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HEAVY METAL ACCUMULATION IN URBAN SOIL: A PHYTOEXTRACTION METHOD REVIEW

By

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Abstract:

Lead (Pb), cadmium (Cd), and arsenic (As) are three common non-essential heavy metals found in urban soils and can prove toxic to animals, humans, and some plants at low concentrations. The main exposure pathways of heavy metals in humans are through ingestion and inhalation of soil particles and ingestion of contaminated food. When dealing with contaminated soil in urban environments, activities like urban gardening can increase the likelihood of these exposure pathways, so heavy metal toxicity from contaminated soil can become a greater risk with the increased interest in urban agriculture. The US EPA created target concentrations for these heavy metals in residential soil, industrial soil, and agricultural soil. If any of these soils exceed their designated concentration, the US EPA has deemed them hazardous to both human health and the surrounding ecosystem. Phytoextraction is being considered and tested as a method to remove heavy metal pollution in urban soils. Two popular forms of phytoextraction are 1) using hyperaccumulator plants and 2) chelate-assisted phytoextraction using metal tolerant species. Hyperaccumulating plants can bioaccumulate 100 to 1000 times the heavy metal concentration of non-hyperaccumulators but have low biomass production/growth rates and are heavy metal specific. Chelate-assisted phytoextraction has higher a growth rate and biomass production, but can be expensive, has a stronger potential for heavy metal trophic transfer, and can lead to leaching of heavy metals off of the contaminated site. Phytoextraction using hyperaccumulating plant species may pose less risk and be suited for smaller sites with specific heavy metal pollution whereas chelate-assisted phytoextraction

may be a better approach for large sites with time sensitive phytoextraction needs, but because this method posed may risks, it needs to be highly monitored.

Introduction:

The accumulation of heavy metals in soil throughout the United States (US) is becoming a serious health concern. Heavy metal accumulation in soil can be an effect of different anthropogenic activities such as emissions from industrial areas, the use of leaded gasoline and paint, the use of fertilizers and pesticides, and waste disposal (Plyaskina and Ladonin 2007). Unlike other soil contaminants, heavy metals are not only toxic to animals in small quantities, but many of them do not degrade, so bioaccumulation can become a threat (Wuana and Okiemen 2011). Although heavy metal accumulation happens in soils throughout the US, the contamination of soils in urban areas is important to address due the high population density in these areas. According to the US Census Bureau, an urbanized area contains 50,000 people or more and in 2010 there were 486 different areas encompassing 71.2% of the US population (US Census Bureau 2016). Because urban areas have limited space and high population densities, certain heavy metals will accumulate in greater quantities due to human activity (Clark *et al* 2006). Three different exposure pathways in humans are through the ingestion of soil particles on hands or produce (children playing in soil, eating unwashed vegetation), the inhalation of soil particles (aggravating soil), and ingestion of contaminated grains and vegetables (Filippelli and Laidlaw 2010).

Urban Agriculture is a growing trend across the US because it offers and affordable way of eating heathy. According to the United States Census of Agriculture, there has been an increase of urban farms in the US between 2002 and 2007 (Rogus and Dimitri 2015) and because of this increase, there is a higher risk of exposure to contaminated soil. Urban gardening increases the risk of soil ingestion, soil inhalation, and contaminated vegetation ingestion, so its implementation on lots with high heavy metal accumulation is important to address.

Three common heavy metal/metalloids found in urban environments are lead (Pb), cadmium (Cd), and arsenic (As) which is actually a metalloid but herein is referenced as heavy metal. All three of these metals have a relatively high awareness because they are non-essential to the human metabolism and are dangerous in very low quantities. Pb is introduced into the soil mainly by emissions from leaded gasoline and the use of leaded paint; it is dangerous if inhaled or ingested and can lead to serious neurological disorders and even death (Filippelli and Laidlaw 2010). Cd is mainly introduced to the soil through petroleum products, battery waste, and fertilizers; is dangerous if ingested and can lead to metabolic disorders including kidney failure (Wuana and Okiemen 2011). As can be introduced to soil through fertilizers and coal combustion and it is dangerous if ingested leading to increased risks of cancer, circulatory problems, and death (Karimi *et al* 2013). Because exposure to these heavy metals can prove toxic for humans, target quantities have been established to classify soil conditions. The US EPA created the following minimum target levels to reach in remediation: for residential soil (Pb- 400 mg/kg soil, Cd- 70 mg/kg soil, and As- .68 mg/kg soil), for industrial soil (Pb- 800 mg/kg, Cd- 800 mg/kg, and As- 2.4 mg/kg), and for agricultural soil(70 mg/kg, Cd- 1.4 mg/kg, and As-12 mg/kg) (Anon C 2016).

There are many methods for soil remediation including physical methods such as extraction and biological methods such as phytoremediation. One of the most popular phytoremediation methods is called phytoextraction. Phytoextraction is a plant mediated uptake and translocation of contaminants from soil to above soil plant tissue (Liang *et al*. 2008).

In phytoextraction of heavy metals, the uptake of these heavy metals by plants is then paired with the harvesting of contaminated plant tissue as an attempt to eliminate further accumulation. Two types of phytoextraction are: 1) natural phytoextraction using hyperaccumulating plant species and 2) induced phytoextraction using metal tolerant plant species and soil chelating agents. Both types of phytoextraction have their pros and cons which need to be assessed before a remediation method is chosen for a specific site.

This report will discuss the main concerns of Pb, Cd, and As accumulation in urban soil, how people can come in contact contaminated, and the heavy metal pathways inside the human body. It will then discuss the two types of phytoextraction (the use of hyperaccumulators and the use of metal tolerant species with chelating agents) including their ability to affect the terrestrial food web and their likelihood of re-contaminating additional soil. The two alternative hypotheses addressed are:

HA1. The accumulation of one or more of three heavy metals: Lead, Cadmium and/or Arsenic, in soils in urban environments can lead to increased toxicity levels in people who come in contact with these soils.

HA2. When comparing chelate-assisted phytoextraction and hyperaccumulator phytoextraction, chelate-assisted phytoextraction presents a larger threat of off-site heavy metal transfer through soil leaching and trophic transfer.

Methods

Research of this report was done specifically through internet databases Michigan Technological University had access to from May 2016- July 2016. When searching for sources on the internet, the search engines that were uses included MTU Van Pelt Library Database Search, Google, and Google Scholar. The Databases used in this report were ProQuest SciTech Collection and Elsevier ScienceDirect journals. Any article that could not be found in these databases was accessed through a ILLiad (Interlibrary loan) at the MTU library. The types of resources used for this report were peer reviewed scholarly articles, government websites/published documents, and EPA websites/published documents.

Of the 74 sources used in this report, four of them were government sources, two of them were EPA sources, and 68 were peer-reviewed articles. From these peer-reviewed articles, five of them were review papers, and fifteen were used to obtain background information on the topic. Keywords used to find sources for this paper include the following:

For HA 1. “heavy metals”, “urban soil”, “lead”, “cadmium”, “arsenic”, “bioavailability”, “urban agriculture”, “exposure pathways”, “heavy metal toxicity”,

For HA2. “phytoremediation”, “phytoextraction “terrestrial bioaccumulation”, “chelating agent”, “hyperaccumulators”, “metal tolerant species”, “trophic transfer”, “Cheating agents- heavy metal leaching”, “phytoextraction efficiency”

Results

Heavy metal soil contamination in urban environments

Although heavy metal accumulation in soils can pose a threat to any community, accumulation in urban environments can be considered very dangerous because of the large number of people that can potentially come in contact with it on a daily basis. According to the US Census Bureau, the average population density in a metropolitan area in 2000 was 320.2 people per square mile while the average population density outside of a metropolitan area was 0.05 people per square mile (US Census Bureau 2016). This being said, it can be deduced that a contaminated lot in an urban environment has the potential to affect a large amount of people if there is activity on it such as a play structure or an urban garden (Filippelli *et al*. 2010). Because urban areas are hubs for industrialization and human activity, the heavy metal by-products of such activities can accumulate in urban soils creating an exponentially growing problem (Anon 2013). Although many environmental regulations have been enacted to prevent additional accumulation of dangerous heavy metals in soil, these metals take a long time it degrade unlike organic compounds so removal necessary (Wuana and Okieimen 2011).

Human contact with contaminated urban soil has been addressed in previous studies, and although contaminated soil on a specific site might seem like it is geographically contained, it is commonly carried into residences and work places by human and animal activity (example: human or pets walking through contaminated yard into a carpeted house) (de Burbure *et al*. 2006). The most common methods of exposure to contaminated soil are through ingestion and inhalation of soil particles (Anon 2013).

Ingestion of soil particles happens in both children and adults through various activities. Children most commonly ingest soil particles by intentionally eating soil because of nutritional deficiencies, playing on contaminated lots, eating something with contaminated soil particles on their hands, or eating/ drinking something with soil particles on it (Filippelli *et al*. 2010). Adults mainly ingest soil particles when they work on contaminated lots (yard work), by not properly washing produce grown in contaminated soil, and by not washing hands before they eat (Filippelli *et al*. 2010). Inhalation can occur in both children and adults through breathing in airborne soil particles on contaminated sites (Anon 2013) and by breathing in contaminated dust inside the home or work place (de Burbure *et al*. 2006).

Although not as prevalent, consuming contaminated vegetation can also be a cause of heavy metal exposure to people living in urban areas. Many houses in urban environments are on lots that have high levels of some type of heavy metal, gardening and consuming vegetables not planted in a raised soil bed can be a common source of heavy metal contact in unsuspecting households (Clark etal 2013). According to The US Census of Agriculture, there has been an increase of urban farms between 2002 and 2007; although there is no self-identified urban farms reported on the census, the increase of urban farms can be seen through the decrease of farm land acreage and the increase of total farms registered (Rogus and Dimitri 2013). With this increase in urban agriculture, exposure to contaminated soil may increase due to greater chances of heavy metal exposure. Because each heavy metal is bound differently to the soil and each plant has a different affinity for heavy metal uptake, the risk of exposure to a particular heavy metal through consumption of vegetation grown in contaminated soil varies (Clark *et al*. 2006).

Common heavy metals found in urban environments

Three common heavy metals found in urban environments are Pb, Cd, and As. All three of these heavy metals are by-products of industrialization and anthropologic activities and their accumulation in soil impacts living organisms.

Lead

Lead is a naturally occurring cationic metal usually found in a compound with different elements such as oxygen or sulfur. Pb is the fifth most industrially produced metal and used in many industries including battery and ammunition production, mining and coal burning, leaded paint manufacturing, and leaded gasoline production (Anon 2013). Although Pb is used in many industries, the main source of topsoil contamination in urban areas comes from the previous overuse of leaded paint and leaded gasoline emissions (Filippelli *et al*. 2010; Clark *et al*. 2013). Peak usage of Pb paint occurred in 1925 (Clark et al 2006) when Pb used for additional paint pigmentation and increased paint durability and flexibility (Clark et al 2013). The peak usage of leaded gasoline was in 1979 (Clark et al 2006) in which Pb was used in the form of tetraethyl-Pb, an anti-knock agent (Clark et al 2013). Both of these products were phased out due to U.S. regulation by the end of the 70's but because Pb does not degrade, its accumulation in urban soil became a real threat (Clark et al 2006). Although Pb paint is no longer used, natural weathering and chipping of older houses that contain Pb paint is still a factor that leads to soil Pb accumulation today (Clark *et al.*2013).

Similar to soil, Pb accumulates in the human body over time because there is no metabolic use for Pb in the body and it is not able to be broken down making it very toxic at low levels (Huff *et al.* 2007). Chronic exposure to Pb-contaminated soil can lead to high Blood Lead Levels (BBL) (Clark *et al.*2013). The tolerance threshold for Pb in an adult human body is 10 µg/dl of blood and only 5 µl/dl of blood in children (Clark *et al.*2013; Anon 2013). Once Pb enters the human body, it is accumulated in organs such as the brain and kidneys which can lead to organ failure (Wuana *et al.*2011). Pb accumulation has been known to negatively affect the cardiovascular, renal, and hepatic systems, increase bone deterioration, and lead to lower IQ (Saad *et al*. 2014; Anon 2013; Khan *et al*. 2007). Similar to other heavy metals, Pb damages cellular components by elevating the level of oxidative stress (Khan, *et al*. 2007). Pb-induced oxidative stress is created by the introduction of Pb molecules in the cell which forms Reactive Oxygen Species (ROS) and depletes the cell's pool of antioxidants (Saad *et al*. 2014). This happens because Pb inhibits the enzyme gluthathione reductase (GR) which helps create antioxidants as well as inhibiting ∂-aminolevulinic acid dehydrogenase (ALAD) which helps to inhibit ROS (Saad *et al*. 2014).

Children are more sensitive to Pb exposure due to their smaller size, early brain and nervous system development, and the higher absorption rate of ingested Pb; the absorption rate in adults is less than 5% compared over 50% in children (Filippelli *et al*. 2010). The average percent of children with Pb poisoning in the US in 2006 has dropped to 2.2% but it remains at 15% in urban areas (Clark *et al.*2006; Filippelli *et al*. 2010). Pb poisoning in children can lead to severe mental conditions including a low IQ and attention deficit disorder (Filippelli *et al*. 2010). Chronic exposure to Pb can also lead to problems in school and increased learning struggles. In a study published in 1990 it was determined that children with tooth dentin Pb levels over 20ppm had higher high school dropout rates and increased reading disorders than children with dentin Pb levels under 10ppm (Needleman *et al*. 1990). Pb poisoning is a major threat for children in older, low income areas because there is naturally more Pb in the soil (due to Pb based paint chipping on older buildings and the extended time frame from leaded gasoline emissions), there is a greater chance for poor nutrition, and a higher probability of inadequate education and access to health care (Filippelli *et al*. 2010).

Cadmium

Cadmium is a cationic heavy metal that is found naturally in the United States as cadmium sulfide (Cd=S). Naturally, it is not as abundant as other heavy metals with concentrations ranging from 0.1 to 1ppm of the earth's crust (Thevonod *et al*. 2013). Because Cd is found mixed with other metal ores such as zinc and copper, one of the main ways it is introduced to urban soils is through emissions from smelting (Saad *et al*. 2014; Anon 2013; Roussel *et al*. 2010). It is also introduced into urban soils by the use of manufacturing batteries, fertilizers/pesticides, coal combustion, sewage sludge, and pigmentation (Saad *et al*. 2014; Anon 2013). The United States production of Cd began in 1907 and peaked in 1969 (Roussel *et al*. 2010). Although many uses of Cd started to decrease in the 1970's, Cd use in battery production actually increased; in 1970 Cd use in batteries was 8% and in 2000 it was 75% (Roussel *et al*. 2010). Because illegal dumping is a large issue in many urban areas, improper Cd battery disposal adds to the Cd soil accumulation.

Cd exposure to humans from contaminated soil happens from ingestion of soil particles, inhalation of dust particles, and through consumption of crops grown in contaminated soil. Research has shown that Cd has the ability to easily bioaccumulate and 90% of Cd exposure in non-smokers is through food (Hou *et al*. 2013). Crop uptake is affected by Cd mobility and bioavailability so soils that are more acidic may lead to higher Cd toxicity in the surrounding population (Hou *et al*. 2013).

Both chronic and acute exposure to Cd is harmful to humans. Cd is not metabolized in humans and because it cannot be degraded inside the body, it accumulates in the human body. Cd accumulates in the kidney, lungs, brain, liver, and nervous system (Saad *et al*. 2014) and has been classified as a #1 category human carcinogen by the International Agency for Cancer in the United States (Saad *et al.* 2014). Organ failure due to Cd happens at a cellular level. Cd ions compete with essential metal ions for entry into a cell and disrupt normal cell functioning (Hou *et al*. 2013). Cd is also known to interfere with the calcium metabolism which causes brittle bones and painful joints (Hou *et al*. 2013). Although Cd is unable to create its own free radicals, it can replace Iron and Copper in cytoplasmic membranes and the dislodged, unbound metals will increase the oxidative stress in a cell (Saad *et al*. 2014). If the oxidative stress overwhelms the cell, cell death pathways will be initiated leading to organ failure. If the oxidative stress does not signal cell death but continues for an extended period of time (chronic exposure), cells may lose control of their adaptive mechanisms and malignancy is common (Hou *et al*. 2013).

Arsenic

Unlike the two heavy metals previously discussed, arsenic is an anionic compound and is naturally found fused with oxygen in the earth’s crust (Anon 2000). Inorganic As can be introduced into urban soils through a variety of different industries including coal and fossil fuel combustion, manufacturing and disposal of pharmaceuticals and pharmaceutical waste, wood preservatives, and the use of pesticides (Anon 2013; Wuana et al 2011). Because As is anionic, its mobility in soil decreases as pH decreases meaning that the ability for it to migrate into plants or drinking water is low in the presence of other cationic metals or organic matter (Anon 2013; Wuana et al 2011). This being said, the presence of As in soil can create complications for various heavy metal remediation techniques such as adding stabilizing agents for cationic metals which mobilizes As (Anon 2000). Inorganic As-based pesticides (lead arsenate, calcium arsenate) were used extensively in the 20th century in both urban and rural areas and because As does not easily degrade, its presence is still in the soil. Unlike Pb soil accumulation, soil As cannot be linked to poverty, in fact, in a study done in 2015, higher concentrations of As were found in urban clusters with higher income due to the wood preservatives found in their outdoor wooden structures (Dewalt *et al*. 2007).

The most prevalent way for As in urban soil to enter the body is through ingestion of contaminated soil and inhalation of soil particles (Anon 2013; Wuana et al 2011). Although As poisoning from food does happen, arsenic does not accumulate in food crops very easily. In order for As to be mobile in soil, the level of acidity would not be suitable for growth in a majority of plants (Anon 2013). Once inside the body, As can cause many health problems including multiple organ failure, skin lesions, and cancer (Bhadauria *et al*. 2007). Characteristic skin lesions are the most common sign of As poisoning; the skin first undergoes melanosis (change in pigmentation) and then keratosis (dry, rough, skin lesions) (Rahman *et al*. 2009). Organ failure (including heart, lung, liver, brain and kidney) happen on a cellular level; in the presence of As, reactive oxygen species are released and lipid peroxidation occurs in a cell which leads to cell death (Bhadauria *et al*. 2007). Lipid peroxidation is the oxidative deterioration of polyunsaturated fatty acids which are needed for cell functions (Bhadauria *et al*. 2007). Although all of the pathways of cancer induction are not known, the introduction of As to the cell increases the stress level as previously mentioned and can affect the DNA-repair mechanism which can result in malignancy (Bhadauria *et al*. 2007).

Bioavailability of heavy metals within soil

Although the total concentration of heavy metals in soil is important to address when determining if a lot is contaminated, the bioavailability of the metals measured may be significantly different. The National Research Council describes bioavailability as the fraction of total soil contaminant that is readily available for uptake by an organism (Navarro *et al.* 2005). Although a total concentration of a particular heavy metal might be high, if the bioavailability of that heavy metal is low, there will be little uptake possible by plants. The bioavailability of different metals can be influenced by soil characteristics such as soil acidity, mineral composition, organic matter content, and cation-exchange capacity (Farrag *et al.* 2012). If a metal is negatively charged like Pb and Cd, its mobility will increase with a decrease in pH (Wuana *et al* 2011). If a metal is positively charges like As, its mobility will decrease with a decrease in pH (Wuana *et al* 2011). Soils with high organic matter concentrations tend to decrease metal mobility because of the formation of stable complexes with humeric substances (Farrag *et al.* 2012). Mineral composition also has the ability to affect the heavy metal mobility; in clay like soils, there is less metal mobility and in sandy soil there is greater mobility (Farrag *et al.* 2012). Because the soil composition is directly related to metal mobility, it is important to analyze the soil before picking a specific phytoextraction method.

Phytoextraction methods

Phytoextraction is one of the most popular methods of phytoremediation because of its ability to remove a large variety of contaminants and the effectiveness of its removal. Phytoextraction is becoming a popular mode of remediation because it is thought to be environmentally friendly and low cost (Sarma 2011, Thakur *et al*. 2016) but it is also generally a slower method of treatment, and its heavy metal removal efficiency can vary greatly (Sarma 2011). The four main factors that determine the phytoextraction efficiency are the heavy metal uptake potential, the concentration of heavy metals a plant can withstand, the biomass production of a particular plant, and the bioavailability of heavy metals within the soil (Chaney *et al*. 2007). The remediation of heavy metals using phytoextraction can vary due to the soil composition, climate, addition of different soil contaminants, and types of plants used (Chaney *et al*. 2007). There are two common methods of heavy metal phytoextraction: the use of hyperaccumulaing plant species, and the use of metal tolerant plant species and a soil chelating agent. Both methods of phytoextraction have their own specific benefits and potential issues which will be addressed below.

Phytoextraction using Hyperaccumulators

Metal hyperaccumulating plants are defined as plants that are able to uptake large amounts of heavy metals (100-1000 times that of a non-hyperaccumulating plant) and translocate them to above-ground vegetation (shoots and leaves) (Sarma 2011; Rascio *et al*. 2011; Kazemi-Dinan *et al*. 2015). Hyperaccumulators are classified by 3 common traits: the capability of heavy metal uptake, effective root-to-shoot translocation, and ability to detoxify heavy metals in their leaves (Rascio *et al*. 2011). As of 2011, researchers have found over 500 different hyperaccumulating plant species in 101 different families (Sarma 2011; Kazemi-Dinan *et al*. 2015). To date, there are no known natural hyperaccumulators for Pb but non-specific hyperaccumulators in the Brassica family that are known to uptake Zinc and Cd have also been known to uptake Pb as well (Table 1) (Chaney *et al*. 2007). Hyperaccumulators for Cd, Pb, and As are plants that can survive in soils with heavy metal concentrates being >.1 mg/g soil, >1mg/g soil, and >1mg/g soil respectively (Rascio *et al*. 2011)

Heavy metal translocation is specific to each plant/metal combination but the basic pathway in nearly all hyperaccumulators is: heavy metal uptake by the roots, translocation from the roots to the shoots/ leaves, and finally detoxification/sequestering within the leaf cells (Rascio *et al*. 2011). Because each hypeaccumulator is able to uptake over 100 times the average heavy metal concentration of a normal plant, their root system is phenotypically different (Kellwe *et al*. 2003). Normally hyperaccumulator root systems have genes hyper-expressed for specific metal uptake which increases the following: heavy metal binding on the root cell walls (Rascio *et al*. 2011), excretion of natural chelate agents (malate and citrate) to lower the pH for easier heavy metal uptake (Rascio *et al*. 2011), excretion of different amino acids to help uptake (Rascio *et al*. 2011), and have natural rhyzobacteria that help the sequesterization (Kellwe *et al*. 2003). The uptake of heavy metals into the roots is either by passive diffusion or active transport (Thakur *et al*. 2016). Once heavy metals have entered the root cells, they attach to different protein shuttles and are transported up the shoot xylem into the leaf where they are either stored in a vacuole or are placed into the cell wall for sequestering (Rascio *et al*. 2011). It has been accepted that the efficient metal root-to-shoot transfer in hyperaccumulators is due to overexpression of genes coding for transport (Rascio *et al*. 2011). Cd binds to the ZIP (Zinc-regulated transporter Iron-regulated transporter Protein) on the root cell wall, is transported through the xylem by Heavy Metal Transporting ATPase, and is stored in a vacuole in the leaf cells (Rascio and Navari-Izzo 2011). As binds to phosphate transporters on the root cell wall, is transported up the xylem by Nodulin 26-like Intrinsic Proteins to be stored in a vacuole in leaf cells (Rascio and Navari-Izzo 2011).

Hyperaccumulators are one of the main plants used for phytoextraction because they have the ability to uptake extremely high concentrations of heavy metals. Because of this, there is normally no need to add soil amendments (chelating agents) to increase availability of certain heavy metals. This makes hyperaccumulators a less expensive option. Unlike other heavy metal contaminated vegetation, hyperaccumulators have the ability to uptake such a large concentration of heavy metals that they can use it as a deterrent for herbivores and pathogens (Kazemi-Dinan *et al*. 2015; Rascio *et al*. 2011). The "elemental defense" hypothesis suggests that the increased concentration of heavy metals on the leaves of hyperaccumulators discourages generalistic herbivores from eating the leaves or laying eggs on them (Kazemi-Dinan *et al*. 2015). Although hyperaccumulators do not discourage specialist herbivores with metabolisms modified to ingest high quantities of heavy metals (Kazemi-Dinan *et al*. 2015), if introduced to a site for remediation purposes, it is likely that the many of the local herbivores would be deterred. By decreasing the likelihood of herbivory, introduction of hyperaccumulators in urban environments would decrease the possibility of heavy metal bioaccumulation in the terrestrial food web as well as decrease the possibility of plant death due to herbivory. If hyperaccumulating plant species can decrease herbivory, the phytoextraction efficiency will not be negatively affected by the potential phytotoxic effects of herbivory.

Although hyperaccumulators have many benefits, their phytoextraction potential can be less than first anticipated. Because of the extreme conditions they live in, hyperaccumulators normally have a low annual biomass yield and low growth rates (Rascio *et al*. 2011) which affects their practical application. Although they can maintain extremely high metal concentrations in their above ground biomass the metal removal from the contaminated soil is still limited by the above ground biomass or growth. Other problems found with hyperaccumulators is that they are normally heavy metal specific meaning that they are able to tolerate high concentrations of only one or two elements. If they were planted on a site that had high concentrations of different heavy metals (many urban contaminated lots) they would likely experience phytotoxic effects similar to non-hyperaccumulators (Rascio *et al*. 2011; Sarma 2011). Hyperaccumulators natively grow in areas with high levels of a specific heavy metal, if used for phytoextraction, the best results would likely be if the contaminated soil in question had one particular heavy metal accumulation problem (Sarma 2011). Although heavy metal trophic transfer might be less feasible with hyperaccumulators, the leaf litter of hyperaccumulators does contain bioavailable heavy metals (Zhen-guo *et al*. 2002) that can re-contaminate the soil after the leaves degrade, or can be transferred to another area by wind, human removal and disposal, and animal activity. Unaffected environments are at risk if hyperaccumulator biomass it not collected and disposed of properly (Sarma 2011).

Chelate-assisted phytoextraction with heavy metal tolerant plant species

Although heavy metals enter and accumulate in soil in various elemental forms, once introduced into the soil matrix, most heavy metals are no longer bioavailable (meaning that plants do not uptake) (Schmidt and Ulrich 2003). In order for metal-tolerant plants to uptake heavy metals bound in the soil matrix, the concentrations of soluble heavy metals needs to be increased (Schmidt and Ulrich 2003). Organic chelating agents are often added to the soil to increase the solubility of heavy metals accumulated within the soil of a particular site (Schmidt and Ulrich 2003). Chelating agents are artificial or naturally occurring agents that increase extraction efficiency by forming water-soluble metal-organic complexes (Schmidt and Ulrich 2003). Some common chelating agents are synthetic agents like EDTA, DTPA, HEDTA EDDS, CDTA, and EGTA (Liu *et al*. 2002) and naturally occurring agents like nitrilotriacetic acid (NTA), citric acid, oxalic acid, and acetic acid (Schmidt and Ulrich 2003). Synthetic chelating agents increase the solubility of heavy metals at a higher rate, but increased solubility can also lead to heavy metal leaching (Schmidt and Ulrich 2003). Natural chelating agents that increase the pH of the soil will release cationic metals from the soil matrix, but will not prove effective for metalloids like As because its mobility decreases as the soil acidity increases (Anon 2000).

The addition of chelating agents to soil makes phytoextraction using metal tolerant species just as effective if not more effective than the use of hyperaccumulators. There are many metal tolerant plant species that are usually non-metal specific and have high annual biomass yield (Kellwe *et al*. 2003). Some non-food crops that are proven to be high-biomass, metal tolerant species include perennial grasses such as switch and vetiver, and trees such as willow and poplar (Paz-alverto *et al*. 2007, Chen *et al*. 2011). Plant species that would be beneficial for chelate-assisted phytoextraction should have an extensive root system, robust stature, high biomass yield, and be soil/climate tolerant (Chen *et al*. 2011). When choosing to use chelate-assisted phytoremediation, there are more plant species options and the use of native species is a viable option as long as the plant fits the metal-tolerant specifications (Wuana and Okieimen 2011).

The advantages of using chelate-assisted phytoextraction are apparent. By increasing the bioavailability of heavy metals in contaminated soil combined with the use of large biomass yielding plants the total phytoextraction potential increases. Naturally, non-hyperaccumulating plants have more difficulty uptaking heavy metals through their roots and then translocating them into their leaves due to limited metal binding and transportation pathways. However chelating agents change the structure of heavy metals making it easier for the plants to uptake and translocate them (Sarma 2011). Chelate- assisted phytoextraction also increases the range of heavy metal remediation; because there are no known Pb hyperaccumulators, chelate-assisted phytoextraction has the greatest potential for the phytoextraction for Pb. Because Pb is not bioavailable in the soil matrix when there is sufficient phosphorus present, uptake by many plants does not occur. The addition of PbEDTA, to Pb contaminated soils creates Pb compounds that are able to be absorbed by most plants even when phosphorus is present (Chaney *et al*. 2007). With the addition of chelating agents, the uptake by the Zinc/Cadmium mechanism in plants is much greater because of the increased bioavailability which leads to greater Cd removal (Rascio *et al*. 2011).

The use of chelating agents also has its downfalls. One of the reasons phytoextraction is popular is because of its relatively inexpensive application. The use of chelating agents like

EDTA increases the expense greatly. In one study it was estimated that the total cost for EDTA for 10mmols EDTA/kg soil would be $30,000/ha (Chaney *et al*. 2007). Not only are some chelating agents expensive, but they also increase the potential for heavy metal leaching off-site, into ground water, or into surface water (Zhen-guo *et al.* 2002, Chaney *et al*. 2007, Schmidt and Ulrich 2003). Because chelating agents make heavy metals water soluble, once these metals are mobile, the metals that do not get absorbed by plants move down through the soil and can reach underground water sources (Zhen-guo *et al*. 2002). Most chelating agents are not specific to any metals, so leaching of important nutrients can also happen, decreasing the heath of the treated soil (Abruzzese *et al.* 2001). The degradation rate of metal chelates is dependent on microbial activity and metal concentrations but in general it takes about 2 weeks for chelates to degrade (Zhen-guo *et al*. 2002). If a site were to be over-treated with a chelating agent, there is a large risk of contamination spread to other sites or ground water.

Bioaccumulation of heavy metals in the food web is also an area of concern when dealing with non-hyperaccumulating phytoextraction. Metal tolerant plants used for phytoextraction normally have a larger biomass with lower concentrations of heavy metals in their plant tissue. These lower levels of metal accumulation will not likely be high enough to deter herbivore consumption, meaning that there is a greater possibility of heavy metal tropic transfer (Rascio and Navari-Izzo 2010). Because heavy metals do not degrade, a steady diet of plants containing low levels of heavy metals can lead to accumulation within an organism (Gall *et al*. 2015). Although heavy metal trophic transfer is an alarming possibility, present research shows that bioaccumulation through the food web, although it does happen, is not as easy as many might believe (Gall *et al*. 2015). Each organism has its own defense mechanisms for heavy metal poisoning; some mechanisms include avoidance due to taste and sickness (if it does not taste good or it makes an animal feel sick, they will stop eating it), metal detoxification methods (used mainly by invertebrates), and excretion (Sarma 2011). These mechanisms decrease the trophic transfer of heavy metals, but transfer still happens because some animals have the natural ability to withstand higher heavy metal concentrations with limited effects on their metabolism (Szolnoki *et al*. 2013). In specific studies, some invertebrates such as snails have been known to maintain high amounts of heavy metals in their tissue with almost no negative effects to their metabolism (Nica *et al*. 2012). Bioaccumulation of heavy metals has also been seen in mammals. In fact, some studies report higher concentrations of metals in the organs of secondary consumers than in organs of primary consumers in the same region, supporting the theory of biomagnification (Szolnoki *et al*. 2013; González *et al*. 2008). It can be suggested that secondary consumers might have higher concentrations of specific metals in their organs than primary consumers because the transfer of metals from plants to animals is lower than animals to animals (González *et al*. 2008). Although heavy metal trophic transfer is still a new theory, research does support the idea that some metals have the ability to travel up the food chain, and that animal to animal transfer is possible. In urban areas with high heavy metal soil concentrations trophic transfer is a possibility in the surrounding ecosystem.

When addressing the hypotheses presented at the beginning of the report, it can be seen that heavy metal toxicity can be an effect of increased contact with contaminated soil as long this contact presents an exposure route for the heavy metal into the human body. It can also be seen that although chelate-assisted phytoextraction may have a higher phytoextraction potential, heavy metal leaching and trophic transfer are more probable, making this form of phytoextraction more harmful to the environment that it is implemented in.

Discussion

Pb, As, and Cd are three common heavy metals found in urban soils. Each heavy metal impacts specific organs differently and continuous exposure through ingestion and inhalation can lead to chronic toxicity (Rhaman *et al*. 2008, deBurbure *et al*. 2006). Soil exposure in urban environments happens in a number of ways, but a rising concern is the exposure due to urban gardening since residential yards in urban areas have been known to have high levels of these heavy metals (Dewalt *et al*. 20015) and gardening in contaminated soil is an exposure pathway in humans (Clark *et al*. 2006). In urban gardens, exposure to heavy metals is possible through the ingestion of soil particles on hands or vegetables and through the ingestion of contaminated fruits and vegetables (Clark *et al*. 2006). Accumulation of heavy metals in fruits and vegetables is dependent on many different factors including the soil pH, amount of organic matter, heavy metal concentration in garden soil, and the type of fruits and vegetables planted (Szolnoki and Farsang 2013). Because accumulation of heavy metals in vegetation intended for human consumption is possible, it is important to know what heavy metals are actively accumulated in plants and what types of vegetation have an affinity for heavy metal accumulation.

In a study done in India (Bvenura and Afolayan 2012), the accumulation of heavy metals (copper (Cu), magnesium (Mg), zinc (Zn), lead (Pb), and cadmium (Cd)) was examined in the following vegetables: *Brassica oleracea* (cabbage), *Soinacia oleracea* (spinach), *Daucus carota* (carrot), *Allium cepa* (onion), and *Solanum lucopersicum* (tomato). Although the Pb and Cd soil concentrations were lower than the maximum permissible limit for soil in India (Bvenura and Afolayan 2012), the uptake of Cd in carrots, spinach, and tomatoes was high enough to surpass Food and Agriculture Organization/World Health Organization permissible limit for metal concentration within vegetation (Bvenura and Afolayan 2012). This study was able to show Cd had a high uptake potential in some plants and that three types of vegetables (leafy, root, and fruiting) have the ability to uptake toxic amounts of some heavy metals. It was also able to show that the accumulation of Cd in the vegetation was not dependent on the concentration in the soil, although all three sites tested in this study had different Cd concentration levels, each type of vegetable for the different sites contained roughly the same concentration of Cd.

In a bioaccumulation study by Massaquoi *et al*. 2014 both vegetables and cereals were used. It was determined that cereals accumulate lower concentrations of heavy metals than vegetables when grown in soil watered with wastewater containing similar concentrations of heavy metals. In this study, various types of crops *Capsicum annuum* (bell pepper), *Cumumis sativus* (cucumber), *Solanum melongena* (eggplant), *Triticum aestivum* (wheat), *Zea mays* (maize), *Allium chinense (*green onion), and *Vigna unguiculata* (Chinese long bean)) were planted in soil watered with clean water and wastewater containing concentrations of As, Cd, chromium (Cr), Cu, manganese (Mn), nickel (Ni), Pb, and zinc (Zn). This study was able to show that there was relatively little difference between the heavy metal concentrations within the different types of vegetation and that Pb, As, and Cd concentrations within the vegetation were similar.

The two-methods of phytoextraction discussed in this paper are relatively new areas of research and although there are no current studies directly comparing the remediation potential of natural hyperaccumulators and metal tolerant species with soil chelating agents, there have been many independent studies which can prove informative when deciding what treatment can be beneficial in a particular urban setting.

When determining if the use of hyperaccumulators is the most desirable phytoextraction method for a specific urban site, both its remediation potential and impact on the environment need to be addressed (Table 2). The potential for heavy metal phytoextraction by hyperaccumulators is limited by the following: types of heavy metals in soil, soil characteristics, and the length of the growing season (van der Ent *et al*. 2012). Because specific hyperaccumulating plants have not been identified for many of these metals, hyperaccumulator phytoextraction potential is limited. Of the three heavy metals discussed in this paper, Pb has no known hyperaccumulator specific to its uptake. Two common Cd hyperaccumulating plant species are *Thlaspi caerulescens* and *Arabidopsis halleri* (Reeves *et al*. 2003). In a study by Schwartz *et al*. (2003), *Thlaspi caerulescens* was used in addition to Cd-tolerant species *Lolium perenne* and *Lactuca sativa* to determine the mechanisms of Cd acquisition in this particular hyperaccumulating species~~.~~ In field trials, *Thlaspi caerulescens* removed 10-15 times more soil Cd than the Cd-tolerant species. It was determined that the higher ability of *Thlaspi caerulescens* to uptake Cd was due to the differences in its root structure (they proliferated in areas with higher concentrations of Cd) and had a higher uptake rate due to their root morphology (Schwartz *et al*. 2003).

Although there are less known As hyperaccumulating plant species, one common plant known to be an As hyperaccumulator is *Pteris vittata* (Reeves *et al*. 2003). In a study by Kertulis-Tartar *et al*. (2006), *Pteris vittata* was used to remediate soil contaminated with chromated copper arsenate, a common wood preservative. Within 3 years the addition of *Pteris vittata* was able to remove 19.3 grams of surface soil As, reducing the surface soil As concentration from 190 mg/ kg to 140 mg/ kg. Although there are no known specific Pb hyperaccumulators, there have been studies that relate *Pteris vittata* to the removal of Pb in addition to As. Because Pb and As are often found in the same environments, it is believed that *Pteris vittata* located in these environments has adapted to uptake both. One study by Wan *et al*. (2013), suggests that soil Pb concentrations can actually lead to the increase of As accumulation in *Pteris vittata* (Chinese brake fern species). In this hydroponic study, *Pteris vittata* was harvested from contaminated environments and placed in hydroponic chambers containing different concentrations of As and Pb. This experiment correlated a higher frond As concentration to a higher Pb solution concentration (Wan *et al*. 2013).

The phytoextraction potential of hyperaccumulators is also dependent on soil type. In a phytoextraction study by Hammer and Keller (2003) using *Thlaspi caerulescens* to remediate soil Cd, two different soil types were compared (calcareous-pH 7.3 and acidic-pH 5.2) containing similar Cd concentrations. The acidic site was located in Caslano, Switzerland and the calcareous site was located in Dornach, Switzerland. It was determined the *Thlaspi caerulescens* grown in the acidic soil had a higher biomass (Caslano dry matter yield: 2.1 ± 0.2 tons/ha, Dornach dry matter yield: 0.9 ± 0.3 tons/ha) and was able to remove more soil-Cd than the *Thlaspi caerulescens* grown in the calcareous soil (Caslano metal removal yield: 539 ± 127 g/ ha, Dornach metal removal yield: 128 ± 19 g/ha) (Hammer and Keller 2003).

The length of the growing season of certain hyperaccumulators can also change their phytoextraction potential. McGrath *et al*. (2005) developed a study using *Thlaspi caerulescens* and *Arabidopsis halleri* to determine the effects of the length of the growing season. In this study it was deduced that *Thlaspi caerulescens* was able to uptake more Cd when it had a longer growth period. The mean Cd uptake of *Thlaspi caerulescens* grown for 4 months in 2000 was 1.3% and whereas the mean uptake of *Thlaspi caerulescens* grown for 14 months in 2001 was 8.7% (McGrath *et al*. 2005).

The two environmental risks associated with hyperaccumulators discussed by Coleman *et al*. (2005) are the reintroduction of bioavailable heavy metals to the environment from leaf litter or dead biomass and the potential for heavy metal trophic transfer. The "Elemental Defense" hypothesis has been addressed in various studies, but very few have been conducted using the heavy metals as discussed in this paper. In 2005 a study was done on the survivability of Diamondback moth (DBM) larva with a liquid artificial diet of stock solution containing concentrations of heavy metals. In this study, it was shown that hyperaccumulator concentrations of Pb (1000 µg/ g dry biomass) had 20% larval survivability and hyperaccumulator concentrations of Cd (100µg/ g dry biomass) had 0% larval survivability supporting the elemental defense hypothesis (Coleman *et al*. 2005).

The phytoextraction potential of metal tolerant species with the use of soil chelating agents depend~~s~~ on the metal tolerant plant chosen and the type and amount of chelating agent. Although there are many plants that are metal tolerant, they all have different root characteristics so it is important to research a plant's morphology before using it for phytoextraction. Pas-Alberto (2007) conducted a study using three different metal tolerant grasses grown in Pb contaminated soil to determine which grass had the greatest soil-Pb uptake. Twenty plants of each grass (*vetiver, cogon, and caraboa*) were used in a pot experiment using 50 kg of soil containing 75 mg Pb/kg soil and 150 mg Pb/kg soil. At the end of the 6 week experiment, it was determined that the initial soil-Pb concentration did not affect the Pb uptake in the plants and the average Pb content found in *vetiver, cogon,* and *carabao* grasses were 31.5 ± 9.1 mg Pb/kg , 2.3± 0.5 mg Pb/kg, and 0.3 ± 0.03 mg Pb/kg respectively (Paz-Alberto 2007) The significantly higher Pb absorption of soil-Pb by *Vetiver* grass was attributed to *vetiver's* large biomass and robust root structure.

It is also important to note that most metal tolerant plant species are non-metal specific, and although large biomass production is an important quality when choosing a plant for phytoextraction, its root structure and depth is also very important (Keller *et al*. 2003). When choosing a plant for phytoextraction, the depth of the soil contamination should be addressed to determine an appropriate plant choice. Keller *et al*. (2003) conducted a study in which root systems of four plants were assessed for their impact on phytoextraction potential. Four high biomass producing plants (*Brassica juncea, Nicotiana tabacum, Zea mays*, and *Salix viminalis*) and one hyperaccumulating plant (*Thlaspi caerulescens*) were used in a field study to determine how their root structure affected the uptake of Zn, Cu, and Cd. In this study the depth of the heavy metal contamination was between 0.2 and 0.7 meters and it was shown that the only plants that showed a significant reduction of Cd in their soil blocks were the hyperaccumulator *T. caerulescens* (179 g/ha), the willow *S. viminalis* (44 g/ha), and the tobacco plant *N. tabacum* (41.7 g/ha) (Keller *et al*. 2003). It was determined that although the high biomass species were not able to uptake the same amount of soil Cd as *T. caerulescens*, their increased ability for uptake was due to the deeper location and high density of their root systems when compared to the other metal tolerant species tested.

The type and quantity of soil chelating agents also play a large role in the phytoextraction potential of different metal tolerant plant species. Chelating agents can prove especially important in some cases because heavy metals such as Pb naturally have a strong association to organic matter making their solubility and phyto-availability low (Shen *et al*. 2002; Cao *et al*. 2008). In a study by Shen *et al*. (2002), the phytoextraction ability of cabbage was compared using different kinds and concentrations of chelating agents. Soil containing 10,600 ± 800 mg Pb/kg treated with chelating agents: EDTA, STPA, HEDTA, NTA, and Citric Acid was tested for soluble Pb concentrations three days after their application. EDTA was suggested to help release from the soil the highest quantity of soluble Pb at over 900 mg Pb /L and citric acid had the lowest release at under 200 mg Pb/L. The concentrations of EDTA were (0, 1, 1.5, 3, 5, and 10 g/pot) in the soil studied. It was determined that there was a positive correlation between the increase of soil EDTA and Pb concentration in cabbage leaves but a negative correlation between the increase of soil EDTA and the cabbage biomass production suggesting that EDTA did increase the absorption of soil Pb but decreased the biomass production of the plants (Shen *et al*. 2002).

Some of the negative environmental effects that should be addressed before choosing phytoextraction using metal tolerant species and chelating agents are the leaching of soluble heavy metals off of the contaminated site and the potential of heavy metal trophic transfer.

Soluble heavy metal transfer is a potential byproduct of the use of chelating agents in the soil. Abruzzese *et al*. (2001) conducted a study using contaminated soil treated with EDTA (5mmol/kg dry soil) and underwent a series of five washes with water to determine the concentration of soluble metals at different soil depths. Not only did the EDTA move soluble Pb as far at 70 cm into the soil, but it was also able to solubilize macronutrients causing them to move away from the site where they were needed for plant growth and therefore reducing soil fertility.

Terrestrial trophic transfer is also a concern when dealing with heavy metal plant accumulation with less than fatal concentrations of heavy metals. Because this theory is still new, there is little research determining if trophic transfer is feasible for plants with elevated concentrations of Pb, Cd, or As in their leaves. Because these heavy metals are toxic at low concentrations, the “elemental defense” hypothesis can also be used to determine the risk of some metal tolerant plant species on heavy metal trophic transfer. In the same ‘elemental defense’ study discussed earlier in this paper, the survivability of ~~d~~iamondback ~~m~~oth (DBM) larvae eating a diet containing concentrations of Pb and Cd caused low survivability rates at Pb and Cd concentrations lower than what a hyperaccumulator is capable of containing. It was determined that the minimum toxic level for DBM larvae (60% survival) was 7.5 µg Cd/g dry biomass and 15 µg Pb/g dry biomass (Coleman *et al*. 2005). This evidence suggests that even small amounts of Pb and Cd can cause toxicity and death to DBM larvae reducing the risk of trophic transfer by this moth in this experiment.

Although both hyperaccumulators and metal tolerant species have the potential to accumulate high enough concentrations for the “elemental defense hypothesis” to prove accurate, heavy metal trophic transfer is still a possibility. Even with high concentrations of heavy metals present in their vegetation, most plants will still fall victim to some type of herbivory and the surviving herbivores can become prey to higher trophic predators. In a study by Cheruiyot *et al*. (2013) the weight, metal accumulation, and survival rate of a generalist predator (the spined soldier bug *Podisus maculiventris*) fed a diet of herbivorous prey (the beet armyworm *Spodoptera exigua*) was monitored. In this experiment *S. exigua* were fed an artificial diet of food containing the minimum sub-lethal and minimum lethal concentrations of Cobalt (Co), Cu, Ni, and Zn. It was determined that both Cu and Zn underwent biomagnification and that the lethal concentration in the diet caused higher concentrations to be found in both the predator and prey.

Conclusion

The accumulation of Pb, Cd, and As in urban areas is an increasing area of concern. When addressing the first hypothesis in this paper, it can been deduced that contaminated soil is a possible exposure pathway for humans. It can be shown that it heavy metal accumulation in urban settings leads to increased body burdens in both adults and children. Chronic heavy metal toxicity can be caused by exposure to contaminated soil or vegetables grown in contaminated soil. When addressing the second hypothesis, it can be shown that metal accumulating plants might have a higher possibility of trophic transfer, but because the heavy metals addressed in this paper are very toxic to most animals when ingested, the possibility of trophic transfer is low. Although metal tolerant plant species do accumulate less metals in their leaves than hyperaccumulators, there is still a low chance of herbivory due to the toxicity of the metals accumulated. The addition of chelating agents to the soil when using metal tolerant plants can prove dangerous however, by making heavy metals mobile, the transfer of metals into non-contaminated areas is possible and can increase contamination risk. Both types of phytoextraction should be researched before choosing the right method for a particular contaminated urban site. Although both have their negative side effects, many still believe that phytoextraction will prove a beneficial type of soil remediation

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Table 1. Cadmium and Arsenic Hyperaccumulators

Species	Metal	Reference
Arobiodopsis halerii	Cd	Sarma 2011; van der Ent *et al*. 2012
Pelargonium sp.	Cd	Sarma 2011
Arabis gemmifera	Cd, Zn	Sarma 2011
Sedum alfredii	Cd	Sarma 2011; van der Ent *et al*. 2012
Thlaspi caerulescens	Cd, Zn	Sarma 2011; van der Ent *et al*. 2012
Tamarix smyrnensis	Cd, Zn	Sarma 2011
Brassica napus	Cd	Sarma 2011
Arabidopsis thaliana	Cd, Zn	Sarma 2011
Lemna gibba	As	Sarma 2011
Pteris vittata	As	Sarma 2011
Viola baoshanensis	Cd	van der Ent *et al*. 2012
Arabis paniculata	Cd, Zn	van der Ent *et al*. 2012
Pteris sp.	As	van der Ent *et al*. 2012
Pityrogramma calomelanos	As	van der Ent *et al*. 2012

Table 2. Chelate-Assisted Phytoextraction vs. Hyperaccumulator Phytoextraction- Implementation Conditions

Implementation Conditions	Chelate-Assisted Phytoextraction	Hyperaccumulator Phytoextraction
Budget	High budget	Low budget
Monitoring	A lot of monitoring needed	Some monitoring needed
Time frame	Shorter time frame	Longer time frame
Lot size	Larger lot size	Lower lot size
Heavy metal soil condition	Mixed/ all heavy metals	Heavy metal specific
Off-site metal transfer	Leaching, trophic transfer, contaminated vegetation	Contaminated vegetation

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