/kg	2.59	1.33	1.94
HM Concentration in root, g/kg	0.09	0.009	0.16
HM Conc. in solution, mg/mL	0.033	0.006	0.081

3.3.5. Growth and Transpiration

Many field crops show a logistic growth curve. The initial growth is exponential, but towards ripening, the growth slows down and finally stops. Accordingly, the change of plant mass M (kg) with time t (d) can be expressed as:

$$\frac{dM}{dt} = k \times M\left(1 - \frac{M}{M_{max}}\right) \qquad (3.5)$$

where; k is the rate constant for exponential growth (1/d), and M_{max} is the max. plant mass (kg).

Plant mass as a function of time, M(t), can be calculated by integrating the growth function. With the initial plant mass, M_0, M(t) can be determined as:

$$M(t) = \frac{M_{max}}{1 + \left(\frac{M_{max}}{M_0} - 1\right) \times e^{-kt}} \qquad (3.6)$$

About 2/3 of precipitation (rain, snow, fog) is evapotranspired, and 2/3 of that evapotranspired is transpired by plants (Trapp, 2013). The Sorghum transpiration ratio is 1:310, meaning that the plant uses 310 parts of water to produce one part of the dry matter. The Sunflower transpiration ratio is 1:577, meaning that the plant uses 577 parts of water to produce one part of the dry matter. Transpiration of plants is closely related to growth via the transpiration coefficient T_c (L/kg), (Rein et al. 2011) which can be calculated as:

$$Q = T_C \times \frac{dM}{dt} = T_C \times k \times M\left(1 - \frac{M}{M_{max}}\right) \qquad (3.7)$$

where; Q is the water flux through the roots and out of the stem (L/d)

3.4. Model Calibration and Validation

Model calibration is the process of modifying the input parameters of a model until the output from the model matches an observed set of data. Therefore, calibration is an essential step in every modeling practice to obtain better and more accurate results. The search for the best parameter values can be carried out by following a trial and error procedure, which is one of the most used approaches in the calibration process. The soil-water partitioning coefficient (Kd) is the most effective parameter governing the plant uptake process, and its range is quite broad as given in Table 3.3. so there is a need for careful calibration of this parameter. For this purpose GoldSim's built-in optimization functionality is used to automatically adjust model parameter values within ranges reported in the literature, to attain better agreement between simulated and observed data.

On the other hand model validation refers to the testing of the model output to confirm the results that should be produced in reality. Calibration and validation require some measurement of how well the model represents the field measurements which is known as goodness-of-fit-statistics. The Nash and Sutcliffe (1970) model-efficiency measure is commonly used:

$$NS = 1 - \frac{\sum_{i=1}^{n}(Oi - Mi)^2}{\sum_{i=1}^{n}(Oi - \overline{O})^2} \qquad (3.8)$$

where; O is the observed, and M is modeled value, respectively.

This equation is a measure of the square error to the observed variance. If the error is zero, then NS=1, meaning the model represent a perfect fit.

Model is calibrated and validated via Cu, Zn and Pb concentrations measured from the soil samples, before and after the planting periods of Sorghum and Sunflower, as outlined in Table 3.1. A split dataset approach was undertaken for the calibration and validation purposes. For calibration purposes summer data of 2011 and 2012 was used; whereas validation was achieved using winter data of 2011 and 2012. It should be noted that soil heavy metal concentrations before planting and post-harvest are assumed as model input and output, respectively.

The model’s validity was tested by taking into account the reductions in soil heavy metal concentrations as a consequence of phytoextraction process by plants. A summary of the calibration and validation procedure is illustrated in Figure 3.7.

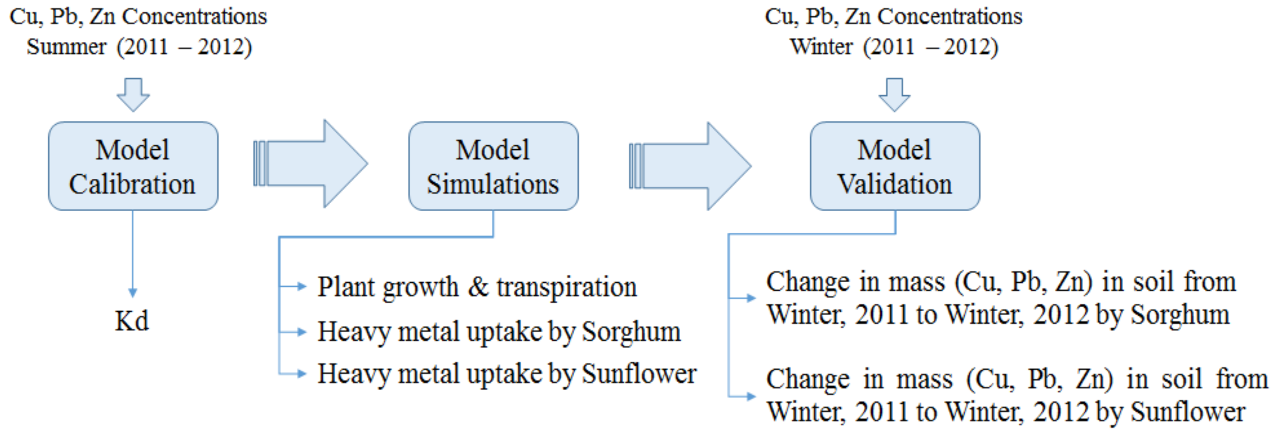

Figure 3.7. Calibration and validation procedure

3.5. Sensitivity Analysis

Sensitivity analysis can be described as the process of determining the sensitivity of model output to changes in the input parameters. If changing a particular input value causes a significant change in the model output, then the model is said to be sensitive to that particular parameter.

Sensitivity analysis of a mathematical model is often associated with its uncertainty as it investigates how the uncertainty in the output of a model can be apportioned to different sources of variation in the model input. Sensitivity analysis methods can be categorized as mathematical, statistical and graphical.

Mathematical methods simply include determining the range in output variation in relation to the changes in input variation of parameters under investigation. This is usually in the form of one-at-a-time parameter sensitivity analysis, which means altering the value of one input parameter, while holding the others fixed, and observing the model output.

Statistical methods involve running simulations in which inputs are defined as probability distributions and estimating the effect of variance in the input and output distributions. This is usually done via Monte-Carlo simulations, and enables the modeler to identify the effect of interactions among multiple parameters.

Graphical methods can give a visual indication of how an output is affected by variation in input variables and integrate the results of mathematical and statistical methods for better representation (Frey and Patil, 2002).

4. RESULTS AND DISCUSSION

This section presents the results of model calibration, model simulations, and model validation. Model calibration is based on the determination of the best values of Kd for Cu, Zn and Pb. Model simulations aims at presenting how heavy metal uptake is influenced by plant growth and transpiration. Finally, model validation provides both qualitative and quantitative descriptions of the model's ability to simulate real conditions. Finally, the significance of three different parameters (plant mass, partitioning coefficent and transpiration rate) are evaluated in terms of their sensitivities in affecting the residue soil heavy metal concentrations.

4.1. Results of Model Calibration

Solid–liquid partitioning of metals in soil (Kd) is a critical parameter used to predict the fate of metals in soil, namely their mobility and availability. Kd, of a metal varies mainly due to differences in soil properties; pH, soil organic matter and origin of the metals. The model is calibrated based on the Kd coefficient regarding three different heavy metals; Cu, Zn, Pb. This is achieved using GoldSim's optimization tool. Calibration results for Cu, Zn and Pb are given in Figures 4.1, 4.2 and 4.3, respectively. In the figures Nash and Sutcliffe Efficiency measure (NS) of '1' corresponds to a perfect match between the modeled and observed data, where as an NS value '0' indicates that the model predictions are completely incapable of simulating the observed behaviour.

Soil heavy metal concentrations from the winter and spring 2011 and 2012 data sets and Kd values of heavy metals used for calibration and validation are shown in Table 4.2. Calibration results for NS versus Kd coefficient regarding three different heavy metals; Cu, Zn, Pb are presented in Appendix A.

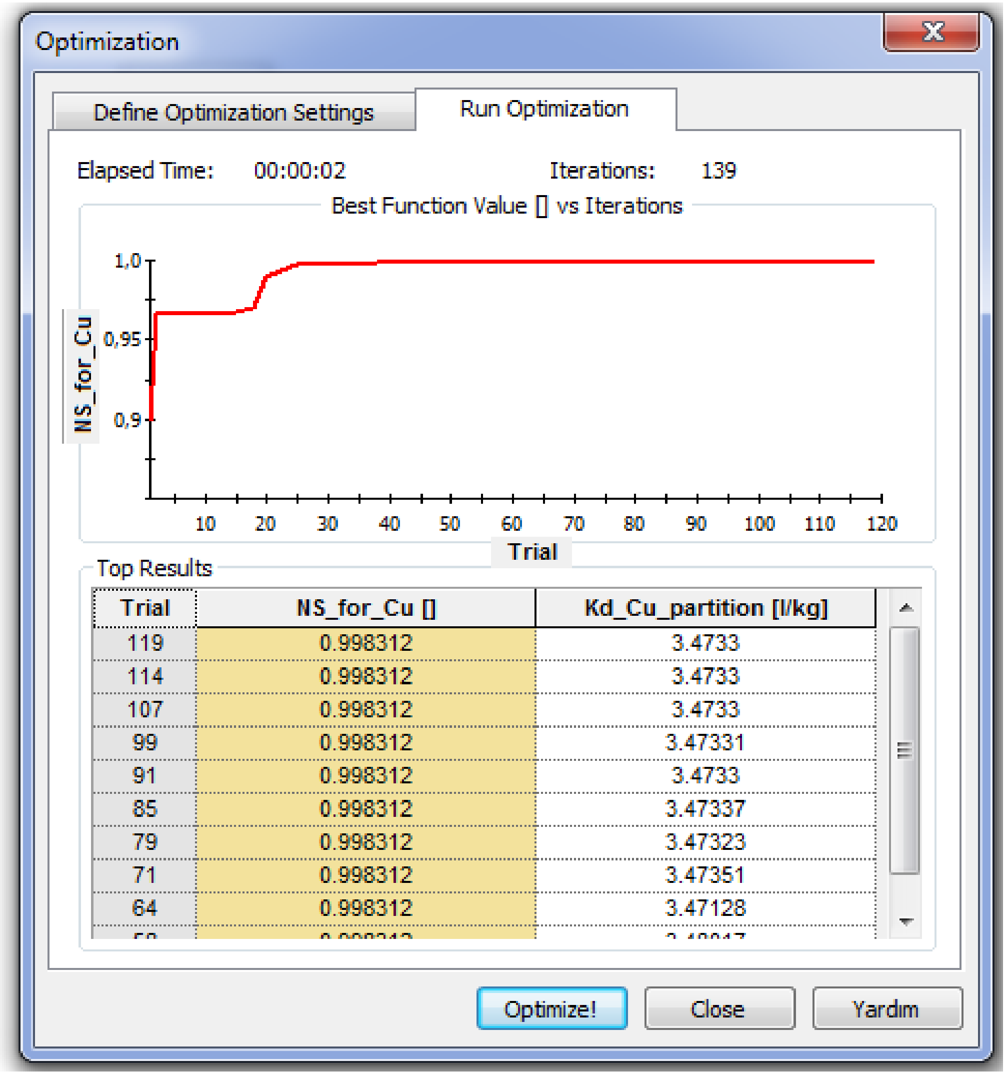

Figure 4.1. Optimum Kd values for Cu.

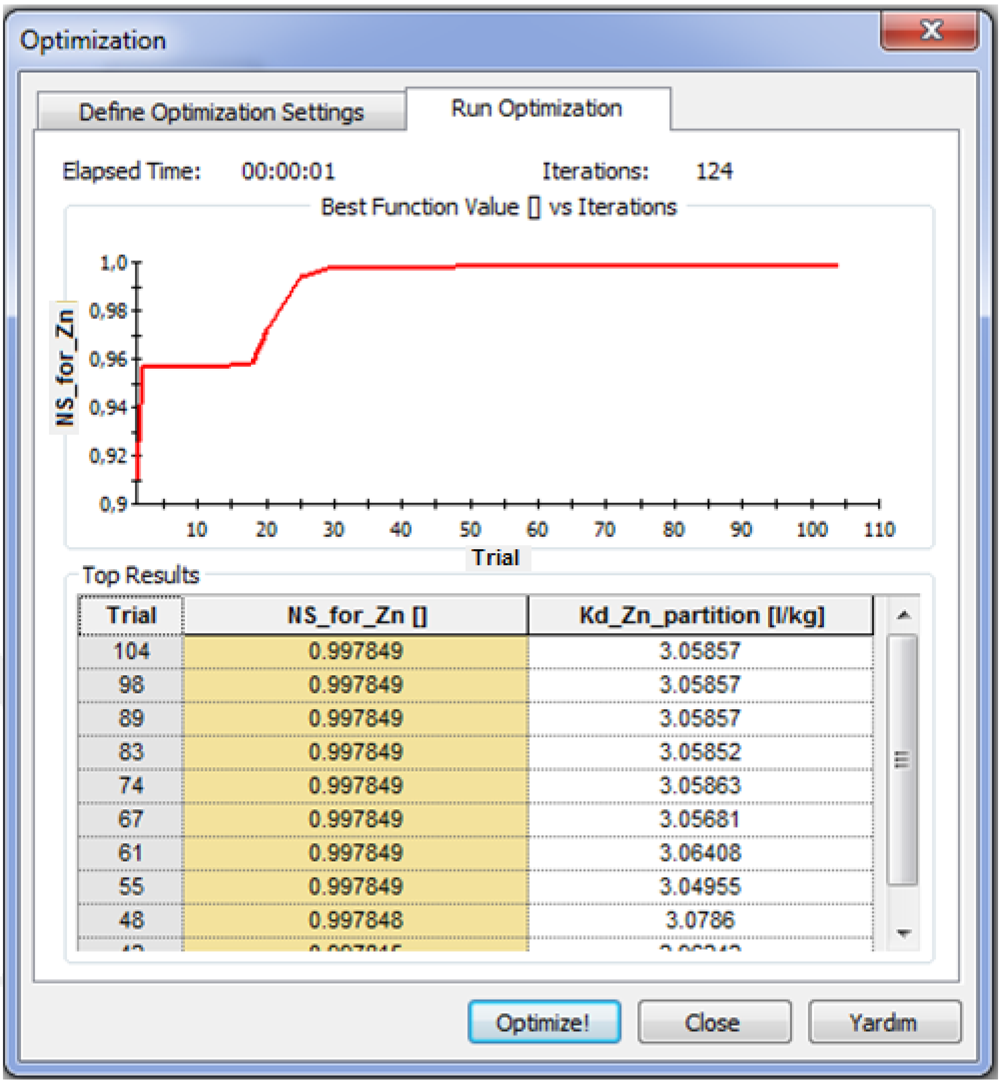

Figure 4.2. Optimum Kd values for Zn.

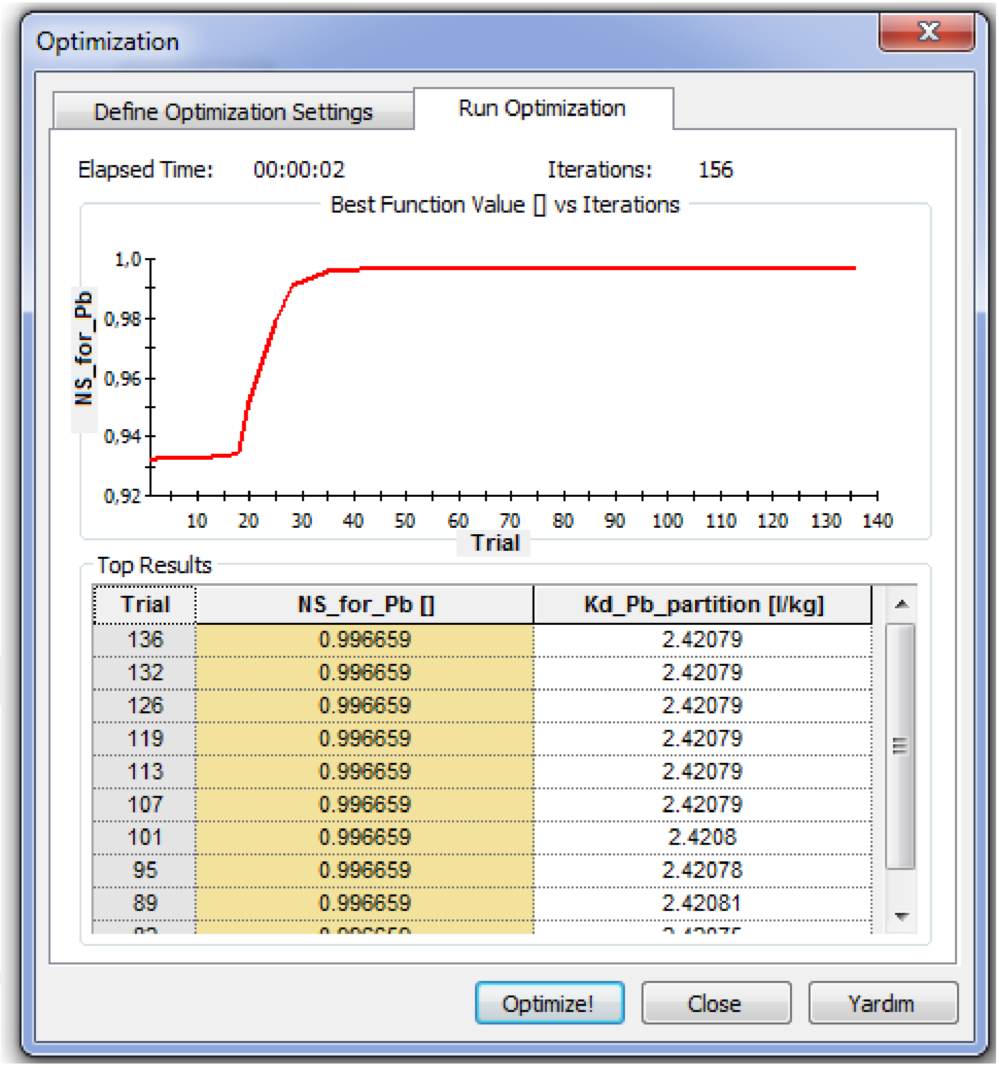

Figure 4.3. Optimum Kd values for Pb.

Table 4.1 summarizes the calibrated Kd values for the heavy metals and corresponding removal rates of those heavy metals by Sorghum and Sunflower. Lower Kd values indicate higher uptake rate of heavy metals by plants, which means an increased heavy metal removal rate from the soil.

Table 4.1. Calibrated Kd values and heavy metals removal rates.

Parameter	**Value**	**NS**	**Removal Rate** (from observed data)	
			Sorghum	Sunflower
Kd_{Cu}	3.47 L/kg	0.998	16 %	18 %
Kd_{Zn}	3.05 L/kg	0.998	18 %	26 %
Kd_{Pb}	2.42 L/kg	0.997	26 %	27 %

This result is in agreement with previously published literature. According to a former experimental research, the Kd value for Pb is found to be the highest as 900L/kg, followed by Zn and Cu, with the values 62, and 22 L/kg, respectively (EPA, 2005).

Change in Cu, Zn, and Pb concentrations from summer, 2011 to 2012, after Sorghum planting, are given in Figure 4.4. Dashed lines represent the observed concentrations obtained from the field. Left and right axes indicate the soil heavy metal concentrations in summer, 2011, and 2012, respectively. For the simulations, summer, 2011 and 2012 data are taken as model input and output, respectively. Accordingly, modeled and observed heavy metal distributions (Cu, Zn, Pb) after planting Sorghum are shown Figure 4.5.

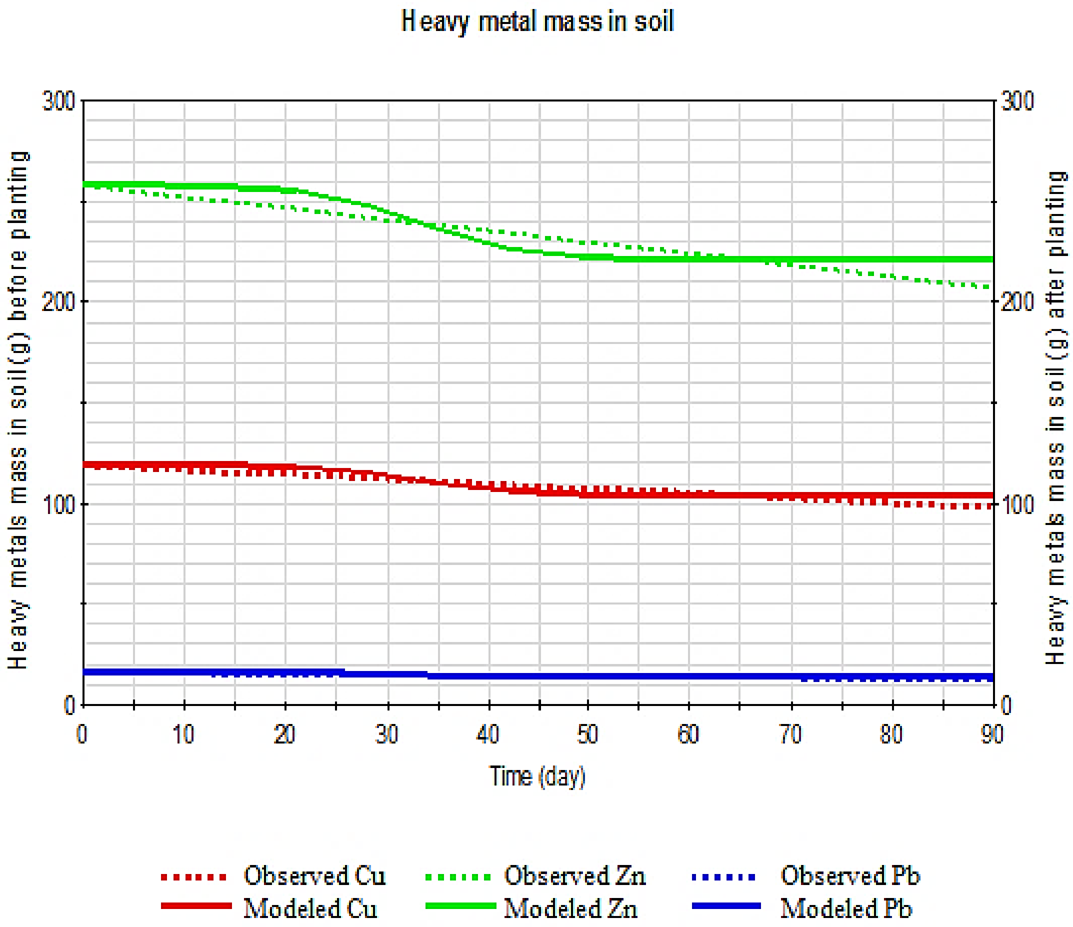

Figure 4.4. Change of heavy metal mass in soil from 2011 to 2012 summer by Sorghum.

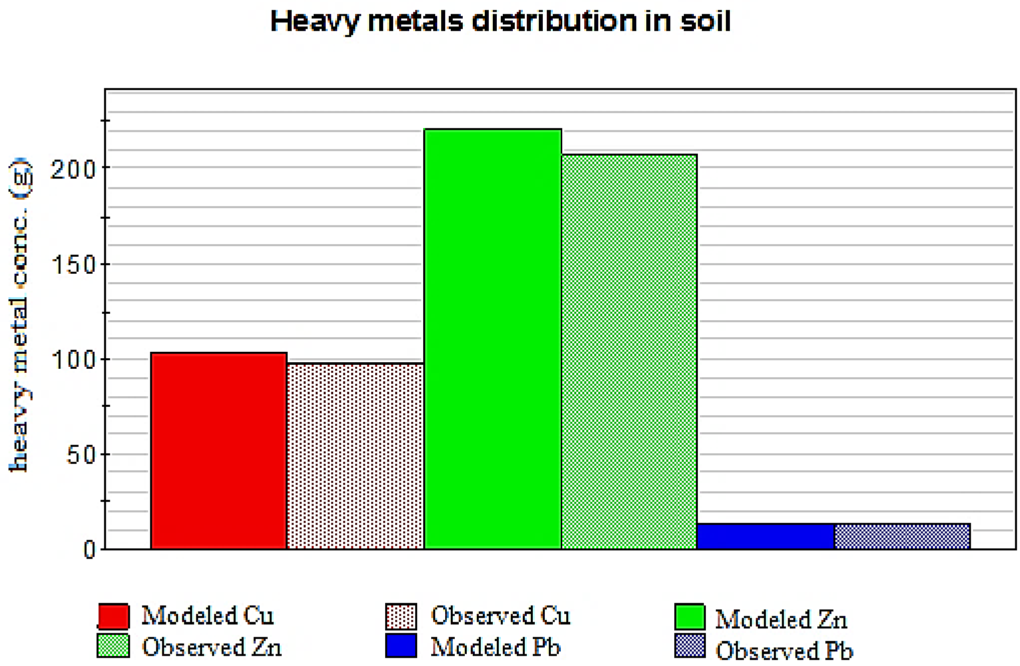

Figure 4.5. Heavy metals distribution in soil by planting Sorghum in 2011 summer.

Similarly, change in Cu, Zn, and Pb concentrations from summer, 2011 to 2012, after Sunflower planting, are given in Figure 4.6. Dashed lines represent observed concentrations of heavy metals in soil while solid lines represent modelled concentration when growing Sunflower. Left and right axes indicate the soil heavy metal concentrations in summer, 2011, and 2012, respectively. For the simulations, summer, 2011 and 2012 data are taken as model input and output, respectively. Accordingly, modeled and observed heavy metal distributions (Cu, Zn, Pb) after planting Sunflower are shown Figure 4.7.

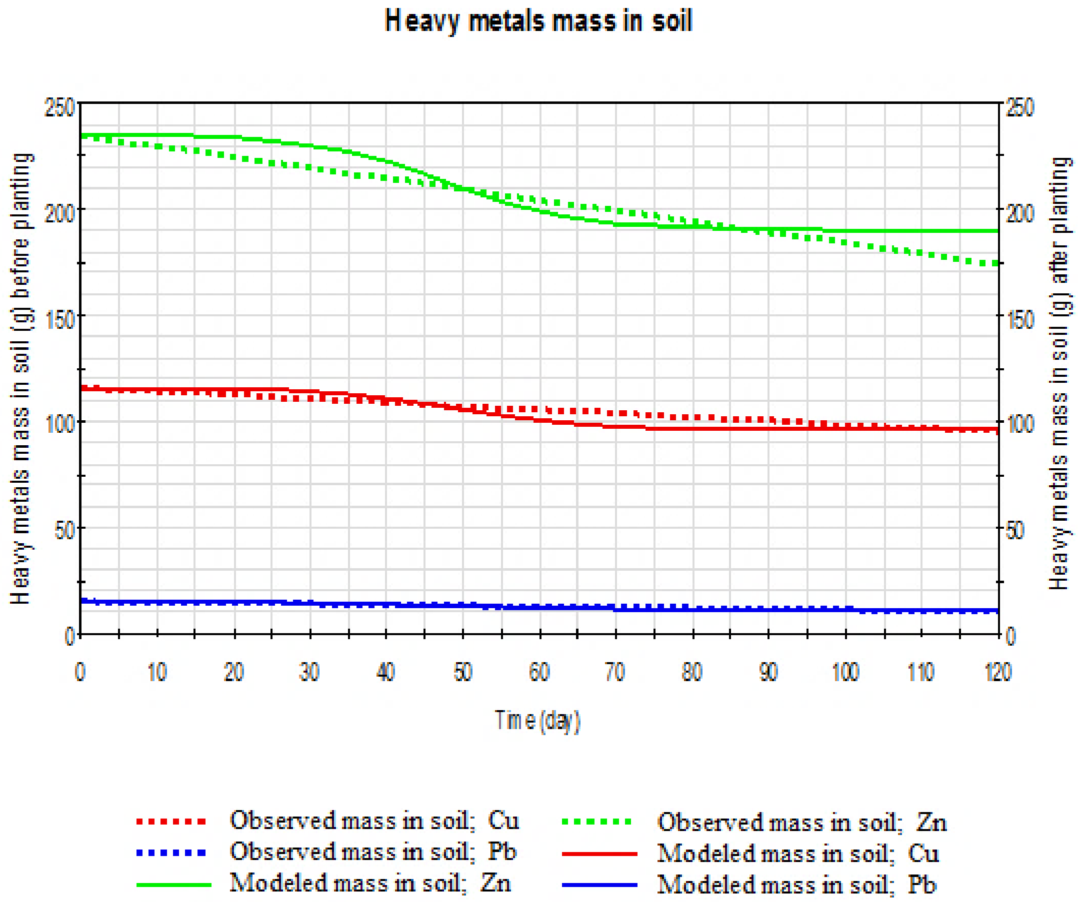

Figure 4.6. Change of heavy metals mass in soil from 2011 to 2012 summer by Sunflower

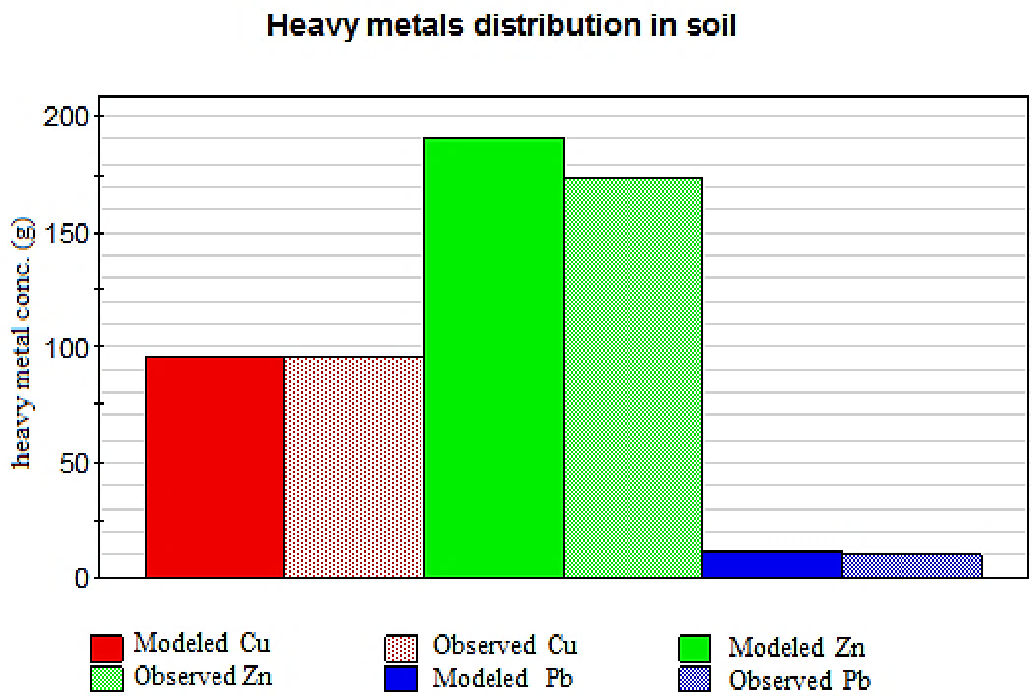

Figure 4.7. Heavy metals distribution in soil by planting Sunflower in 2011 summer.

Based on the calibration and simulation results, Table 4.2 summarizes Kd values and comparison of observed and simulated soil concentrations of heavy metals for different seasons.

Table 4.2. Calibration data for the plant uptake model.

Parameter, units		**Heavy Metals**		
		Cu	Pb	Zn
Kd, min, L/kg		1.26	1	0.1
Kd, mean, L/kg		71	708	100
Kd, max, L/kg		3981	100000	100000
Kd, opt, L/kg		3.47	2.42	3.05
For calibration **Sorghum** 2011-2012 Summer	$\mathbf{C_{in}}$ initial conc. on soil, gr/1000kg	119	16.5	258
	$\mathbf{C_{ob}}$ Observed conc. on soil, gr/1000kg	98	12.50	207
	$\mathbf{C_{sim}}$ Simulated conc. on soil, gr/1000kg	103	13.59	220
For validation **Sorghum** 2011-2012 Winter	$\mathbf{C_{in}}$ initial conc. on soil, gr/1000kg	135	15.3	238
	$\mathbf{C_{ob}}$ Observed conc. on soil, gr/1000kg	116	11.0	199
	$\mathbf{C_{sim}}$ Simulated conc. on soil, gr/1000kg	117	12.60	203
For calibration **Sunflower** 2011-2012 Summer	$\mathbf{C_{in}}$ initial conc.on soil, gr/1000kg	116	14.8	235
	$\mathbf{C_{ob}}$ Observed conc. on soil, gr/1000kg	95	10.3	174
	$\mathbf{C_{sim}}$ Simulated conc. on soil, gr/1000kg	96	11.3	190
For validation **Sunflower** 2011-2012 Winter	$\mathbf{C_{in}}$ initial conc. on soil, gr/1000kg	129	13	214
	$\mathbf{C_{ob}}$ Observed con. on soil, gr/1000kg	106	10	156
	$\mathbf{C_{sim}}$ Simulated conc. on soil, gr/1000kg	107	10	173

4.2. Model Simulation Results

Two different plants for the purpose of phytoremediation, Sorghum and Sunflower, were planted in the summer and winter seasons of 2011 and 2012 respectively. Following planting, the soil heavy metal concentrations were compared, and the results suggested that Sunflower is more effective in the uptake process of heavy metals, compared to Sorghum. This may be attributed to the fact that the transpiration rate of Sunflower ($Tc = 577\ L/kg_{dry}$) is higher than that of Sorghum ($Tc = 310\ L/kg_{dry}$).

Sorghum's growth and transpiration curves, which are derived from plant mass, M(t) and transpiration, Q, equations given by Equations 3.6 and 3.7, are illustrated in Figure 4.8 together with the schematic representation of the growth stages shown in Figure 4.9. Simulation period was set to 90 days to be able to cover the full Sorghum crop growth period. Similarly, sunflower's growth and transpiration curve, which is derived from plant mass, M(t) and transpiration, Q equations given by Equations 3.6 and 3.7 are illustrated in Figure 4.10 together with the schematic representation of the growth stages shown in Figure 4.11. This time, simulation period was set to 120 days to be able to cover the full Sunflower crop growth period. According to Figures 4.8 – 4.11, it becomes possible to suggest that plant transpiration occurs more during the growth stage than during the ripening stage, when the plant has a higher mass.

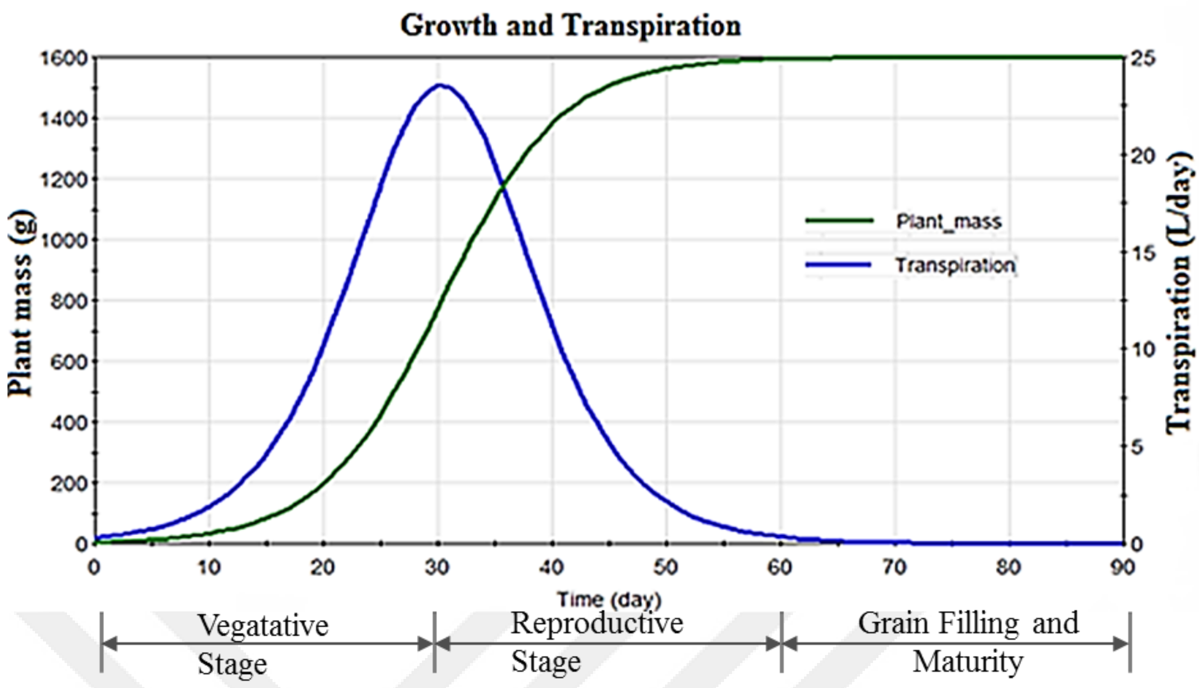

Figure 4.8. Sorghum Growth and Transpiration curve obtained from GoldSim.

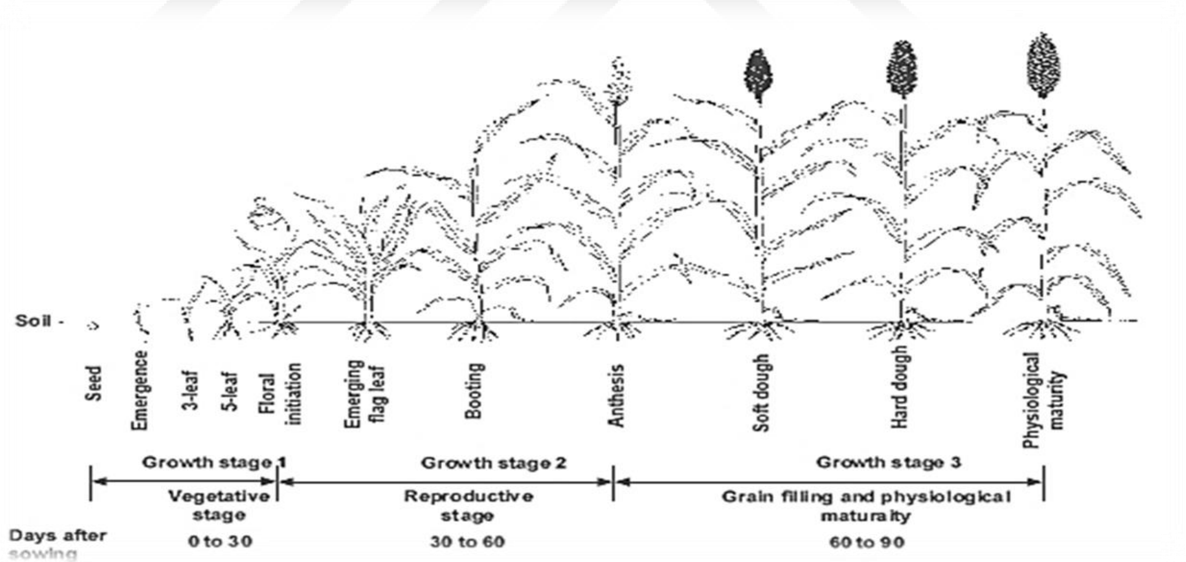

Figure 4.9. Schematic representation of Sorghum growth stage.

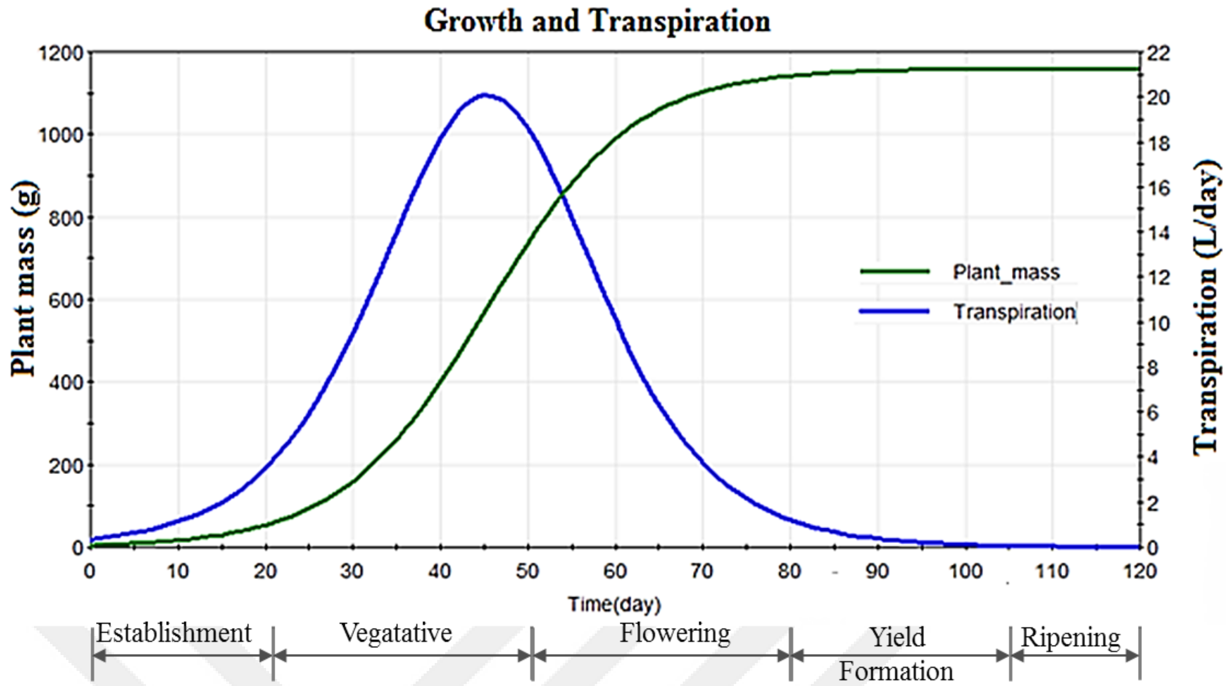

Figure 4.10. Sunflower Growth and Transpiration curve obtained from goldsim.

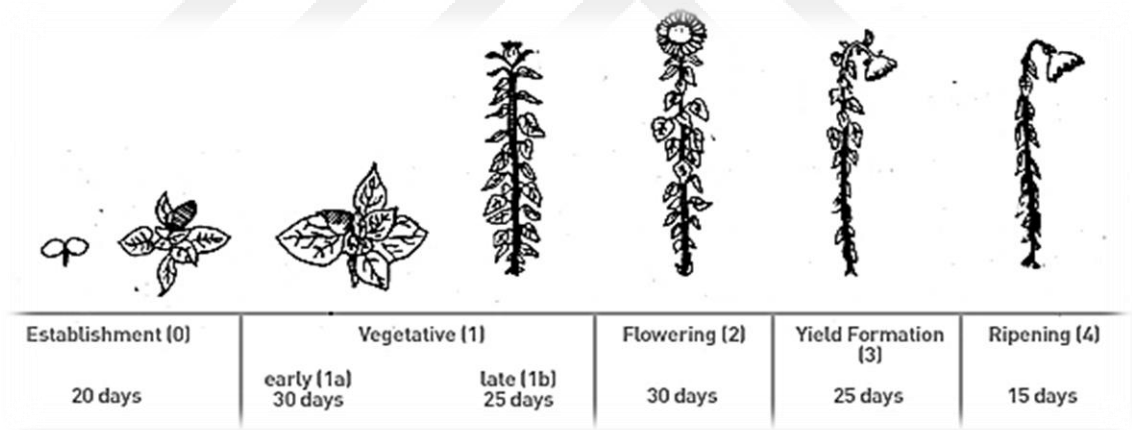

Figure 4.11. Schematic representation of Sunflower growth stage

One of the main aims of this study is to model the uptake of heavy metals by plants. Yet, there is lack of the data information regarding the heavy metal concentrations in the plants. This difficulty is overcomed by the assumption that the heavy metal loss in the soil is directly associated with the increase in heavy metal concentration in the plant. Based on this assumption, the estimated concentration of heavy metals in plants were derived from differences in Summer, 2011 and 2012 soil heavy metal concentration data obtained from the field.

The solid and dashed lines in figures 4.12 and 4.13 indicate the modeled and estimated heavy model concentrations corresponding to Sorghum and Sunflower planting, respectively. Results indicated that, plant transpiration occurs more during the growth stage than during the ripening stage, therefore, heavy metal uptake during the fisrt 80 days is higher, and approaches to zero after the 80 days period.

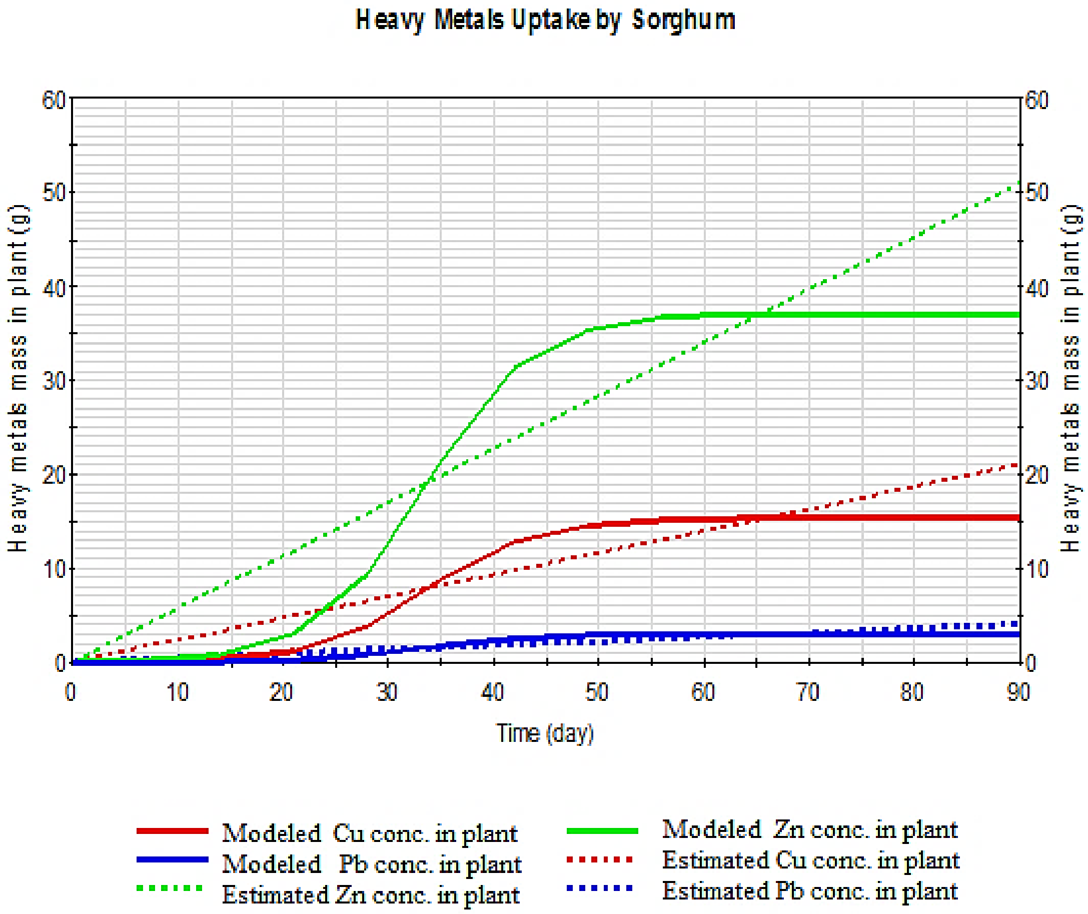

Figure 4.12. Heavy metals uptake from soil to Sorghum with time.

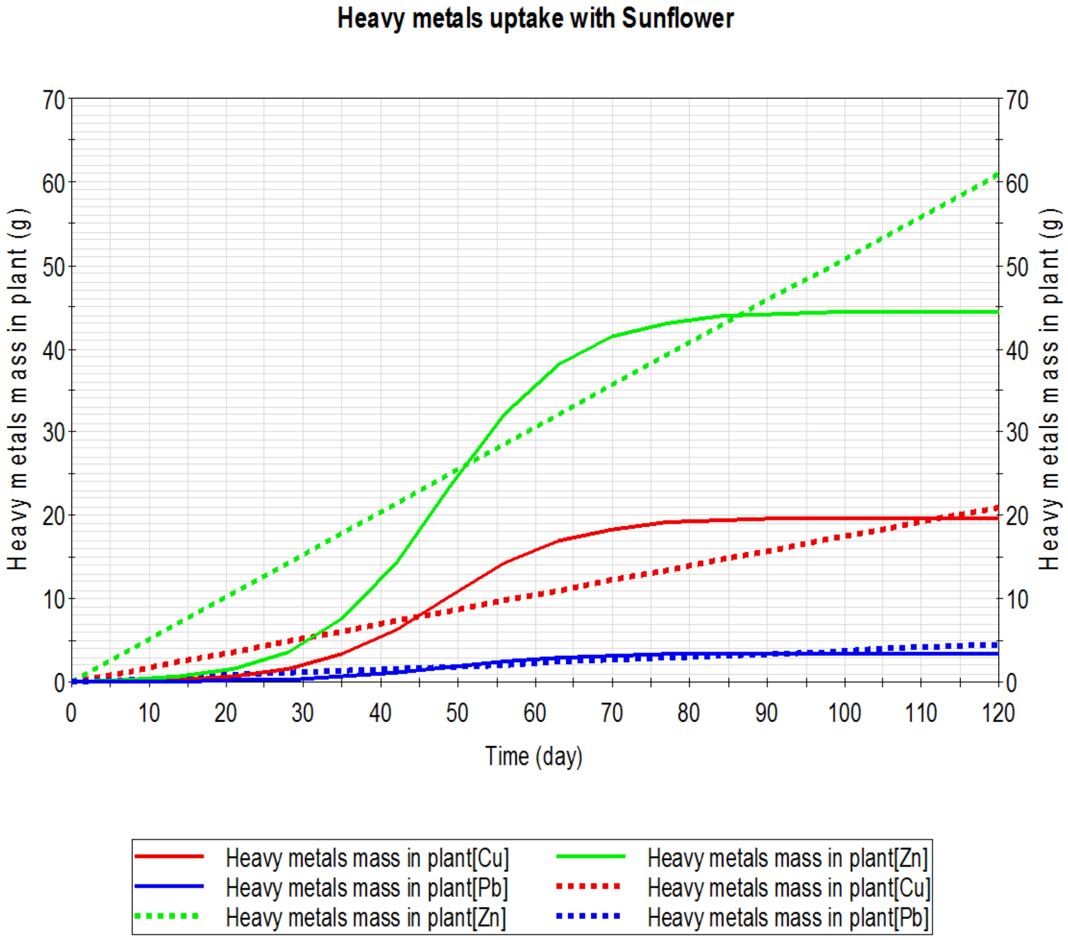

Figure 4.13. Heavy metals uptake from soil to Sunflower with time.

4.3. Results of Model Validation

As discussed earlier in the Methodology Chapter, model validation uses winter data regarding the years 2011 and 2012. In this season, removed heavy metals observed and modeled concentrations from soil to the plants and associated NS values are given in table 4.3.

Table 4.3. Removed heavy metals concentration from soil.

Heavy metals, units	**Removed heavy metals from soil**			
	by Sorghum		by Sunflower	
	Observed	Modeled	Observed	Modeled
Cu, mg/kg	19	18	23	22
Pb, mg/kg	4.3	2.7	3	3
Zn, mg/kg	39	35	58	41
NS of validation	0.968		0.813	

Variations in soil Cu, Zn and Pb concentrations are demonstrated in Figures 4.14 and 4.16 for Sorghum and Sunflower, respectively. Solid and dashed lines represent the modeled and observed concentrations of heavy metals in the soil, respectively. Left and right axes represent the Winter, 2011 and Winter, 2012 data, which corresponds to model input and output, respectively.

Soil heavy metal distributions are also given in Figures 4.15 and 4.17 for Sorghum and Sunflower, respectively.

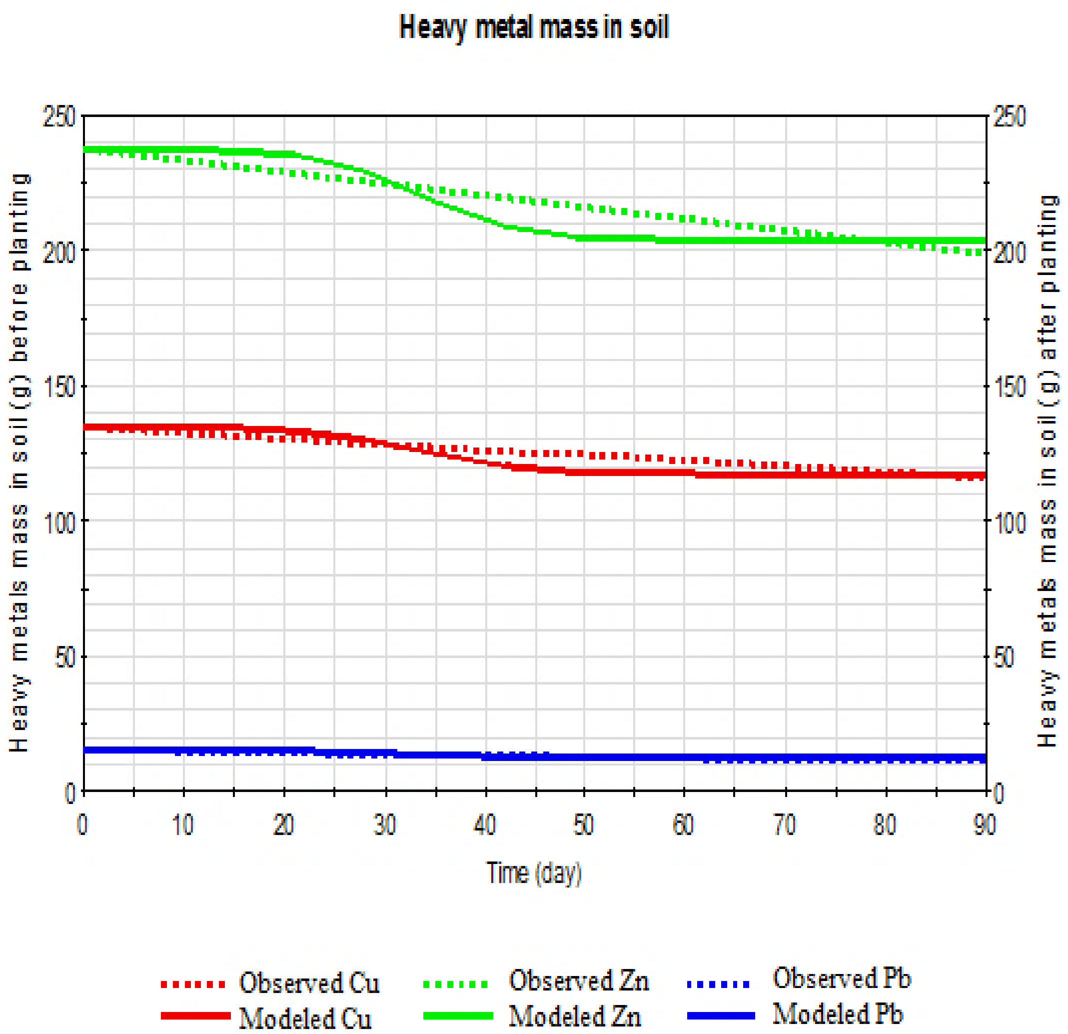

Figure 4.14. Change of Heavy metals mass in soil from 2011 to 2012 winter by Sorghum

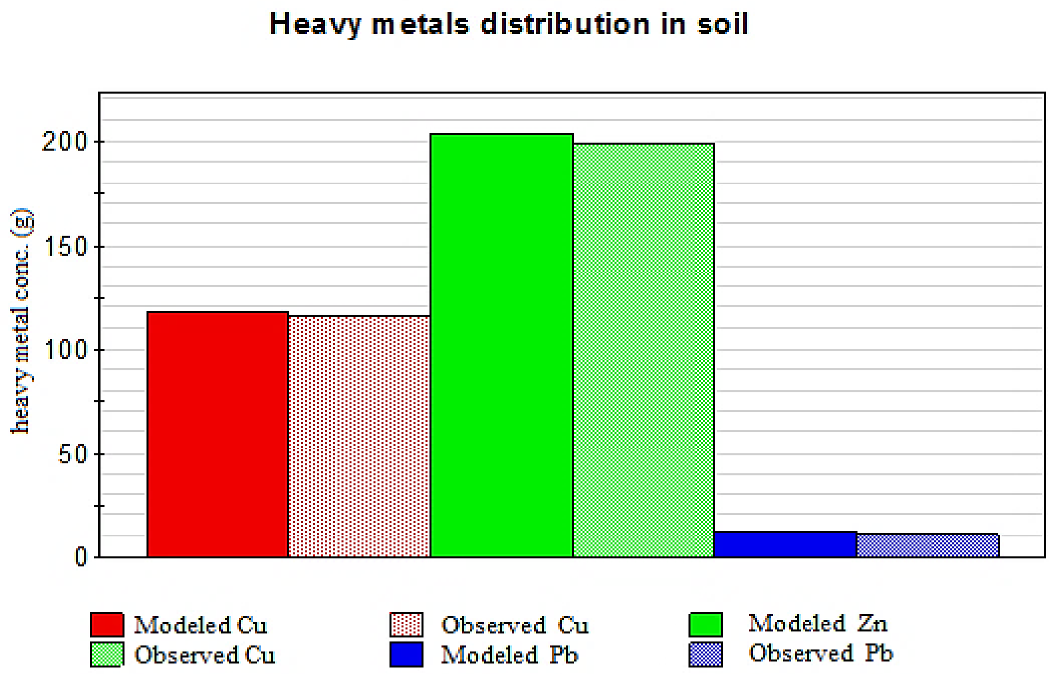

Figure 4.15. Heavy metals distribution in soil: Phytoremediation by Sorghum

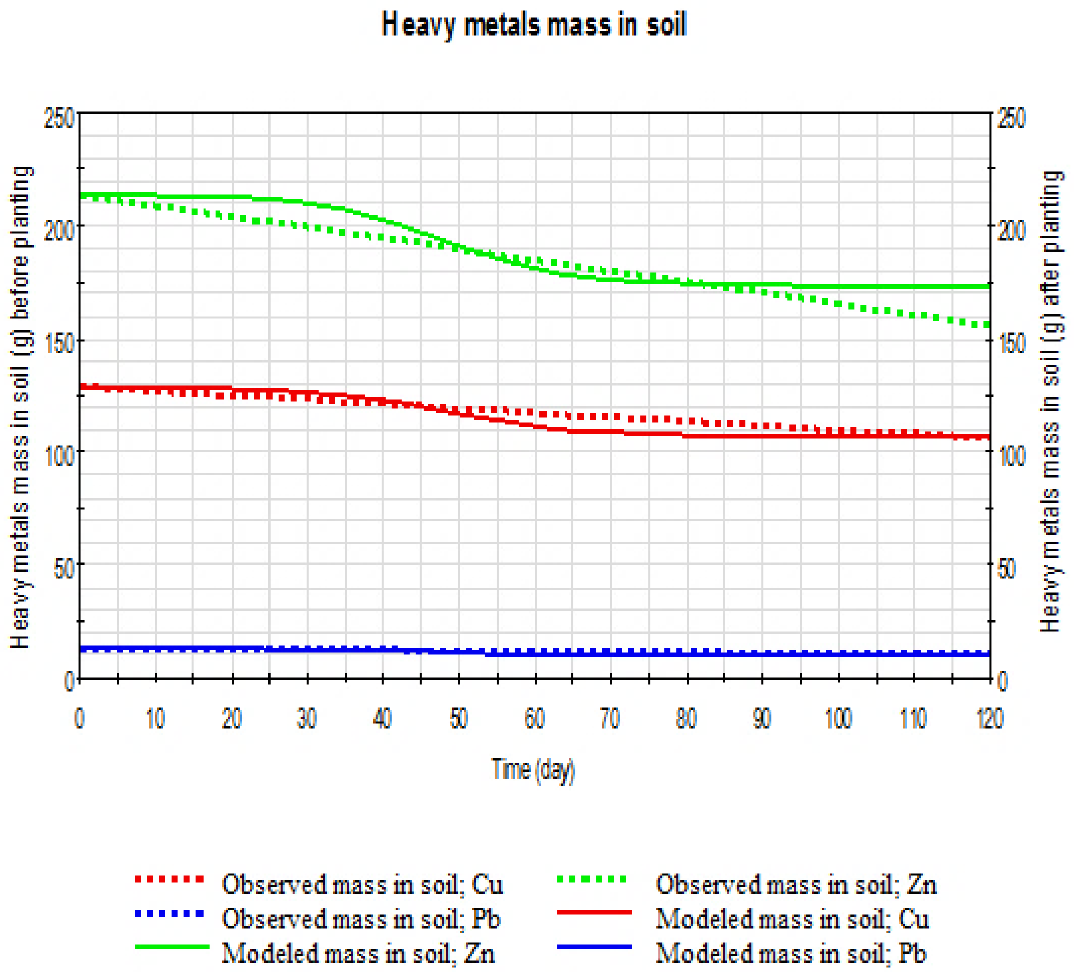

Figure 4.16. Change of Heavy metals mass in soil from 2011 to 2012 winter by planting Sunflower

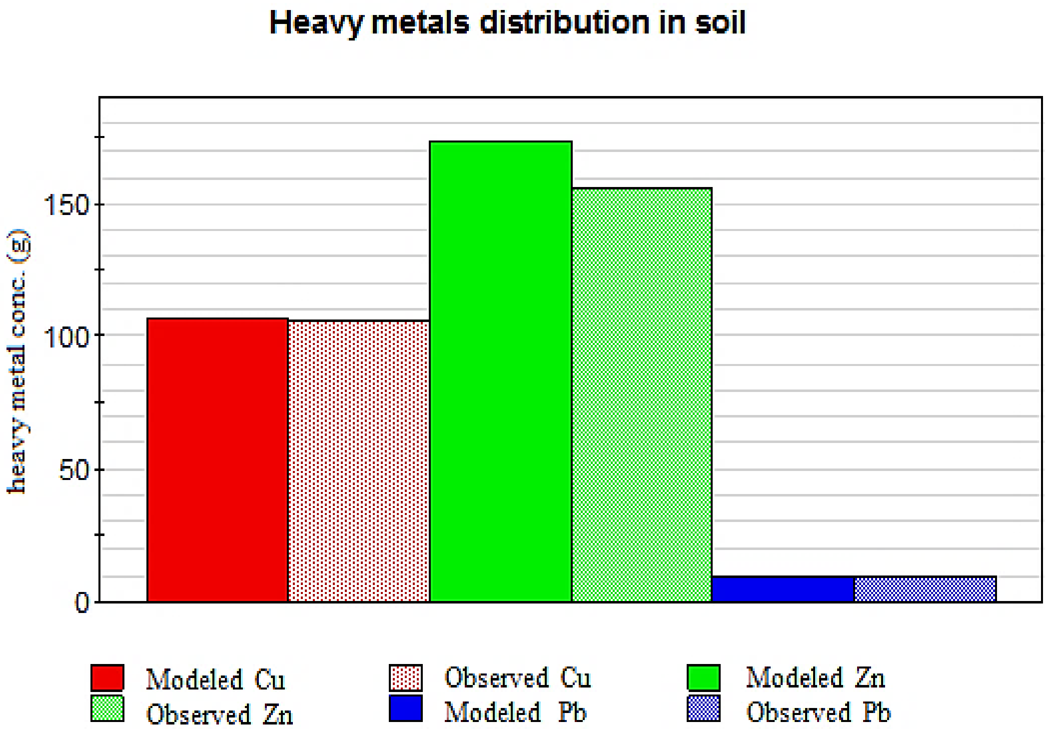

Figure 4.17. Heavy metals distribution in soil: Phytoremediation by Sunflower.

Overall, results produced from the model presented here showed good aggrement with previously published studies (EPA, 2005; Nawab et al., 2015). For example, in a recent experimental study determining the heavy metal contamination in a mine affected soil, and its phytoremediation by Sorghum, concentrations of Cu, Pb, and Zn are found to be 8.42, 4.41, and 88.2 mg/g in plant, and their corresponding soil concentrations are found to be 180, 104, and 40 mg/kg. These findings are similar to the model outputs presented here, especially in terms of relative abundance of different metal groups.

4.4. Results of Sensitivity Analysis

The sensitivity analysis was undertaken by changing one input variable at a time, while holding all others constant. GoldSim runs the model multiple times, systematically sampling each variable over a specified range, while holding all of the other variables constant to produce sensitivity plots (i.e, a tornado chart or X-Y function charts). This is to graphically identify the variables in the model to which the results are most sensitive.

The model runs a series of deterministic simulations, varying one independent variable at a time through a range of values. The x-axis of a tornado chart represents the values of the result for different values of the independent variables.

Each bar represents the range of result values produced when each independent variable is set to lower bound, central value, and upper bound (with the other variables being held constant). A light blue bar indicates that the value was produced by the lower bound (Low), and a dark blue bar indicates that the value was produced by the upper bound (High). The solid vertical line represents the value of the result, when the central values are used for all independent variables.

An X-Y function chart can be hold all other independent variables at their central value and at their deterministic values, the first independent variable is varied from its lower bound to its upper bound. The process is repeated for each independent variable.

The y-axis of an X-Y function chart represents the values of the result for different values of the independent variables. There is one line for each variable. Each line illustrates how the result changes when that independent variable is varied from its lower bound to its upper bound (with the other variables being held constant). Because each variable likely will have different units and a different range, the x-axis does not represent actual values, rather it represents normalized values (range from 0 to 1)

$$\text{Normalized Value} = \frac{(\text{Value} - \text{Lower Bound})}{(\text{Upper Bound} - \text{Lower Bound})} \qquad (4.1)$$

The normalization differs depending on whether the range of the independent variable was specified as quantiles or was specified directly.

The sensitivity of three parameters, namely, partition coefficient, Kd; plant mass, M(t); and transpiration rate, Tc were tested in terms of their sensitivities in simulating model output, which are residue heavy metal concentration in the soil.

The x-axis in the tornado chart represents the residue heavy metal concentration in the soil. The x-axis in the normalized function plots represent the normalized values. When the lower bound of the parameter has a low value, then the normalized values are near 1, and when the lower bound of the parameter has a high value, then normalized values are near zero. Bounds value of the parameters used in the model are given in table 4.4.

Table 4.4. Sensitivity analysis parameters' bound values

Parameters, Units		**Lower Bound**	**Central value**	**Upper Bound**
Kd partitioning, l/kg	**Cu**	1.26	3.47	3981
	Pb	1	2.42	100000
	Zn	0.1	3.05	100000
Tc transpiration rate, l/kg		250	310	550
M(t) Plant Mass, kg		1	1.6	2.5

According to the results of the sensitivity analysis, the model output is more sensitive to the lower values of Kd and plant mass, but more sensitive to the higher values of transpiration rate. Amongst the three parameters, plant mass is the most significant one. This can be attributed to the fact that plant transpiration occurs more during the growth stage than during the ripening stage, when the plant has a higher mass. Results showed that residue heavy metal concentrations in the soil decrease with increasing transpiration rate. Generally, although the degree may differ, M(t) seems to be the most significant parameter, followed by Kd, and Tc, for each type of heavy metal.

Tornado charts and normalized plots of sensitivity analysis for Cu, Zn, and Pb are provided in Figures 4.18. to 4.23. respectively.

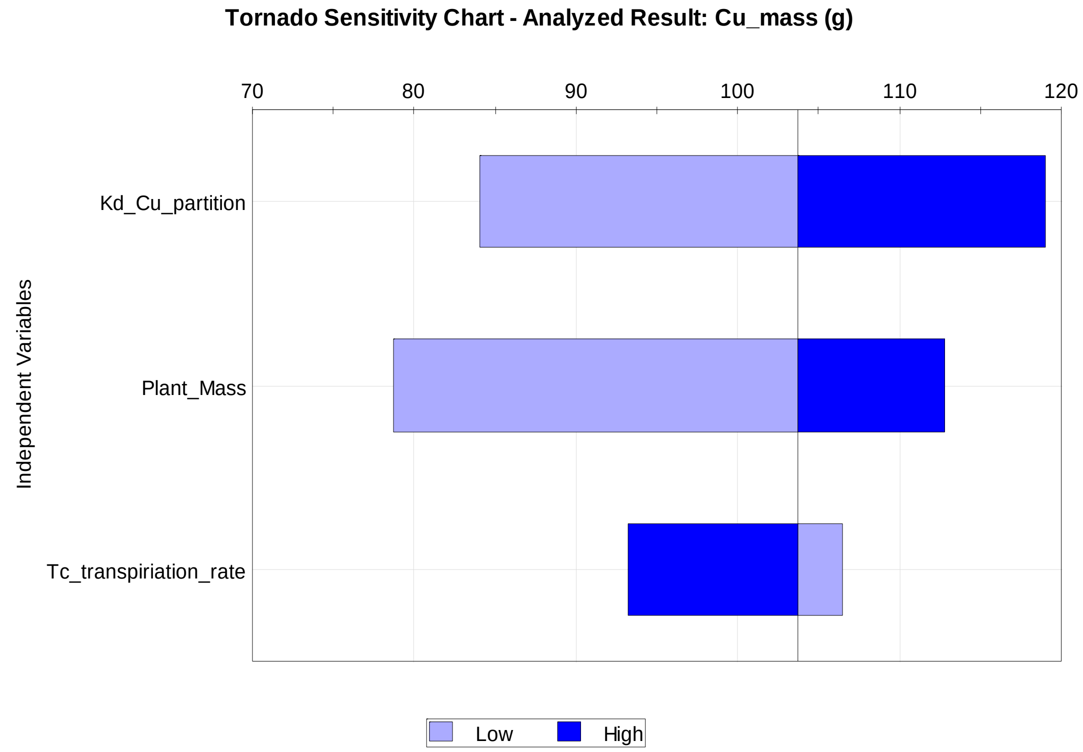

Figure 4.18. Sensitivity analysis of model parameters for Cu concentration by Tornado Diagram

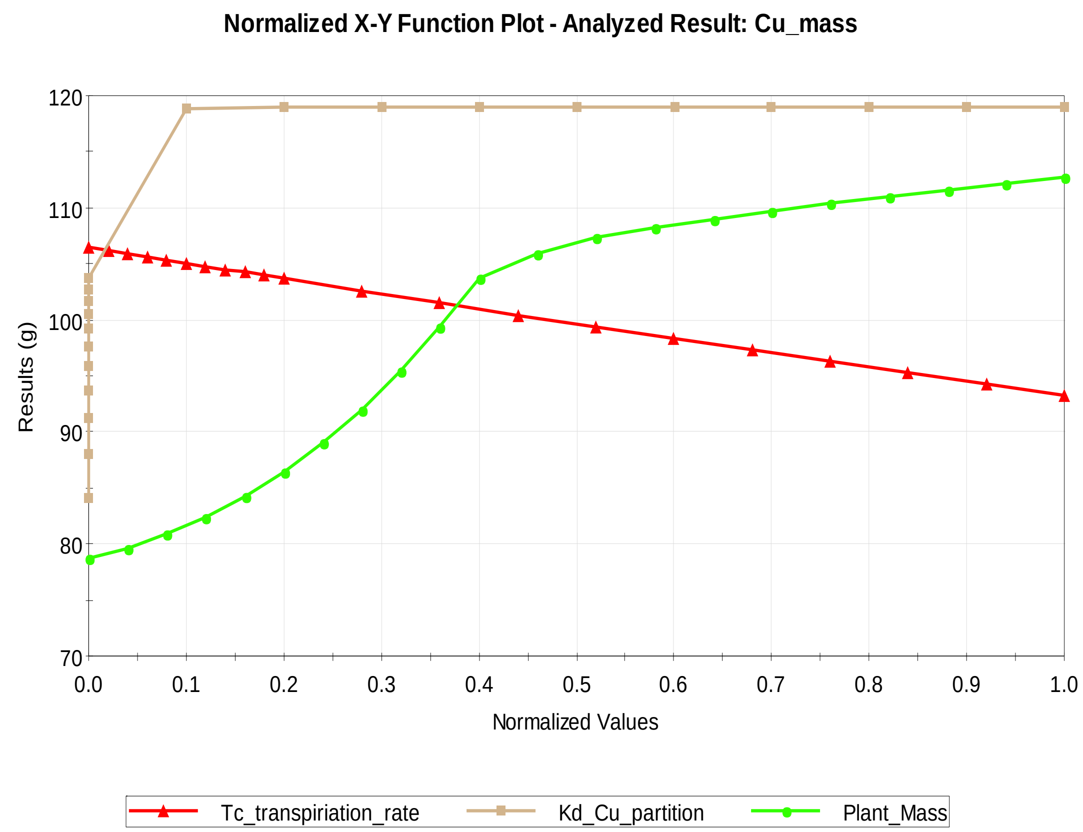

Figure 4.19. Sensitivity analysis of model parameters for Cu conc. in soil by X-Y func. chart

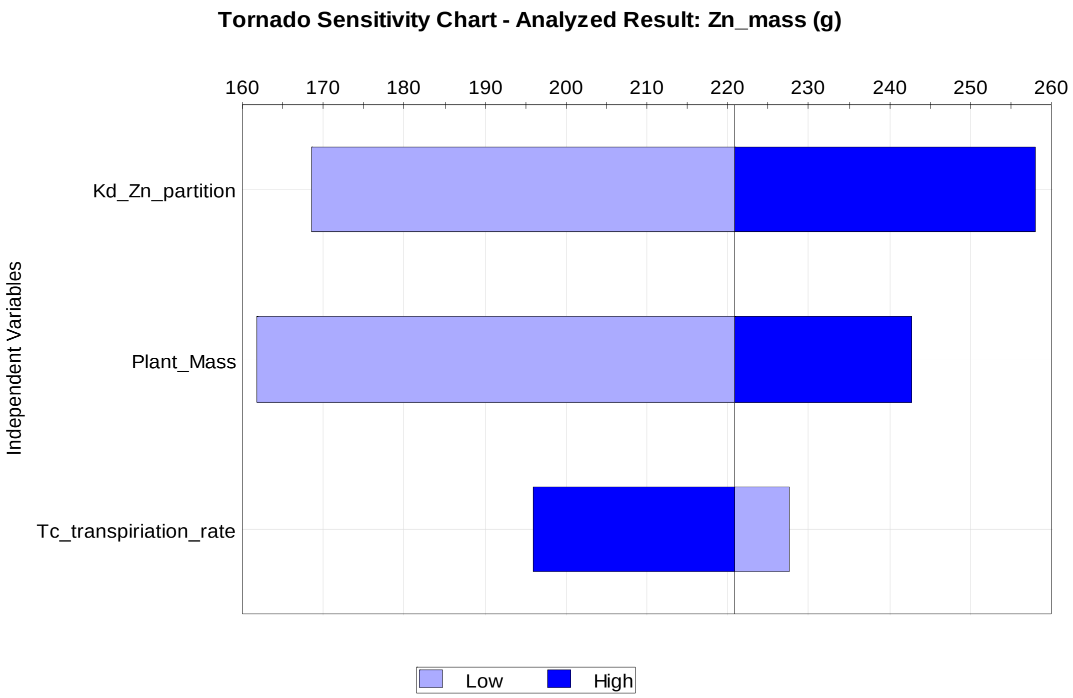

Figure 4.20. Sensitivity analysis of model parameters for Zn conc. in soil by Tornado Diagram.

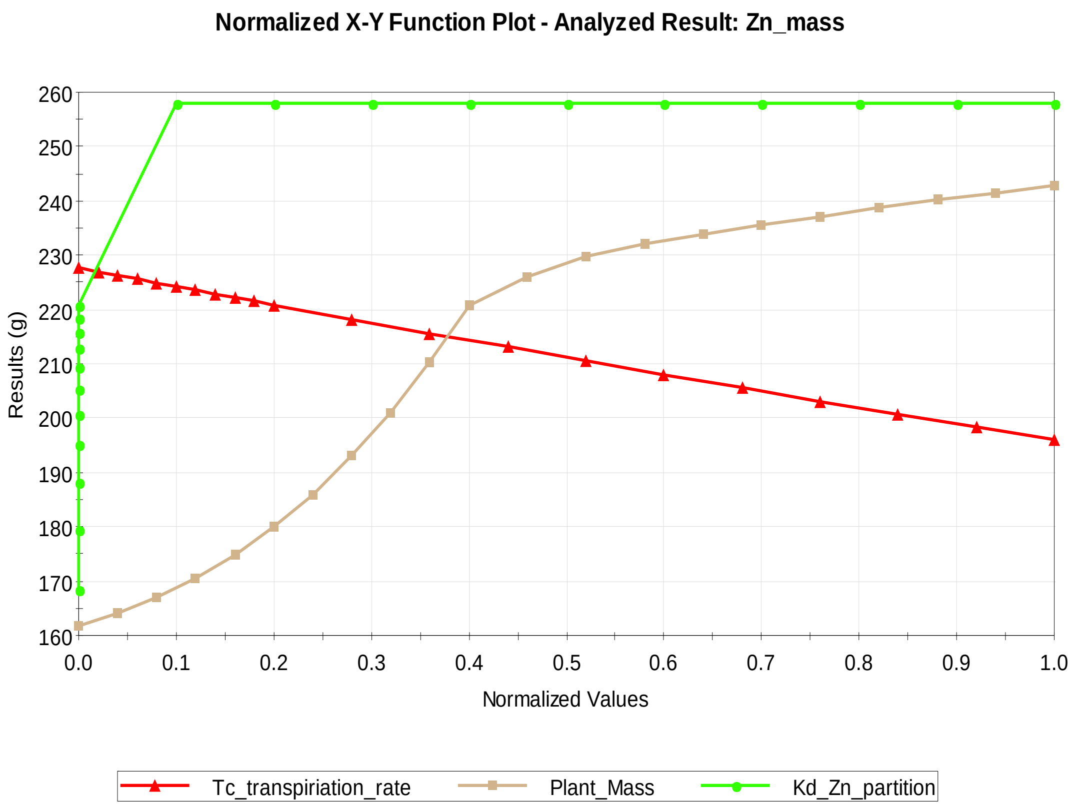

Figure 4.21. Sensitivity analysis of model parameters for Zn concentration in soil by X-Y chart

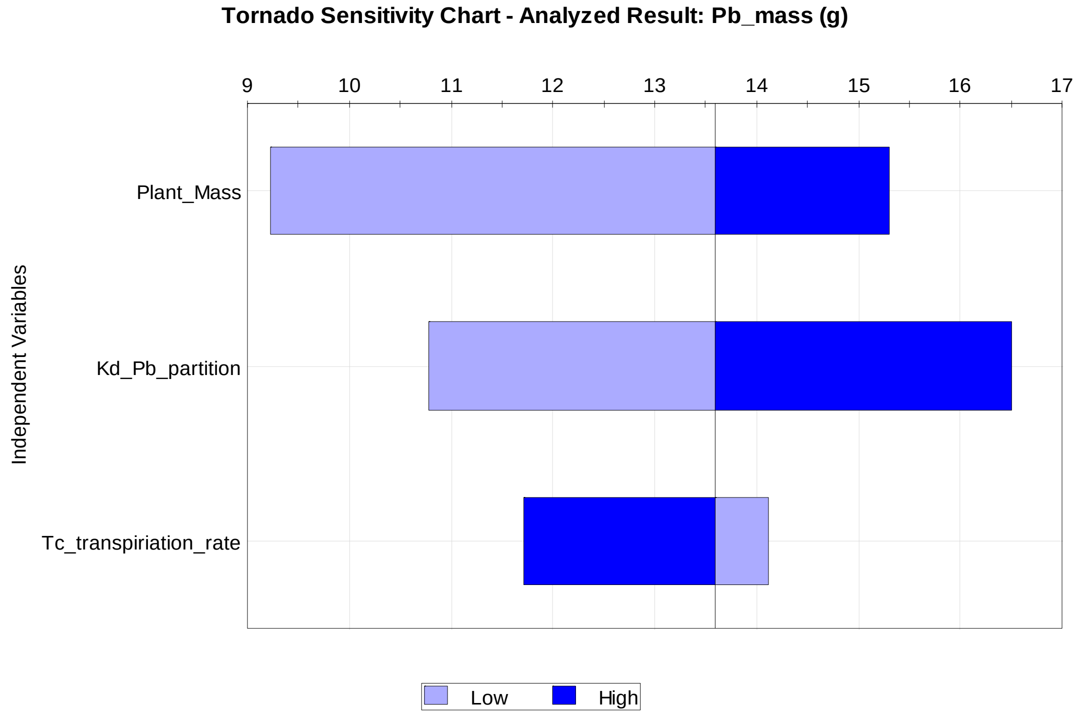

Figure 4.22. Sensitivity analysis of model parameters for Pb conc. in soil by Tornado Diagram

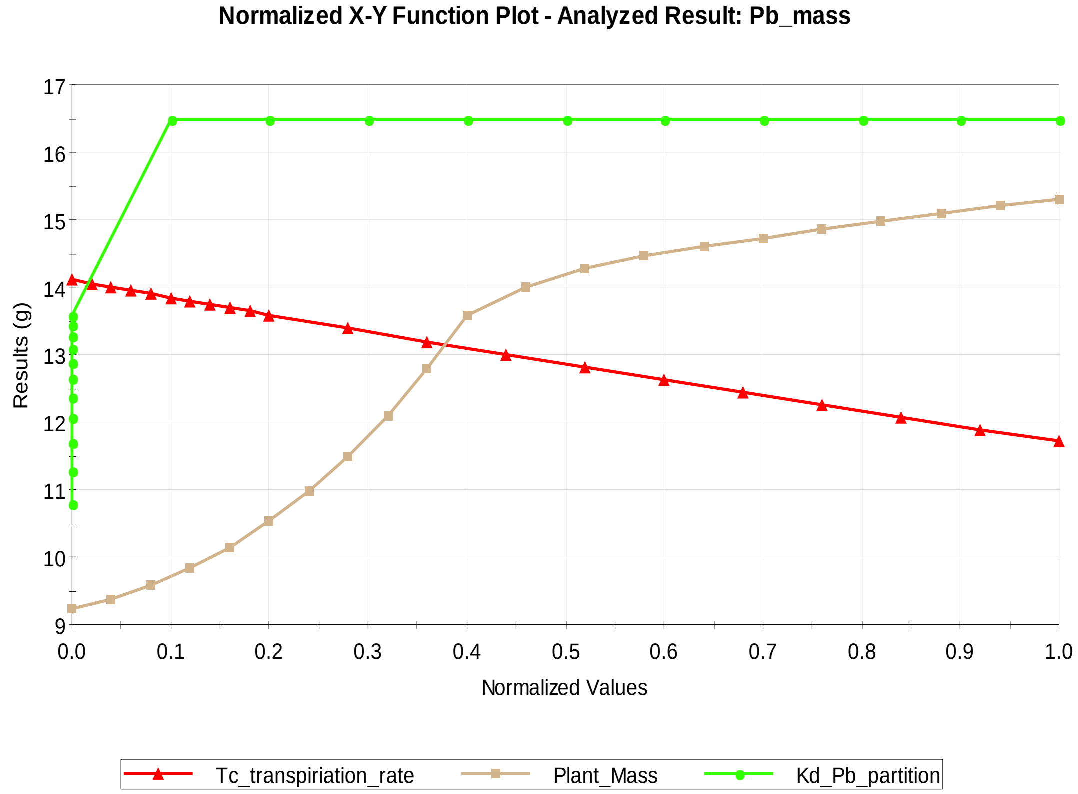

Figure 4.23. Sensitivity analysis of model parameters for Pb concentration in soil by X-Y function chart

5. CONCLUSIONS AND RECOMMENDATIONS

The focus of this study was to develop a process-based mathematical model of heavy metals (Cu, Pb, Zn) uptake from soil into plants using the field data obtained from the Kilis region, where Sorghum and Sunflower were planted in the years 2011 and 2012.

The model contains only one plant compartment and assumes passive uptake of heavy metals with soil water into the plant via transpiration and growth. Moreover, plant roots are considered as a part of the soil, because they remain in the soil after harvesting. There are, however, some processes that have been neglected in this study. Amongst these, leaching movement of water, the posssible complexation of heavy metals in the soil solution by organic substances, and the distribution of the absorbed heavy metals over the different parts of the plant have not been considered in the current model.

The main conclusions that can be drawn from the study are:

i. Decreasing Kd values increase the uptake of heavy metals by plants or removal of heavy metals from the soil. This is successfully simulated by the model.
ii. The uptake rate of Sunflower is higher than that of Sorghum.
iii. Kd values for Cu, Zn, and Pb are found to be 3.47 L/kg, 3.05 L/kg, and 2.42 L/kg; respectively.
iv. NS number for validation of Sorghum and Sunflower are found to be 0.968 and 0.813 respectively.
v. Plant mass is found to be the most sensitive parameter, followed by partition coefficient and transpiration rate.

The solid-liquid distribution of heavy metals largely affects their mobility and bioavailability in the soils. Higher Kd values reduce the uptake of heavy metals into the plant due to their lower concentrations in soil water.

Transpiration may be regarded as one of the main process for the plant uptake model. Higher transpiration rates lead to increased heavy metal removal from the soil. Moreover, plant mass per cubic meter is also as effective as transpiration. According to the model results both transpiration and, hence heavy metal uptake rate is higher in Sorgum, compared to Sunflower.

The comparisons between simulated and measured concentrations in soils are in good agreement. Further research may focus on planting different plants in this area for the identification of other suitable plants for the phytoremediation of heavy metals. More detailed studies, investigating the effects of various planting cycles on heavy metal removal efficiency may be undertaken. Moreover, microorganism contribution for heavy metal removal can be evaluated through more extensive field studies.

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APPENDIX A: Optimum Kd Values

Table A.1. Optimum Kd values for Cu

Trial (low precision)	**NS for Cu**	**Kd Cu [l/kg]**
15	0.998052	3.8539
13	0.96672	276.464
10	0.966179	695.864
8	0.965945	1986.32
2	0.965882	3971.65
1	0.89826	1
Trial (medium precision)	**NS for Cu**	**Kd Cu [l/kg]**
62	0.998312	3.47303
55	0.998312	3.47514
49	0.998312	3.46672
44	0.998312	3.48356
38	0.99822	3.69082
32	0.998219	3.27629
26	0.997672	4.10535
20	0.994094	2.44724
17	0.993821	5.76345
13	0.979366	15.9672
Trial (high precision)	**NS for Cu**	**Kd Cu [l/kg]**
79	0.998312	3.47323
71	0.998312	3.47351
64	0.998312	3.47128
58	0.998312	3.48017
52	0.998312	3.46239
45	0.998311	3.49796
38	0.99828	3.35569
32	0.997958	3.92478
25	0.996803	2.7866
20	0.990196	7.33932
Trial (maximum precision)	**NS for Cu**	**Kd Cu [l/kg]**
119	0.998312	3.4733
114	0.998312	3.4733
107	0.998312	3.4733
99	0.998312	3.47331
91	0.998312	3.4733
85	0.998312	3.47337
79	0.998312	3.47323
71	0.998312	3.47351
64	0.998312	3.47128
58	0.998312	3.48017

Table A.2. Optimum Kd values for Pb

Trial (low precision)	NS for Pb	Kd Pb [l/kg]
15	0.967802	8.1699
13	0.933102	693.051
10	0.932789	1746.71
8	0.932655	4988.75
2	0.932619	9976.51
1	0.931679	1
Trial (medium precision)	**NS for Pb**	**Kd Pb [l/kg]**
69	0.996659	2.42138
62	0.996659	2.42006
56	0.996659	2.42535
50	0.996659	2.41477
42	0.996657	2.43593
36	0.996446	2.26669
30	0.996418	2.60516
23	0.9938	1.92823
20	0.984255	4.63592
17	0.956749	12.9673
Trial (high precision)	**NS for Pb**	**Kd Pb [l/kg]**
89	0.996659	2.42081
82	0.996659	2.42075
73	0.996659	2.42098
67	0.996659	2.41735
61	0.996659	2.42461
54	0.996658	2.41009
47	0.996642	2.46817
41	0.996344	2.23584
35	0.996138	2.70051
28	0.990946	1.77118
Trial (maximum precision)	**NS for Pb**	**Kd Pb [l/kg]**
136	0.996659	2.42079
132	0.996659	2.42079
126	0.996659	2.42079
119	0.996659	2.42079
113	0.996659	2.42079
107	0.996659	2.42079
101	0.996659	2.4208
95	0.996659	2.42078
89	0.996659	2.42081
82	0.996659	2.42075

Table A.3. Optimum Kd values for Zn

Trial (low precision)	**NS for Zn**	**Kd Zn [l/kg]**
15	0.983122	8.1699
13	0.956899	693.051
10	0.956652	1746.71
8	0.956546	4988.75
2	0.956517	9976.51
1	0.909656	1
Trial (medium precision)	**NS for Zn**	**Kd Zn [l/kg]**
25	0.997849	3.05927
20	0.996738	3.73625
17	0.976236	12.0683
13	0.963645	37.7056
10	0.957934	195.473
8	0.956907	680.912
6	0.956688	1427.74
5	0.956599	2576.71
4	0.956571	3460.53
3	0.956557	4140.39
Trial (high precision)	**NS for Zn**	**Kd Zn [l/kg]**
83	0.997849	3.05852
74	0.997849	3.05863
67	0.997849	3.05681
61	0.997849	3.06408
55	0.997849	3.04955
48	0.997848	3.0786
42	0.997815	2.96242
36	0.99779	3.19477
29	0.997394	2.73007
25	0.993954	4.58889
Trial (maximum precision)	**NS for Zn**	**Kd Zn [l/kg]**
104	0.997849	3.05857
98	0.997849	3.05857
89	0.997849	3.05857
83	0.997849	3.05852
74	0.997849	3.05863
67	0.997849	3.05681
61	0.997849	3.06408
55	0.997849	3.04955
48	0.997848	3.0786
42	0.997815	2.96242