PHYTOREMEDIATION BY AROMATIC PLANTS TO REMOVE HEAVY METALS FROM CONTAMINATED SOIL: CASE STUDY OF TAIPING LANDFILL

by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABREVIATIONS

Abbreviation	*Description*
ANOVA	Analysis of Variance
As	Arsenic
BS	British Standard
Cd	Cadmium
CEC	Cation Exchange Capacity
Co	Cobalt
CPCB	Circumvents the Earth and is named as Troposphere
Cr	Chromium
CSBT	Concentration Soil Before Treatment
Cu	Copper
DTPA	Diethylenetriaminepentaacetic Acid
EC	Electrical Conductivity
EDTA	Ethylenediaminetetraacetic
EDTA	Ethylenediaminetetraacetic Acid
EPA	Environmental Protection Agency (USA)
Fe	Iron
HS	Humic Substances

Abbreviation	*Description*
ICP (OES)	Inductively Coupled Plasma/Optical Emission Spectrometry
Li	Lithium
LOF	Lack of Fit
Mn	Manganese
MTBE	Methyl Tertiary Butyl Ether
Ni	Nickel
NOM	Natural Organic Matter
NTA	Nitrilotriacetic Acid
OM	Organic Matter
PAHs	Polycyclic Aromatic Hydrocarbons
Pb	Lead
PCBs	Polychlorinated Biphenyls
PDA	Pyridinedicarboxylic Acid
PMCP	Percentage of Moved Concentration by Plants
TCE	Trichloroethylene
TNT	Trinitrotoluene
USDA	United States Department of Agriculture
V	Vanadium
WHO	World Health Organization
Zn	Zinc

PEMULIHAN PHYTO MENGGUNAKAN TANAMAN AROMATIK UNTUK PEMBUANGAN LOGAM BERAT DARIPADA TANAH TERCEMAR: KAJIAN KES KAMBUS TANAH TAIPING

ABSTRAK

Pencemaran logam berat adalah kejadian yang meluas yang menyebabkan pelbagai masalah persekitaran. Isu ini perlu di ambil kkira untuk memastikan persekitaran yang selamat dan bersih. Penggunaan spesies tanaman untuk mengeluarkan pencemaran daripada tanah selalunya ditakrifkan sebagai pemulihan phyto. Pemulihan phyto adalah endah alam sekitar dan teknologi muncul yang membersihkan tanah dan air dengan takat yang meluas. Mengikut penyelidikan terkini, selain daripada tanaman makanan, dengan menanam spesies aromatik boleh dilaksanakan. Keluaran akhir adalah bebas daripada logam-logam berat dan tanaman aromatic boleh dipertimbangkan sebagai pilihan yang baik untuk pemulihan phyto.

Kajian ini menilai potensi penggunaan Thyme (Thymus vulgaris), Selasih (Ocimum basilicum or Sweet basil), Marjoram (Origanum majorana), and Gelang Pasir (Portulaca oleracea) untuk pemulihan phyto untuk logam berat As, Co, Cr, Cu, Li, Mn, Ni, Pb, V, dan Zn. Biji ditanam dalam enam pasu media tumbuhan, termasuk SN1, SN4, SN8, NN1, NN2, and NN4, dengan tahap masing-masing dalam reka bentuk blok tak lengkap terawak dengan tiga replikasi. Selepas 60 hari, tanah dan pokok Thyme, Selasih, Marjoram and Gelang Pasir dikumpulkan dan disiasat untuk logam berat daripada enam pasu tanah daripada tanah timbus dan sekelilingnya. Logam berat tersebut telah diekstrak daripada sample dengan menggunakan kaedah cerna asid dan dianalisa melalui plasma berganding (secara) aruhan (PKA)-pancaran optik spectrometer. Kajian pada ciri-ciri tanah menunjukkan pengambilan logam berat tumbuhan tanaman bolah menjadi kaedah yang

berkelebihan dan praktikal. Kajiselidik di tapak tanah timbus menunjukkan tanah tersebut tercemar dengan As. Cr. Cu, Li. Mn. Ni. Pb. V. dan Zn. Tahap pencemaran melebihi had yang dibenarkan. Selepas menuai semua empat tanaman, analisa menunjukkan pengambilan maksima berlaku untuk pencemar Zn dan minima untuk pencemar Cu. Untuk spesies tumbuhan tanaman. logam terkumpul khususnya dalam akar, kecuali untuk Mn dan Zn, yang terkumpul dalam tunas. Bukti yang diperolehi daripada ujikaji menunjukkan yang semua empat species adalah pengumpul yang efektif dalam pemulihan phyto tanah tercemar untuk Zn dan Mn kerana faktor translokasi (TF) yang melebihi 1. Logam berat tidak terhantar kedalam minyak pati semasa proses sulingan stim; iaitu minyak tersebut bebas daripada logam. Tahap logam minyak pati boleh di abaikan.

Satu perbandingan peratusan kepekatan penyingkiran logam dalam tanah menunjukkan penumpuk Thyme mempunyai tahap-tahap berikut untuk logam berikut; Li .As dan V .Co . dan Ni .Kajian ini juga menunjukkan yang Selasih adalah efektif dalam pemulihan phyto untuk As daripada enam olahan (61%). Marjoram menunjukkan pengambilan efektif untuk keseluruhan logam berat. iaitu as Li. Mn. Cu. Gelang Pasir adalah pilihan yang baik sebagai pengambilan Li ,Cu , Cr , dan Mn. Secara ringkasnya. Marjoram dan Gelang Pasir menunjukkan ruang penerimaan pelbagai logam surih.

PHYTOREMEDIATION BY AROMATIC PLANTS TO REMOVE HEAVY METALS FROM CONTAMINATED SOIL: CASE STUDY OF TAIPING LANDFILL

ABSTRACT

Heavy metal pollution is a widespread occurrence that causes serious environmental problems. This issue has to be addressed to ensure a safe and clean environment. The use of plant species to remove contaminants from soils is generally described as phytoremediation. Phytoremediation is an environment-friendly and emerging technology that purges contaminated soil and water to a large extent. According to current research, instead of growing edible crops, growing certain aromatic species is feasible. The final product is free from heavy metals so that such aromatic crops are considered to be an excellent choice for phytoremediation.

This study evaluates the potential application of Thymus vulgaris, sweet basil, Origanum majorana, and Portulaca oleracea in the phytoremediation of As, Co, Cr, Cu, Li, Mn, Ni, Pb, V, and Zn. Seeds were planted in six different growth media pots, including SN1, SN4, SN8, NN1, NN2, and NN4, their levels in a completely randomized block design with three replications. After 60 days, the soil and plants of Thymus vulgaris, sweet basil, Origanum majorana, and Portulaca oleracea were gathered and investigated for metals of six soil samples from the Taiping landfill and its vicinity. The heavy metals were extracted from the samples using the acid digestion method and were analysed through an inductively coupled plasma-optical emission spectrometer. Studies on soil properties show that the heavy-metal uptake of the cultivated plants promises to be an advantageous and practical technique.

The survey of the landfill site showed that the soil was contaminated with As,

Cr, Cu, Li, , Ni, Pb, and Zn. The levels of contamination were above acceptable standards. After harvesting all four plants, analysis shows that the maximum uptake occurred for the Zn contaminants and the minimum uptake for the Co contaminants. In the cultivated plant species, metals primarily accumulated in the roots, except for Mn and Zn, which accumulated significantly in the shoots. The evidence provided by this experiment indicated that all four plant species are effective accumulators in the phytoremediation of Zn- and Mn-polluted soils because their translocation factor (TF) was greater than 1. Heavy metals are not transmitted into the essential oils during the process of steam distillation; that is, the oils were free of metals. The levels of metals in essential oil were negligible.

A comparison of the concentration percentage of metal removal in the soils shows that the Thymus vulgaris had maximum uptake in the following metals: Li As and V ,Co , and Ni, study evidently shows that sweet basil was very effective in the phytoextraction of As from six treatments. Origanum majorana exhibited an effective uptake of most heavy metals, such as Li, Mn and Cu. Portulaca oleracea was a good choice as an accumulator of Li, Cu, Cr, and Mn. Briefly, Origanum majorana and Portulaca oleracea offer region discovered of multi trace metals.

CHAPTER 1

INTRODUCTION

1.1 Background

The importance to the environment has also increased significantly due the world growing population. One of the effects is the excessive use of pollutants in the agricultural sector where pesticides with different chemical composition such as lead, arsenic, calcium, arsenate and copper sulfate is used to control disease fungus and arthropods (Malakuti, 1996). In addition, previous problems are enhanced by the incremental growth of sewage sludge which includes too much organic and inorganic contaminated substance in the agriculture (Kabata- Pendias and Pendias, 2000).

In Malaysia, studies were carried out at waste disposal sites such as Pulau Burung, Gemencheh and Taiping demonstrated decreased- groundwater quality because of the leachate leaking into the groundwater system. One of the practicable methods to modify this matter improves of natural soil as a barrier to sequence minimizing of migration of pollutant into the ground water (Samuding, 2010).

One method is the use of plants for the pollution load reduction, filtration, consolidation and control polluted environment. The aim of phytotechnology is the absorb pollution or its control by plants. Phytoremediation is a collection of techniques that utilizes plants for eliminating contamination of soil, sludge, groundwater and surface water (Kazemzade and Noori, 2012).

Currently, phytoremediation is a widespread green technology which is an interchangeable process for cleaning the contaminated soil and wastewater it is an effective cost, environment-friendly and aesthetically pleasing temper and executable equal for the removal of both organic and inorganic contamination stocks of soil, water and air (Bruce et al., 2007). Thus, phytoremediation is compatible with nature and environmentally sustainable which can be introduced as a convenient method.

Aromatic and medicinal plants commonly used in the food, confectionery, condiment, soap, mouthwash, and other industries. The essential oils generated from the aromatic plants by the process of distillation, or extraction with suitable organic solvents show a complex mixture of several compounds. The world production of essential oils is growing at more than 10 percent annually and at present it is estimated at about 1,100,000 tons valued at over 11 billion US dollars (Sheela et al., 2008).

This research is aimed to investigate the effects of the four aromatic and medicinal plants i.e Thymus vulgaris, Ocimum basilicum, Origanum majorana and Portulaca oleracea, on the heavy metal uptake in the polluted soil. These plants were selected due to their essential oil which is end product have not been contaminated with heavy metal, Zeljazkov et al., (2006) said *"some of these species are able to grow in metal contaminated sites without significant yield reduction"*.

1.2 Problem statement

The major metals are classified as the almost hazardous materials for that biota in the environment as a result of high toxicity and constancy (Alkorta, 2004). The heavy metals have a tendency to adsorb quite tightly towards soil matrix, as soon as introduced to the environment; it won't reduce like organics simply by microbial task or perhaps via chemical oxidation (Beiergrohslein, 1998). Individual action including: smelting, exploration, electroplating, etc. could lead to toxic metals contamination connected with soil. A study by EPA (1984) concluded heavy metals were the most popular pollutant in the 395 therapeutic practice webs in the US.

Smith (1981) found that when a trace metal is added to the soil, it may attract on soil particle, precipitated as an unsolvable compound, leached to lower depths in the soil profile, lost to the atmosphere, metabolized by soil fauna or microbes and absorbed by plant roots.

Phytoremediation can be an expanding technique which makes use of plants as well as their own associated microbes to the remediation regarding to contaminants. This will be economical with no developing disorder on the landscape (Itanna and Coulman, 2003). From studies on different type of soils shows heavy metal concentration in soils are increasing especially lead and cadmium (Rahmani, 1995; Agusa et al., 2004; Amini et al., 2004; Diagomanolin et al., 2004; Pais and Benton, 1997).

Persistence and high mobility of some heavy metals cause to enter environmental risk factors to solution phase and soil available phase that are absorbed by the plants. The production of heavy metals in the plant and food chain are endangering human health animal and poultry (Fattahi- Kiasari, 2007; Gallego et al., 1996). Cunningham and Ow, (1996) said *"Heavy metals do not degrade and are generally persistent in the environment"*. Some factors like EDTA (Ethylenediaminetetraacetic Acid) and DTPA (Diethylenetriaminepentaacetic Acid) in detergents such as soap and powder can cause to increase heavy metal solubility and dissolvent in soil (Sorvari and Sillanpa, 1996). Cadmium has high dynamism in soil and intense toxicity potential in organisms so it is considerably in low concentration (Das et al., 1997).

Lead is one of the heavy metals that these days despite of its reduction in the environment it is estimated the accumulation is twenty times more than its outgoing rate in soil (Fattahi- Kiasari, 2007). Particularly this issue is significant in soils which is low cation exchange capacity has a great importance (Zhu et al., 2004). Lead can cause soil pollution in different ways enter in the atmosphere and by precipitation (Rahmani, 1995). A lot of this element enters into the human and animal food chain via the use of pesticide, mining, refinery material, car Battery (Rahmani, 1995; Malakuti 1996; Kalbasi et al., 1995; Shen et al., 2002).

Vast regions of the earth are polluted with organic and inorganic contaminants. Organic contaminants usually are mainly anthropogenic with origin and therefore are released in to the environment via solvent in addition to fuel spills, agriculture activities, armed forces operations, in addition to manufacturing activities. Organic contaminates have been included solvents, like trichloroethylene (TCE), a typical ground-water contaminate' (Newman et al., 1997); herbicides like atrazine (Burken and Schnoor, 1997); combustible material like trinitrotoluene (TNT) (Hughes et al., 1997); hydrocarbons like petrol, benzene, oil, gasoline, toluene, in addition to polycyclic aromatic hydrocarbons (PAHs) (Schnoor et al, 1995; Aprill and Sims, 1990); energy resource chemicals for instance methyl tertiary butyl ether (MTBE) (Hong et al., 2001); and also polychlorinated biphenyls (PCBs) (Harms et al., 2003). Dushenkov (2003) mentioned "*inorganic pollutants, on the other hand, occur as natural elements in the Earth's crust. Inorganic pollutants can be planted micronutrients such as nitrates and phosphates, micronutrients such as Cr, Cu, Fe, Mn, Mo, Ni and Zn, nonessential elements such as As, Cd, Co, Hg, Se, Pb, V, and W, and radionuclides such as 238U, 137Cs, and 90Sr*".

The waste disposal sites or landfills are main sources of releasing large amounts of organic and inorganic pollution via leachate (Tedza, 2001). In humid and semi-humid region, leachate is produced primarily in association with precipitation that infiltrate through the residue in landfill. Contamination of leachate generation at the landfill site will normally result in the migration of the leachate plume into the soil and underlying groundwater zone and pollute them. A diversity of heavy metals are mostly found in landfill leachate, including iron, zinc, copper, cadmium, lead, nickel, chromium and mercury. These metals are either soluble components of the refuse or are products of physical processes such as corrosion. In several instances, heavy metal concentration in leachate increased by time because they are non–biodegradable and they can be accumulated in living tissues and causing various diseases and disorders (Samuding, 2010).

1.3 Objectives

The main objectives of this study are as follows;

1- To evaluate the heavy metal concentration in soil samples of the selected area (Taiping landfill), also determine some physicochemical characteristic of local soil.

2- To determinate the concentration of heavy metals in treated soil after cultivation and elements study to compare the result before and after treatment.

3- To survey plants for heavy metal concentration and consider metals in different parts of plant to find efficiency of phytoremediation.

4- To determine the heavy metals in essential oil as final production of these herbs.

1.4 Scope of study

The scope of this study is focused on the aromatic plant application for lessening the heavy metal pollution in soil and is described in short below:

i) Some species of aromatic plants selected for this study such as Thymus vulgaris. Ocimum basilicum. Origanum majorana and Portulaca oleracea

ii) Collection of polluted soil samples in different distance within the Taiping landfill site.

iii) Soil samples were analysed for their heavy metal content using the ICP-OES which examines 21 elements according to standard solution and to determine basic characteristic of the soil samples. Chemical and physical properties of soil were determined before the treatment.

iv) After treatment soil samples analyzed for metals concentration and also plant tested for determine of metals pollution in different parts with ICP-OES.

1.5 Outline of thesis

This thesis is comprised of five chapters as follows;

Chapter 1, Introduction: introduces the background of the study, problem description, hypothesis statement, list of objectives and scope of the research.

Chapter 2, Literature Review: describes the importance of heavy metal study and brief overview of heavy metal characterization and their entrance to the environment. effective factors to adsorption the heavy metal by plant. some approach as against heavy metal problems and distribution and migration of heavy metal in diverse parts of the plant. Phytoremediation is described which decontamination of soil focus on aromatic plants for treatment and their availability and capability to attract the heavy metal with the advantage of free from pollution in essential oil. In this chapter a short review on ICP-OES is described.

Chapter 3. Material and Methods: describe the field techniques. laboratory experimental program and equipment which are used in this study. Field sampling involved the collection of soil in various spots. Cultivation and growth stages describe totally. All methods to characterize the samples were also presented in this part.

Chapter 4, Result and Discussion: discuss analytical data from experimental work. The investigation and examination of soil samples for heavy metal amount is presented. The physiochemical characteristics of samples are investigated. The soil samples for detection of heavy metal concentration are measured again after treatment. All types plant's tissues in root and shoot parts are determined for absorption of heavy metal pollution in various soils and discussed. All graphs and curves also table of obtaining data, are plotted and discussed.

Chapter 5, Conclusion and Recommendation: describe the conclusion of the findings of the research. Future work is recommended at the end of the chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter is written into three sections. The first section describes the general information of heavy metals, including their presence and importance in the environment and their impact on plants. Furthermore, the detailed information and explanation of targeted heavy metals is mentioned. The second section consists overview of phytoremediation, and investigation of plants effect to minimize the pollution in the soil. The final section reviews aromatic plant species features as adsorbent of contaminated soils and describes their efficiency in reduction of metal concentration.

2.2 Preface of heavy metals

Heavy metals are defined as elements in which the density of elemental form is greater than 5 g/cm^3, (Pais and Benton, 1997; Cameron, 1992). They consist of 38 elements however, in common terminology, they are referred to 12 metals of most generally used and discharged as wastes by industry, cadmium, cobalt, copper, chromium molybdenum, nickel, lead, manganese, tin, iron, mercury and zinc (Adriano, 1988).

Those that may pose the highest potential hazards to humans, animals or plants such as cadmium, lead, copper, mercury, nickel and zinc are discussed in detail here. Knowledge on the metal/metalloid sources is very beneficial in identifying and distinguishing possible perilous site and soil (and also subsurface and groundwater) pollutions, their behavior and migration (Cameron, 1992).

2.3 Importance of heavy metal pollution study

There has been a growing concern in matter of the accumulation of toxic heavy metals in surrounding environment and their impact on both natural environment and public health (Gardea-Torresdey et al., 2004). The significant problem has caused by accumulation of heavy metals in soil is the result of agricultural and industrial practices. Fertilizers from sewage sludge, paper mills and mining waste all chip in to the continuous deposition of heavy metals into soils. Leaching on these contaminated sites has a lot of effect where it is the movement contaminated in to the ground water (Gratao et al., 2005). Live organisms require a trace value of some heavy metals like iron (Fe), copper (Cu), nickel (Ni) and zinc (Zn) and are often mentioned as essential elements (Odjegba and Fasidi, 2004). However, there are some non-essential heavy metals which are of great concern due to their presence in areas of heavy metal pollution such as chromium (Cr), lead (Pb) and mercury (Hg) (Kamal et al., 2004). Due to the damaging nature of heavy metals, the plants valence to concentrate metals has usually been investigated since some plants are directly or indirectly accountable for the amount of dietary uptake of toxic heavy metals by humans (Chaney et al., 1997; Cunningham et al., 1995). The dietary of heavy metals via consumption of polluted crop plants could long term impact on human health (Ow, 1996).

In soils, metals should be observed separately or attached to soil components. This comprises the forms listed below (Blaylock and Huang, 2000);

1. Totally free metal ions as well as soluble metal compositions inside soil solution.
2. Exchangeable ions absorbed into inorganic firm category surfaces.
3. Nonexchangeable ions as well as insoluble or precipitated inorganic metal compositions.

4. Farraginous material by soluble or insoluble natural and organic materials.
5. Metals shut in silicate products.

Propagation of metals in soil profiles is basically governed by number of factors such as containing the solubility of metals, trait of soils, and other environmental conditions in undistributed soils. Natural and undisturbed soils permit the percolation of water, permeated water serves as a vertical resort for the very small amount metal pollutant; metal-adsorbed particulates (and dissolved metals) transported by water and travel along the soil section, while being snared in different layers (Hernandez et al., 2003).

2.4 Heavy metals entrance to environment

Nowadays, there is a great concern of amounts of heavy metal in intact soil, soils affected different fertilizers and consecutive cultivation. Most of these changes resulted from sewage sludge enhancement to agricultural land (Rahmani, 1995).

A number of studies have shown that sewage sludge contains high concentration levels of Lead, Zinc and Cadmium (Pulford and Watson, 2003).

An evaluation between the concentration of metals in landfill and agricultural soil were studied where it was found that a landfill represents higher contamination risk to soil than agricultural and industrial activities (Samuding, 2010). Trace metals from urban sources are initially released through atmospheric emissions (Wong et al., 2003). Upon emission, the heavy metals tend to adhere to particulate matter to form fine particulates and dust (Vesper and White, 2003).

The supply of heavy metals in the environment are (i) from the industrial and urban aerosols, which are made from metal ore refining and fuel ignition, and other industrial operation; (ii) liquid and solid wastes of humans and animals; (iii) mining wastes; and (iv) industrial and agricultural chemicals (Cameron, 1992). Other causes of uptake by the plants are rainfall, atmospheric dusts, plant conservation factor and fertilizers, which are adsorbed through the leaf septum. Since the industrial impurity of agricultural lands and forests is becoming an intensive ecological obstacle, detection of toxic elements in medicinal and aromatic plants, have received many attentions (Abu- Darwish, 2009).

Atlabachew et al (2011) investigated heavy metal absorption and aggregation in plants, to include, heavy metal accumulation in soil, severity and combination of atmospheric deposition, consisting rainfall, phase of plant vegetation. Other similarities such as waste water irrigation demand of pesticides or impact of organic and mineral fertilizers containing heavy metals, which were obtained by agricultural technologies (Mojiri and Abdul Aziz, 2011).

Disparate plant growth and soil cover caused by heavy metal toxicity navigate to metal mobilization in runoff and further deposition into close to water. In addition, bare soils are more susceptible to erosion and deploy of contamination by airborne dust. In such situations the goal of immediate remediation modifies the location by fixing vegetative cover to minimize the erosion and extension of pollution (Lasat, 2000).

Heavy metal contamination of soil poses a major threat to human health and the environment. Toxic heavy metal contamination is widespread within the surface soils at mining and industrial sites (Huang et al., 1997). Heavy metal pollution is a prevalent problem within all industrially developed countries of the world. Past waste disposal practices associated with mining and manufacturing activities have been such that air, soil, and water contamination were common, and as a result there are many metal contaminated sites that pose serious health risks (Roane et al., 1997).

2.4.1 Air pollution

Nearly 95% of the earth's atmosphere occurs in an 8-12 km layer that circumvents the earth and is named as troposphere (CPCB, 1995). Modern industrial society produces dangerous quantities of gases and particles in human, plant and animal life. Under the process of industrialization, events like expansion in cities, traffic growth, rapid economic developments and an increase in energy consumption cause air pollution (Shilpa et al., 2006).

Smith (1981) studied that "*An appropriate definition of air pollutants is materials that occur in the troposphere in quantities in excess of normal amounts. These materials may be solid, liquid, and gaseous in character and they may result from both natural and human (anthropogenic) processes*". Some main causes of air pollution are population, industries, transmission, vehicle population, fuel (natural gas, gasoline and diesel), exhaust emissions, natural sources and etc.Natural sources of air pollution are varied and include volcanic and other geothermal outbursts, fires occur in forests, gases released from vegetation, wind-blown soil and other pieces, pollen, spores, and sea sprinkle particles (Shilpa et al., 2006). Air pollutants efficacy on human health are as follows. Contaminant affecting respiratory system: among the excessively large number of substances in the surrounding air, the major pollutants are nitrogen oxides, ozone and other photochemical oxidants, also Sulphur dioxide and particulate matter. Table 2.1 shows trace metals that may pose health hazards and described below;

1. People sensitive to these conditions have respiratory diseases like asthma, bronchitis, emphysema and heart problems.
2. Pollutants bringing toxic systemic effects: carbon monoxide, lead.
3. Pollutants entail potential carcinogenic effects: polycyclic aromatic

hydrocarbons (PAH is the group of chemicals emitted during the incomplete combustion of fuel), benzene, aldehydes.

4. Materials and cultural heritage affected by air pollution (Shilpa *et al.*, 2006).

Table 2.1: Trace metals that may pose health hazards (Sindhu, 2002)

Element	Atomic No.	Source	Health effect
Boron	5	Coal, cleaning agents, medicinal, glass making and other industry	Micronutrient to plant excess toxic to plants, slightly toxic to animals
Nickel	28	Fuel oil, coal, tobacco smoke, chemicals and catalysts, steel and nonferrous alloys	Lung cancer
Copper	29	Waste pipes, algae control industrial Smoke	Possible liver damage with prolonged exposure ,toxic to plant
Zinc	30	Metal plating, mining, industrial smoke	Possible lung effects, low toxicity in solution
Cadmium	48	Coal, zinc mining, water mains pipes, tobacco smoke	Cardiovascular disease and hypertension in humans
Mercury	80	Coal, electrical batteries and industries	Nerve damage and fatality
Lead	82	Auto exhaust, paints and in water through Lead joint of pipes.	Brain damage, convulsions behavioral disorder, fatality

2.5 Heavy metals description

Specific contaminants of interest are discussed in detail.

2.5.1 Lead

Lead (Pb) is the major contaminant of soil. Lead is adsorbed by roots: containment arises through the plasma membrane, probably involving cationic channels such as calcium channels. Lead adsorption is adjusted by types of plant species, PH, organic matter content cation exchange capacity of soil, as well as transudation and physicochemical parameters (Kibria et al., 2010). Lead continues to be widely used, especially in developing countries; for instance in petrol, television sets, paints, cabling, pigments, ceramics ammunition, computers, protective gear, cosmetics, and many other ways (Fattahi- Kiasari, 2007). Children are at peril of exposure to environmental lead (Landrigan, 1999). Hand-to-mouth activity as part of normal play and grow, constitutes the major direction of childhood exposure to lead rich dust and soil. Even at relatively low concentrations, lead has been shown to participate in human biochemical passages, causing wide-various health effects. At exceedingly high levels of exposure, cerebral edema, coma, ataxia, paralysis and death may result (Needleman and Bellinger, 1991). It has been reported that a few plant types absorb lead in high concentrations in above ground parts; these plants were named as hyperaccumulators (Kumar et al., 1995; Brooks, 1998; Huang et al., 1997; Barlow et al., 2000; Leung and Jarvis, 2002).

2.5.2 **Arsenic**

Studies have shown that arsenic sets a hazardous threat to environmental and human health universally, this heavy metal enter food chain via plant sorption from soils contaminated by activities like mining or polluted irrigation water (Williams et al., 2006).

Natural sources of As consist soil and rock erosion, resolution of minerals and ores, eruptive and biological activities. Anthropogenic resources include municipal waste incineration, oil and coal ignited power plant, non-ferrous metals smelting, cement function, pesticides and herbicides and alloy making lead and copper, (Minganti et al., 2004). The major origins of food chain's arsenic contamination surface water, groundwater and drinking water, sully soils, sediments and sludge

(Frankenberger and Arshad, 2002). Other practical sources of As contamination contain the chemicals used widely in agriculture as pesticides, insecticides, defoliants, wood maintainer, and soil disinfection (Nriagu and Azcue, 1994). Available methods for As polluted soil amend are costly, take time, unsafe for employee, and develop extra waste items (Lombi et al., 2000). Arsenic hyper accumulators are often capable to uptake high levels of arsenic, even in low measure arsenic soils (Ma et al., 2001; Chen et al., 2005; Tu et al., 2002).

2.5.3 Nickel

Nickel (Ni) is one of the toxic heavy metals, and is discussed due to its negative effects on the environment where it bio accumulates and poses a serious threat to human and environmental health. Nickel treatment requires converting toxic nickel ions (Ni^{2+}) into less toxic chemical forms. The aim of such treatment is to decrease the toxicity of Nickel in human health and environment. Phytoremediation is an emerging green technology that bands the plant eco-physiology arrangement, microbiology and chemistry of soil to clean up Ni-polluted soils (Ackmez and Zhi, 2012).

In non- polluted soils, Nickel concentration is between 5-50 mg kg^{-1}, and 0.4-3 mg. Kg^{-1} in the plants (Motesharezadeh and Savaghebi, 2011).

Naturally derived soils from serpentine rocks are rich in Ni; however, different industrial and anthropogenic activities such as mining, refining of Ni ores, burning of fossil fuels and residual oil and sewage sludge other areas conclude in Ni contamination (Nriagu, 1988). Ni disposal cause immutable injury to main nervous system, heart, gastrointestinal tract and lungs (Axtell et al., 2003). Nickel has been categorized one of the necessary micronutrients; hence it is poisonous for raised condensation in plants (Srivastava et al., 2005). Species, such as

Hybanthusfloribundus, A. Bertoloni, Seneciocoronatus, Thlaspimontanum variety of Siskiyouense, Alyssum species are known to hyperaccumulate nickel. These species can potentially be used to treat Ni-contaminated soils (Martens and Boyd, 2002; Leon et al., 2005).

The findings of Mojiri and Abdul Aziz (2013) noted that the Lepidiumsativum is an impressive accumulator plant for phytoremediation of Ni polluted soils. They showed that an optimum condition for removing Ni was 10.8095 mg /Kg

Brassica juncea resulted as ahyperaccumulator of Ni, due to the translocation factor (concentration of aerial part per root's concentration >1) (Panwar et al., 2002).

2.5.4 **Chromium**

There are different industrial uses of Chromium (Cr) and its compounds, in production of resistant steel, electroplating cleaning agents and in output of specialized chemicals and chronic acid. These anthropogenic activities have directed to prevalent contamination that Cr observes in environment and have augmented its bioavailability and bio mobility (Kimbrough et al., 1999). The constant forms of Cr are trivalent Cr (III) and hexavalent Cr (VI) species. However, there is diverse valence conditions which are impermanent and short lived in biological strings. Chromium toxicity perceived at varying levels, from reduced yield, leaf and root growth prevention, deterrence on enzymatic activities and mutagenesis (Salt et al., 1994; Zavoda et al., 2001). Elevated levels of Cr in soil cause retardation of growth, roots detriment, diminish of yield and barricade fertility (Sharma et al., 2003).

2.5.5 **Zinc**

Zinc (Zn) is principal founding between micronutrients for plants and animals. However, zinc is toxic if it exceeds the sufficient level. The total Zn in the natural soil is 10-300 ppm (Lindsay, 1979; Tisdale, 1985). The discovered Zinc containing minerals composition are sulphide (ZnS), carbonate ($ZnCO_3$) (Smithsonite). ZnF_2O_4 (Franklinite). $ZnSO_4$ (Zincosite) and silicate Zn $(OH)_2Si_2O_7$, H_2O (Lindsay. 1979). Zn is considered as impure for Mn and Fe oxides where these minerals have wide surface area sand make the heavy metals more movable compared to silicates. Therefore Zn plays an important role in holding and safeguarding trace elements (Alloway. 1990). In Zn soil solutions. Zn quantity depends on basic parent materials and specific minerals which verify Zn solubility and accessibility. The solubility and accessibility of Zn to plant depends on availability and severity of zinc concentration in the soil solution (Lindsay, 1979).

Attraction of Zn by soil's inorganic and organic compositions is very momentous for plant's nutrition. Zn moves in soil profile to the ground water (Agbenin and Olojo, 2004; Daviscarter and Shuman, 1993; Shuman, 1975). Zn in low organic matter is more impressive in reference to high organic matter (Jahiruddin et al., 1992). Furthermore, Al and Fe oxides improve Zn adsorption (Dang et al., 1994).

Zn interplay with organic matter function in two different ways. In one way, organic matters causes more availability of Zn to the plant, while the second way blocks it strongly and reduces availability to the plant and prevent transudation to the ground water. The binding potency of organic matter (Humus) to heavy metals is in this line Cu >Ca> Mg > Zn (Zunino and Martin, 1977a; Zunino and Martin. 1977b). Other cations in soil solution such as Cd. Cu. Mg and Ca effectively corrival with Zn for sorption and accordingly affect its mobility (Agbenin and Olojo, 2004; Christensen, 1984; Elzinga et al., 1999; Harter, 1992; Voegelin et al., 2001).

2.6 Availability of heavy metals

Metals bioavailability associated in plants are usually affected of several components such as soil and vegetable specification, and different environmental components. The principle soil traits include pH, organic matter content, clay content, cation exchange capacity and presence of hydrous oxides of iron and manganese, phosphate content, soil particle size, redox potential. Irrigation, climatic status, fertilizing replication usually is samples of environmental factors. Plant character, plant age also affects metal absorption (McIntyre, 2003). The metal increase absorption base by plant pertain the concentration of the dissolved and bioavailable proportion of metal in soil solution. This bioavailable proportion in the soil is usually appointed from the Bioavailable Sequential Extraction (PBASE) procedure (Basta and Gradwohl, 2000). Aged soils are stricter to phytoremediate as in an unclean soil; the particular condensation of bioavailable contaminant have a tendency to decrease after time due to chemical, physical and biological operations (Pilon-Smits, 2005). To improve metal solubility in soil solution, artificial chelates such as ethylenediaminetetraacetic (EDTA), nitrilotriacetic acid (NTA), 2,6-Pyridinedicarboxylic acid (PDA), citric acid, nitric acid, hydrochloric acid and fluorosilicic acid in phytoremediation can be useful (Romkens et al., 2002). For degrading phytotoxic level concentration in soil, adding lime or organic matter is beneficial determination to reduce metal solubility (Pilon-Smits, 2005).

The transmission of metals from soil (solid phase) to plant tops, follows five steps shown in Figure 2.1 and discussed (McBride, 1994).

a) Adsorption or dissolution, which related to the solubility of the elements and easiness of desorption.
b) Diffusion and convection, the transmission by diffusion is very slow due to

low concentrations of elements in soil solution, which is very common. For non-trace elements also convection is very important. Evapotranspiration runs the transfer of water from the soil to the plants through the roots.

c) Sorption or settlement, after diffusion and convection, maybe reabsorbed or precipitated by humus and clays before reaching to the roots, which can enormously limit the motion of certain elements. Beside, Cd^{2+} move quickly through the soil matrix because it joins to adsorb in exchangeable form.

d) Passive or active absorption by the roots depends on concentration of the soil solution of that particular metal. Also the rhizosphere of the plant improves the soil solution by exudates and stick to microorganisms.

e) Translocation in plant, the process of metals translocation from root to upper part of plant is beyond soil solution pool, for instance, Cd, Pb and Cu collect in or on roots (McBride, 1994).

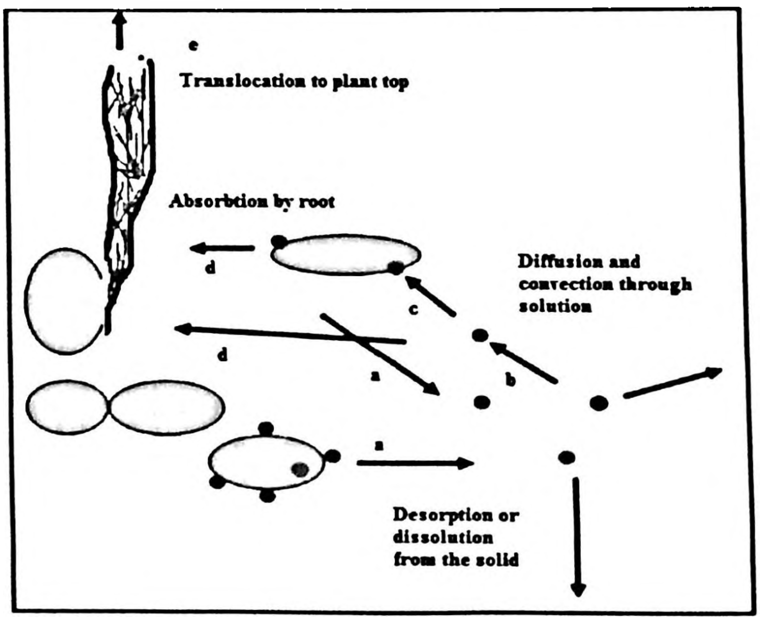

Figure 2.1: Illustrates the five steps for metal to move from soil metal to plants (Modified from environmental chemistry of soils, McBride, 1994)

Heavy metal availability in soil is affected by pH organic matter content, redox conditions, clay type and content, and root exudates (Alloway, 1990). Redox potential and pH execute a principal role in their movement and accessibility (Conkling et al., 1991; Gillespie and Pope, 1990).

2.7 Effective factors in heavy metal absorption by plant

Heavy metal uptake by plants is a complicated process, governed by the numerous factors affecting each other, such as genotype, plant species, availability and mobility of the metals in soil, and soil traits including pH, electrical conductivity (EC), cation exchange capacity (CEC), organic matter and clay content. Influence of soil properties on heavy metal uptake could be very beneficial information when a choice of growing location or possible agro techniques is issued for tillage of these plants (Zheljazkov et al., 1999).

2.7.1 Terrestrial environment

Among terrestrial factors influence of capture and storage of heavy metals in soil can mention some operator like pH, organic matters, cation exchange capacity (CEC), electrical conductivity (EC), iron oxides and hydroxides and inorganic (Amini et al., 2004; Cui et al., 2004 ; Adhikari and Singh, 2003).

2.7.2 pH

Increased pH reduces the solubility of heavy metals like Zn, Cd, Ni and Cu in soil. However, the risk of possible exposure to plants is decreased, when their concentration stays unchanged. Soil pH is an initial parameter for determination of availability of elements in plants concerning heavy metals (Krebs et al., 1998).

Physiochemical characteristics in both soil and soil solution recognize the balance of metals between solid phases and solution. The pH affects extensively metals concentration in soil solution (Adriano, 2001) and has influence on organic and inorganic anions nature (Harter and Naidu, 1995). Values of pH >6 can decrease free metal ion activities in soils due to augment in pH-dependent surface charge on oxides of Mn, Fe, Al,organic matter chelation or sedimentation of metal hydroxides. Heavy metal adsorption by soil is in relation with pH, as result of the surface chemistry of solid materials. Sediments and soils have a PH-dependent or changeable charge associated with reaction of protons, oxide and hydroxide minerals moreover, they are in association with determined functional groups of humic substances (Evans, 1989; Sposito, 1984).

Humic substances (HS) are major incorporation of the natural organic matter (NOM) in soil and water; and in geological organic residuals of brown coals peats, lake sediments, and shale. Humic substances are necessary components of soil that progress soil fertility and affect physical and chemical properties (International Humic Substances Society, 2007).

This dependency of different metals is indeterminate; for example, Cu and Pb are affected irregularly by PH change, while Zn correlates regularly. When pH increases, availability of the Zn decreases (Tyler and Olsson, 2001).An increase in PH (basic range) results in reduction of Pb, Cd and Zn uptake by plants and an increase in absorption of Zn, Cu and Cd into soil particles (Kuo et al., 1985). Conversely, lower pH results in an increase of metal absorption by plants and reduction of metal adsorption in soil (Brown et al., 1994). Therefore, soil pH affects not only metal bioavailability but also amplifies metal uptake of roots. This effect could be metal specific. For Thlaspi caerulescens Zn uptake by root was not dependence of pH whereas, taking up of Cd and Mn by the roots was intensely dependent of soil acidity (Brown et al., 1995). Zinc preservation is positively correlated with PH (King, 1988).

2.7.3 **Organic matters**

Heavy metals can form both inorganic and organic complexes with a range of solutes in soils. Boekhold et al. (1993) found that establishment of inorganic anionic complexes reduces the adsorption of Cd^{2+} by soils. Naidu et al. (1994) indicated that forms a soluble complex of chloride with Cd^{2+}as $CdCl_2$ resulted in slight adsorption of Cd^{2+} on soil particles. In high pH, the carboxyl, phenolic, alcoholic and carbonyl functional groups in soil organic matter dissociate; thereby increased pH, increases affinity of ligand ions for metal cations to form complex compounds. The affinity of ligand to heavy metals to make a complex depends on the type of metal: for example the proximity for metal cations complexes with organic matter is in the following order: Cu^{2+}> Cd^{2+}> Fe^{2+}> Pb^{2+}> Ni^{2+}> Co^{2+}> Zn^{2+} (Adriano, 2001). A number of authors have described positive correlations between pH and copper retention (Tyler and McBride, 1982; King, 1988), and organic matter content (Hickey and Kittrick, 1984). Pb retention with clay content has better correlation (King, 1988). Such significant results were also observed in retention with pH (Jopony and Young, 1994). Some such significant results were also observed in retention with pH between metal adsorption and soil organic matter content (Harter, 1983). Researchers credited this lack of correlation to the fact that total organic matter of wide variety of soils may not be adequately related to their reactive portions to generate a positive correlation.

2.7.4 Electrical conductivity (EC)

Soil Electrical Conductivity (EC) is one of the soil physical properties which have a great connection with the other soil specification. Moral et al (2002) said a higher dependency of the value of Ni as well as Co extracted by chloride salts about the pH as well as salinity had been observed. Therefore, with lowering soil pH and increasing salinity, higher metal extraction proportions were obtained.

Data analysis showed that by increasing the electrical conductivity of irrigation water, the amount of Cd uptake in roots, stems and leaves increased. Therefore, the increase of the electrical conductivity cause to enhance removed- Cd of soil (Salimi, 2012).

2.7.5 Other operators

Root morphology could be mentioned as a main affective factor of heavy metal uptake by the plant if there were no differences between soils; the important factor in metal uptake is root morphology. Thin and numerous roots in comparison to the short and thick roots observe high level of Cd concentration (Das et al., 1997).

Restoration connected for polluted sites employing crops has become to apply although each sample and metal performs different plant. Speedy growth, excessive biomass, stiffness and forbearance to contaminant are some of the favorable plant attributes currently operate for remediation. Among plant uptakes, water and contaminants, plant-microbe interactions, enhanced microbial activity in the rhizosphere, fate and transport of contaminants in the plant root zone, further translocation, and tolerance mechanisms, are of paramount importance in improving phytoremediation technologies (Mellem, 2008).

2.8 Heavy metal distribution in different parts of plants

Chamomile was also able to accumulate significant amounts of Pb and Ni, mainly in the roots. The concentration of Pb in the flowers did not exceed the acceptable levels set by WHO (World Health Organization). In general, the same behavior was observed for chamomile in the presence of Ni; most of the accumulated Ni was stored in roots, whereas leaves and flowers showed lower Ni concentrations (Lydakis et al., 2012).

The accumulation of lead in thyme roots was comparable to that in chamomile roots, and was significantly higher in reference to sage roots. A much larger fraction of lead and nickel was found in the leaves; of course not as large as root concentration. The Pb concentrations used in the experiment (except control) resulted in Pb concentrations in the leaves, which were higher than the WHO levels (Lydakis et al., 2012). High concentrations of Zn were found of some leaves of Thlaspi caerulescens which is considered to be the best known hyper-accumulator (Cluis, 2004) and also finding of Brooks (1998) showed same results.

2.9 Bioremediation

Bioremediation actively enhances the effects of naturally occurring biological processes that degrade contaminants in soil, sediment, and groundwater. In-situ processes involve placement of amendments directly into contaminated media while ex-situ processes transfer the media for treatment at or near ground surface (EPA, 2010). The basic principles behind bioremediation are bioaccumulation, biosorption, and biocrystalisation. Bioremediation using plants are known as phytoremediation (Mathew, 2001).