Sources and Human Health Effects of Arsenic in Urban Soils

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Urban soils often contain relatively high concentrations of heavy metals. Heavy metals such as arsenic (As) can form highly persistent and toxic compounds in the environment While arsenic is released to the environment from natural sources such as wind-blown dirt and volcanoes, releases from anthropogenic sources exceed those from natural sources. Inputs of anthropogenic As has a greater potential to harm the environment in comparison to natural processes. Arsenic exists in both organic and inorganic forms in the environment with trivalent and pentavalent inorganic forms posing the highest level of risk to to human and the environmental health. Inorganic and organic species of As undergo a variety of biological and chemical transformations in soils including adsorption/desorption, precipitation, complexation, volatilization, and methylation. Sorption reactions are particularly important to arsenate and arsenite transport, with soil properties such as amorphous iron and aluminum hydroxide content, clay content and pH affecting As sorption.. Remediation of metal-contaminated sites, specifically As, involves physical, chemical, and biological approaches that may achieve partial or complete removal of As from soil.

Introduction

Urban Soil Properties

What are Urban Soils?

Urban soils are mostly young soils defined as soils that are highly influenced by human activity. Examples may include construction, transportation, manufacturing process, and industrial use sites. These soils are typically located within highly populated cities around major park areas, recreation areas, and community gardens. Activities such as agriculture, silviculture, and horticulture are excluded from the "Urban Soil" category along with natural soils that are located within these larger population cities.

Significance of Urban Soils

Urban soils perform a number of important functions that are similar to those of natural soils. These functions can differ between areas, but the majority can be placed into four categories: hazard prevention, provision of renewable resources, contribution to the performance of urban infrastructure, and functions with relevance to environmental quality and cultural heritage. Urban soils help facilitate water infiltration, protecting against rainstorm damage and flooding events. Urban soils provide renewable resources to those in the surrounding areas by providing water and food supplies through plants and groundwater. Urban soils improve urban infrastructure by being a medium for alternative storm water management, and by creating sites for

recreational activities. These soils are beneficial to the environment by entrapping dust particles, sequestrating carbon in a non-gaseous state, buffering the climate through evaporation, and being the media for public green spaces and gardens. Urban soils provide many beneficial functions to the environment and those in the surrounding areas. (Lehmann, 2006)

However, contamination is a major risk that is associated with urban soils due to the location and infrastructure in the surrounding areas. If the soil becomes contaminated, harmful human effects can result from contaminated plants, water, dust particles, trace gas emissions from the contaminated area. Furthermore, if storm water or flooding infiltration is restricted, the infrastructure can be damaged

Urban Soil Taxonomy

Urban soils are defined under two distinct soil groups under the World Reference Base (WRB) for Soil Resources System: Anthrosols and Technosols. (Nugroho, 2013) Under the WRB soil classification system, soils influenced by cultivation are defined as Anthrosols whereas soils dominated by technical origin are defined as Technosols. (Lehmann, 2006) There is also interest within the National Resources Conservation Services (NRCS) to define all urban soils as Artesols. (Galbraith, n.d.) Anthrosols are soils that have been heavily modified as a result of long-term use in agriculture. Urban soils become Anthrosols by the addition natural soil material for plant growth, loss of material from digging, and compaction. (Lehmann, 2006) Technosols are soils that have been exposed to human activity for industrial purposes and that have properties substantially different from those of natural soil materials or materials moved into a pedon from an area outside of the immediate proximity by human activity. (Spaargaren, n.d.) Artesols are soils that are human altered and either contain artifacts made with skill or the soil body and landform are made with human-altered or human-transported material. The NRCS does not have a soil order to group soils that have been human-altered and human-transported; therefore, a proposal has been announced with the idea to group these soils into Artesols soil order. (Galbraith, n.d.) Anthrosols, Technosols, and Artesols soil orders are all generally known as urban soils or soils that have been altered by humans.

Urban Soil Contamination

Soil plays a vital role in the surroundings of urban areas, whereas, changes to its chemical nature can potentially expose large populations to toxic materials. However, urban areas vary greatly among themselves because the source of pollution depends on a variety of factors, such as: specific industrial, geological, climatic, and sociological conditions. In addition, each factor largely depends on the cities location, size, and extent of urbanization. (Chirenje, 2002) Contamination of Technosols can occur from land fields, construction materials, mine spoils or industrial activities which can lead to contamination of heavy metals such as arsenic (As), copper, lead, and zinc. Anthrosols are typically cultivated land that can be treated with large quantities of agricultural amendments, such as p^{i}hosphorous and nitrogen containing fertilizers or metalloids, such as As and Cu, from fungicides. (Nugroho, 2013) . The most common heavy metals found in urban soils world-wide are Cu, Zn, Pb, Ni, Co, Cr and As.(Szolnoki et al., 2013) Due to the increase in urban areas, As from anthropogenic sources has occurred in many parts of the world, and is being recognized as a global issue.

The Significance of Arsenic Contamination

The History of Arsenic

Arsenic has a long history of being a poison, both intentional and unintentional, to humans due to its odorless and tasteless properties. In the 15th century, As was frequently used in high-profile murders and was commonly referred to as "king of poisons" and "poison of kings". In the 1800s, As was used as a pigment in many products; such as toys, candles, fabric, and wallpaper, resulting in many unintentional As poisoning. Arsenic-based pigment in wallpaper, biotransformed by mold into a toxic As gas, resulted in widespread sickness and even death during this timeframe. (Hughes et al., 2011)

Though As has been known to be a toxic element, As in certain forms has been proven to be beneficial in low quantities especially in plant and animal nutrition. (Mahimairaja et al., 2005) Arsenic has been used to treat certain diseases including malaria, syphilis, asthma, chorea, eczema, and psoriasis. Previous research proved that

arsenical paste treated skin and breast cancer. (Hughes et al., 2011) Farmers tend to benefit from organic As compounds that are included in animal feed for swine and chickens to increase the weight gain rate. Arsenic can also increase the egg production amount in fowl. (European Environment Agency (EEA), 2019) Arsenic has become a useful metalloid in industries worldwide to manufacture products such as glass, ceramics, electronics, cosmetics, and fireworks. (Wilson et al., 2010)

In the late 1900s, arsenic was primarily used as a pesticide specifically for cotton fields or in orchards. (Chou & Rosa, 2003) Due to the toxicity of inorganic As, these compounds are no longer used in agriculture. (Chou & Rosa, 2003) Organic arsenicals were still used in agriculture, primarily on cotton until 2009, when the EPA issued an order to eliminate and phaseout the use of organic arsenical pesticides by 2013. (Bencko & Foong, 2017) However, monosodium methanearsonate (MSMA) an herbicide used on cotton, was an exception to the cancellation order. (Bencko & Foong, 2017) Before the EPA ban of organic As pesticides, cacodylic acid was applied as a herbicide in cotton fields, golf courses, and backyards. (Bencko & Foong, 2017)

Arsenic Speciation

Arsenic is released into the environment as a result of various natural and anthropogenic pathways (Figure 1). (Wilson et al., 2010) Therefore, it returns to the earth by precipitation. (Wilson et al., 2010) Arsenic is naturally present in the lithosphere, hydrosphere, atmosphere, and biosphere. (Jang et al., 2016) In the lithosphere, As is generally linked to metals such as gold, lead, nickel, cobalt, and copper. (Jang et al., 2016) Smelting of coal for fuel, burning fossil fuels, and arsenic waste material release As emissions into the atmosphere along with volcanoes that contribute to the release of As. (Jang et al., 2016) Soil erosion can lead to the weathering of sedimentary rocks or mining which can liberate arsenic. (Jang et al., 2016) Weathering of oceanic rocks containing As and submarine volcanoes can release As into the hydrosphere. (Jang et al., 2016) Arsenic concentrations can vary depending on the natural calamities such as heavy rain, floods, and landslides that enter the hydrosphere. (Jang et al., 2016) Arsenic in contaminated water enters the lithosphere through volatilization, irrigation, etc. (Jang et al., 2016) Additionally, As can be released into the aquatic and soil environment through geothermal water sources. (Jang et al., 2016) Anthropogenic activities may increase the concentration of As in the environment. (Nordberg & Nordberg, 2002) These activities include industrial processes such as mining, wood preservation, urban and industrial wastes, and applications of sewage sludge and fertilizer. (Nordberg & Nordberg, 2002) Inputs of anthropogenic As has a greater potential to harm the environment in comparison to natural processes. (Nordberg & Nordberg, 2002)
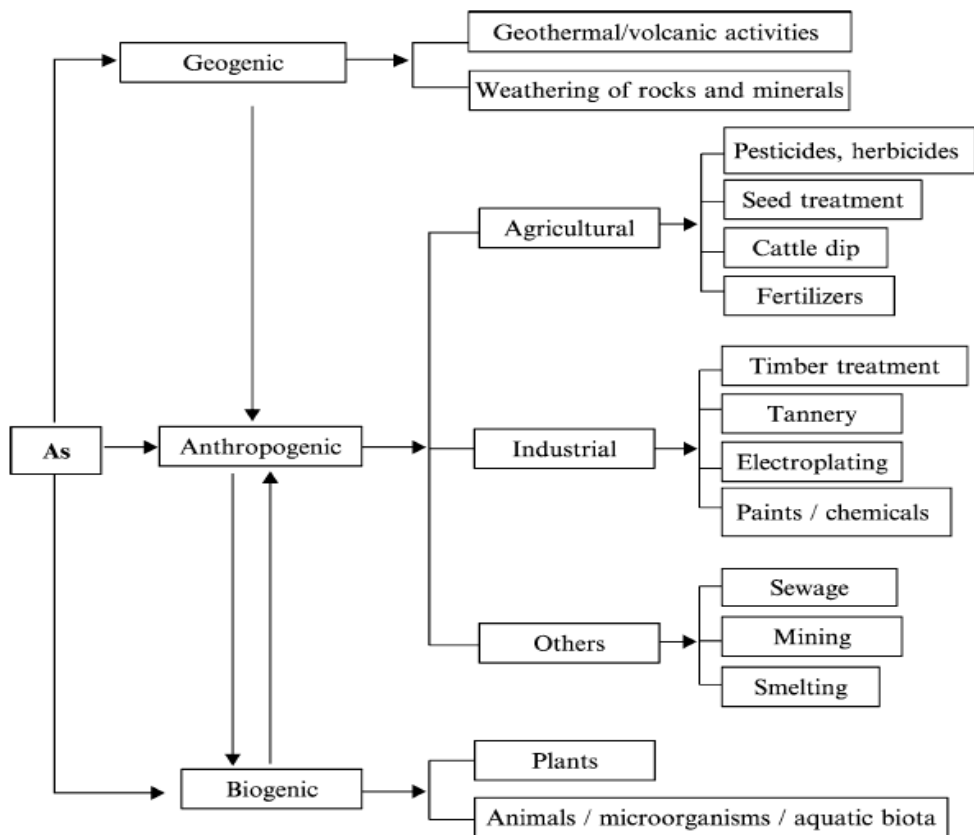
ARSENIC CONTAMINATION AND ITS RISK MANAGEMENT

Figure 1: Major Sources and routes of arsenic in soil and aquatic ecosystems (Mahimairaja et al., 2005)

Arsenic speciation is determined by both biotic and abiotic variables. Speciation is vital not only for understanding the biogeochemical cycling of As in different ecosystems, but also for designing safe disposal options. (Mahimairaja et al., 2005) Arsenic exists in both organic and inorganic forms in the environment. The solubility, mobility, bioavailability, and toxicity of As depends on its oxidation state. (Masscheleyn et al., 1991). Trivalent Ascan exist as arsenous oxide (As_2O_3), arsenious acid (H_3AsO_3), arsenite ions (AsO_4^{3-}), arsenic trichloride ($AsCl_3$), arsenic sulfide (As_2S_3) and arsine (AsH_3). Pentavalent As typically occurs as arsenic pentoxide, orthoarsenic acid, metaarsenic acid, and arsenate ions. Arsenic in the trivalent (As [III]) and pentavalent (As [V]) oxidation states pose the highest level of concern for exposure to humans and the environment. These compounds are considered the number one substance in the most recent Comprehensive, Environmental, Response, Compensation and Liability Act (CERCLA) Priority list of Hazardous Substances. The compounds are based on frequency or occurrence, toxicity, and potential for human exposure. Trivalent arsenic tends to be more toxic than pentavalent arsenic; however, individuals are exposed to both. (Hughes et al., 2011) Inorganic and organic species of As undergo a variety of biological and chemical transformations in soils; such as, adsorption, desorption, precipitation, complexation, volatization, and methylation. (Mahimairaja et al., 2005)

One environmental concern of As is the adsorption of inorganic Arsenate and Arsenite on soil mineral surfaces because it directly affects the fate and mobility of As in soil. (Hughes et al., 2011) Arsenate and arsenite both sorb rapidly and extensively onto iron and aluminum oxides in laboratory studies, suggesting that the two species behave similarly in natural systems. Arsenite is found to be more mobile than arsenate in soils and sediments due to reduction of sorbent oxides to soluble forms followed by reduction of arsenate to arsenite. (Redman et al., 2002) Arsenic mobility in natural systems is controlled primarily by adsorption onto metal oxide surfaces. The most common oxides of iron, aluminum, and manganese appear to be the most important sorbents

of As in natural environments. (Redman et al., 2002) Amorphous iron and aluminum hydroxide, clay content, and pH are the soil properties reported to be most related to As sorption. Arsenate is strongly adsorbed at acidic pH values on amorphous aluminum hydroxide, aluminum oxide, ferrihydrite, and hematite. Typically, As(V) sorption on amorphous Al and Fe oxides is characterized by an apparent sorption maximum at pH 4, whereas As(III) sorption maximum occurs in the pH range of 7 to 8.5. (Mahimairaja et al., 2005)

The qualities of the soil clay content influence the retention of As as well. Soils with higher clay content capture more As , specifically As(V) compared to As(III), than sandy soils with lower clay content. (Mahimairaja et al., 2005) The degree of As sorption onto silicate clay minerals decreases in the order of kaolinite > vermiculite > montmorillonite. (Mahimairaja et al., 2005) The adsorption by clay minerals is impacted by pH. In general, adsorption of As(V) decreases with increasing pH, whereas, adsorption of As(III) increases with increasing pH. (Mahimairaja et al., 2005) Soils with low oxidic minerals, an increased pH has minor impacts on the amount of As(V) adsorbed, however, a soil with high oxidic minerals, adsorption of As(V) decreases with an increased pH. The As(V) decrease is related to two interacting factors: (i) the increasing negative surface potential on the plane of adsorption and (ii) the increasing concentration of negatively charged As(V) species present in the soil solution. (Mahimairaja et al., 2005) A soil under aerobic conditions (100-200 mV vs Hg/Hg_2Cl_2) the primary stable species is As(V), which may occur as a different oxyanions depending on the media's pH. (Ascar et al., 2008) Generally, the pH of soil is from 5-9; therefore, As(V) may be found as arsenate ions. When soil is subject to flooding, it may reach reduced conditions, with redox potential below 100 mV, resulting in the predominate species as Arsenous acid. (Ascar et al., 2008) Previous studies show that Natural Organic Matter (NOM) is an important component that potentially influences arsenic chemistry by being highly reactive towards metals and surfaces. (Redman et al., 2002) Such that As mobility may increase with NOM being present in soil amendments especially if the soils are under waterlogged conditions.(Verbeeck et al., 2020) Research has shown that the maximum adsorption of As(V) on humic acids occurred around pH 5.5 compared to the adsorption of As(III) increased to pH 8. At higher pH, the solubilization of humic substances reduces As retention. Even though there is minimal information regarding the effects of organic matter on As adsorption, it has been shown that humic acid reduces both As(V) and As(III) adsorption on geothite within pH 3 and 9. (Mahimairaja et al., 2005)

Research was conducted on a soil sample (Mollisol Soil Order) in central Chile to determine the influence of redox potential on the mobility and availability of the various arsenic chemical forms. The sample was collected from the surface horizon (0-10 cm). The soil was spiked with As(V) to execute adsorption isotherms. The soil was adjusted to three redox potentials (-200, 0, 200 mV). Under reducing conditions (-200. mV), arsenic increased its mobility. The reduced conditions produced the highest solubility values, and arsenite was the predominate compound. In contrast, arsenic solubility decreased under oxidizing conditions, and was governed by the presence of arsenate. The results also showed that methylated species may contribute to the conversion of arsenate to arsenite because the greatest concentration of organic arsenic species was found under reducing conditions. (Ascar et al., 2008)

According to a study in Louisiana (LA), redox affects the speciation and solubility of As in soil as well. Soil surface samples (0-20 cm) located near an As dripping vat in Kolin, LA were collected for testing. These loamy upland soils consisted of 1.8% organic matter and a pH of 5.6. The Arsenic concentration in these dry soils was approximately 555 ± 18 mg kg^{-1}. (Masscheleyn et al., 1991) Typically, an increase in soluble As upon reduction has been associated with solubilization of ferric arsenate and other forms of iron combined with arsenic. However, the results from this experiment showed that the reduction and release of As may occur before the dissolution of iron oxyhydroxide layer. Also, the observations showed that the dissolution of the ferric hydroxide led to a further increase in As concentrations. Up to 10% of the total As present in this soil became soluble. This study showed that As(V) served as an effective electron acceptor in microbial mineralization of organic matter and thereby became reduced to the more mobile and toxic As(III) species. Because As(V) competed with Fe(III) as a terminal election acceptor in the microbial respiration, may have potentially caused As(V) reduction to become slow and incomplete. (Masscheleyn et al., 1991)

The redox-pH was also studied during this experiment which proved that both redox and pH impact the speciation and solubility of As. Figure 2 shows As species distribution at three pH levels (5, natural, 8) in combination with 4 different redox levels (-200, 0, 200, 500). At redox potentials of 200 and 500 mV, As(V) was the major dissolved As speciation; whereas, at reduction of -200 and 0 mV, As(III) became the major dissolved As species. Figure 2C shows that soluble As concentrations were as much as 3 times higher than those in the equilibrium with lower pH values. Almost all As was present as As(V) which can be attributed to the pH-dependent adsorption characteristics of As(V) onto the oxide surfaces. The decreasing positive surface charge of the oxides with increasing pH facilitated the desorption of arsenate. The results from this test showed that at higher redox levels, As(V) was the predominant As species and its solubility was low. At alkaline conditions and/or reduction of As(V) to As(III) led to a mobilization of As. At reduced conditions (0-100 mV), As solubility was controlled by the dissolution of iron oxyhydroxides. Therefore, to maintain minimal As solubility and mobilization in a situation as such, one must maintain high redox and non-alkaline conditions. (Masscheleyn et al., 1991)
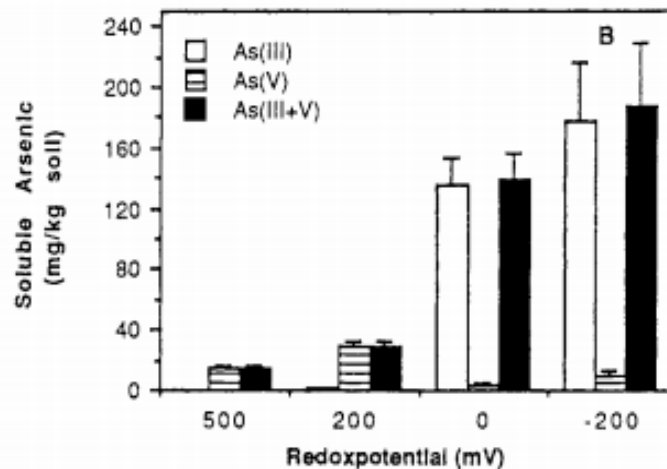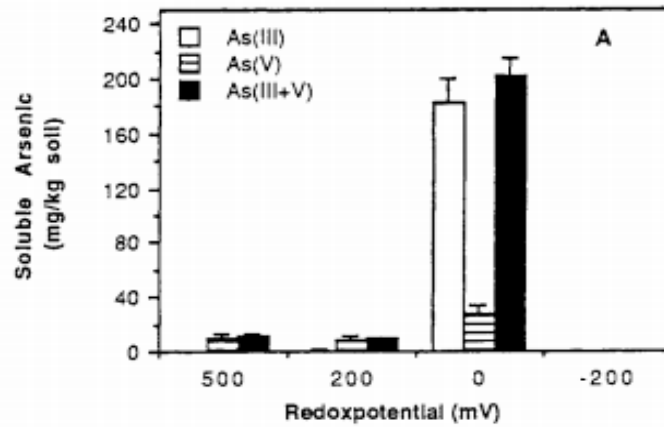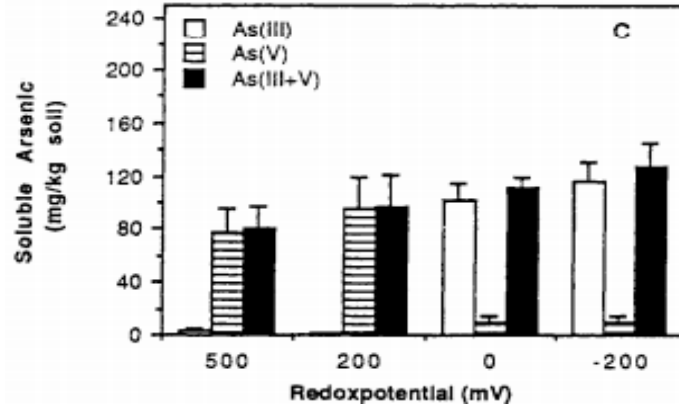
Figure 2: Distribution of soluble arsenic species after a 24-day equilibration period under controlled redox and pH conditions. (A. at pH 5.0, B. at neutral pH (5.2 for 500 mV, 6.7 for 200 mV, 7.0 for 0 mV, and 7.2 for -200 mV) C. at pH 8.0) (Masscheleyn et al., 1991)

Research in California showed that the adsorption of As in soil which has proved that the adsorption of arsenate in soils is correlated with ammonium oxalate-extractable Al and Fe. Whereas, Arsenite adsorption to soil is correlated Fe(III) oxide. Three arid-zone soils from California (Wasco, Fallbrook, and Wyo) were fully characterized as shown in Table 1, then used to compared arsenite and arsenate adsorption on these soils. Chromatographic speciation of As(III) and As(V) showed that the background levels of As were relatively low. Therefore, additional As(V) and As(III) were added to the soil. Oxidation of additional As was not detected below pH 8 in soil suspensions. However, As(III) oxidation was detected at higher pH levels. Wyo had the highest citrate-dithionite extractable Fe and % clay along with the highest affinity for As(III) and As(V), which had similar adsorption behavior similar to pure ferric oxide. Under most conditions, As(V) species adsorbed more strongly than As(III). However, at the low As surface coverage, As(III) displayed a higher affinity for the soil with highest Fe(III) oxide content than As(V).

Measurement	Soil		
	Wasco	Fallbrook	Wyo
EC (ds m^{-1})[†]	0.065	0.045	0.082
pH	5.80	7.10	6.77
E_h (mV)	+96	+64	+88
CEC (mmol$_c$ kg^{-1})	71	78	155
Surface area (m^2 g^{-1})	55.9	28.5	78.2
Clay (%)	14.6	9.2	15.7
Inorganic carbon (mg kg^{-1})	10.0	240	15.0
Organic carbon (mg kg^{-1})	400	310	1370
Selective Dissolution by:			
Ammonium oxalate (pH 3.0)[‡]		mg kg^{-1}	
Al	292[§]	277	492
Fe	364	345	2660
Citrate-dithionite			
Al	648	540	989
Fe	2260	4090	8160

[†]Measurement of EC, pH, and E_h were in 1:10 soil:solution suspensions.
[‡]See Materials and Methods for extraction procedures.
[§]Values are the average of duplicate extractions.

TABLE 1 Selected properties of three California soils

Arsenic Remediation in the Environment

Remediation of metal-contaminated sites, specifically Arsenic, involves physical, chemical, and biological approaches that may achieve with the partial or complete removal of As from soil. A variety of factors determines which type of remedial strategy will be best for the situation. It depends on the extent and nature of As contamination, type of soil, characteristics of the contaminated site, cost of operation, availability of materials, and relevant regulations.

Physical remediation includes capping, soil mixing, soil washing, and solidification. The simplest physical process for As contaminated soil removal is to mix contaminated soil with clean soil resulting in soil dilution. This can be achieved by importing clean soil and mixing it with As contaminated soil or redistributing clean materials already present at the contaminated site. Soil washing also known as extraction can be used to remediate As contaminated soils. This technique uses an acid washing process to extract the bulk of As(V) from highly contaminated soil. Mahimairaja et al., 2005) In Japan, an Andosol soil was collected from horizon A of a forest land. Approximately 1.5 kg of soil was shaken for three months with sodium arsenate solution at pH 4. The artificially contaminated soil (2830 mg As kg-1) was washed with different concentrations of hydrogen fluoride, phosphoric acid, sulfuric acid, hydrogen chloride, nitric acid, perchloric acid, hydrogen bromide, acetic acid, hydrogen peroxide, and 3:1 hydrogen chloride -nitric acid. Phosphoric acid appeared to be the most successful extractant, containing 99.9% As extraction at 9.4% acid concentration. (Tokunaga, 2002) The success of the soil washing primarily depends on speciation of As present in the soil because it is based on the desorption or dissolution of As from the soil inorganic and organic matrix during washing with acids or chelating agents. (Prasad , 2005) The least expensive physical remediation operation is "capping" which is the process of isolating the contaminated soil. The process caps the contaminated sites with clean soil which should prevent upward migration of contaminants through the capillary movement of soil water. (Mahimairaja et al., 2005)

Chemical remediation has a high success rate in adsorption, immobilization, precipitation, and complexation reactions. The issue with the chemical remediation processes is that they are relatively expensive if the contamination site is large. The two primary routes for chemical remediation is (i) immobilization of metals using inorganic and organic soil amendments to reduce their bioavailability, and (ii) mobilization of metals and their subsequent removal through phytoremediation or soil washing. Chemical immobilization is conducted by adsorption/ precipitation of As in contaminated sites through the addition of soil amendments. Immobilization can be accomplished by (i) adjusting the physical properties of the soil, so that As is more tightly bound and less bioavailable, (ii) chemically immobilizing As either by sorption onto a mineral surface or by precipitation as a discrete insoluble compound, or (iii) mixing the contaminated soil with uncontaminated soil increasing the number of As-binding sites. A variety of organic and inorganic amendments are known to immobilize metals including As by Chemical adsorption, which include: ion-exchange resin, ferrous sulfate, silica gel, gypsum, clay minerals, and liming materials. These materials are naturally occurring and nontoxic to the environment. Clay materials are the most reasonable price, and have a simple application. In Australia, a former railroad depot had extensive As contamination with levels exceeding both ecological and health regulations. The As species appeared to be water soluble, resulting in high potential for mobility at this site. The best management option was to immobilize the As through chemical remediation. Ferrous salt was used to immobilize the As which required oxygen to be available to the soil. However, this process generates large amounts of acid, which could be counter proactive to As immobilization in poorly buffered soils. Amending the soil with lime could neutralize the acidity of the acid. After further studies, Iron, Manganese and gypsum was used to stabilize the As contamination site. Phytoremediation uses plants and their associated root bound microbial community to remove, contain, or degrade contaminants. Phytoremediation has been grouped into a variety of categories; such as, phytostabilization, rhizofiltration, and phytoextraction. Phytostabilization is used to immobilize contaminants by reducing leaching, controlling erosion, creating an aerobic environment in the root zone, and adding organic matter to the substrate that binds As. Rhizofiltration is the process where roots can be used to adsorb metals, which are subsequently removed by harvesting the whole plant. Phytoextraction is the process where plants are

grown on contaminated soil to remove the contaminant. Phytoextraction consist of replanting the plant until the metal concentration has reached acceptable levels. (Mahimairaja et al., 2005)

Arsenic goes through biological transformations in soil; therefore, specific microorganisms can be used for the biological remediation process of As. Bioremediation techniques can be grouped into two categories: (i) Intrinsic bioremediation which the process to contain essential nutrients that are required to sustain microbial activity while degrading the targeted pollution, (ii) engineered bioremediation which accelerates the in situ microbial degradation rates to remove the contamination. Bioaccumulation, Microbial redox reactions, and methylation of As can be used as biological remediations strategies to remove As contamination. Bioaccumulation is the process to accumulate As from a substrate containing low concentration of As. This process is accomplished by biosorption of As by microbial biomass and its by products, and by physiological uptake of As by microorganisms through metabolically active and passive processes. Microbial redox reactions can reduce As contamination by microbial oxidation. Heterotrophic bacteria has been found to oxidize toxic As(III) in soils to less toxic As(V) reducing the As concentrations. Because As(V) is strongly adsorbed to inorganic compounds in soil, microbial oxidation could result in the immobilization of As. The remedial process of Methylation can transform inorganic As into metallic hydride or methylated forms, so that it can volatilize into the atmosphere. Two microorganisms, Gallionella ferruginea and Leptothrix ochracea support the biotic oxidation of iron. Iron oxides and the microorganism mentioned previously were deposited in a filter medium, resulting in a suitable condition for As adsorption. This is due to the fact that As in the form of As(III) cannot be efficiently sorbed onto the iron oxides. Potentially, these microorganism have oxidized As(III) to As(V), to facilitate the adsorption on Fe(III). This experiment resulted in the overall removal efficiency of As increased to 95% even with a high inition concentration of As(200 mg/L). Bioremediaton is ecologically safe and natural, and is typically 60-70% less expensive than other remedial techniques. (Nejad, 2018)

Human Exposure to Arsenic

Humans are directly exposed to contaminants in soil through skin contact, inhalation, ingestion, and consumption of plants grown in soil. Indirect effects include interactions between the soil, the soil microbial community, vegetation and the nutritional value of foods and human health. Increasing urbanization leads to intensive anthropogenic activities and consumption of resources and energy in urban areas. Urban soil contaminants are prominent in the green spaces such as parks and gardens which is the locations that people have more direct contact with soil. Not only are parks a primary place for direct contact with contaminated soils, but the population is also exposed to contaminants through the food chain from urban agriculture

In Hubei Province of China, a study was conducted to determine the concentrations and health risk of heavy metals in urban soils around an electronics manufacturing site. The sampling site was divided into four zones within 1 km of the factory: commercial, roadsides, farmland, and residential. The soil properties were characterized by relatively viscous, slightly alkaline, moderate organic matter contents, and low cation exchange capacity. Each sample was a mixture of five subsamples taken from the top horizon (0-10 cm). Seven heavy metals were evaluated during this study which showed the As concentration around the electronics factory ranged from 10.30-73.65 ppm as shown below in Figure 3. This study also showed that the contamination of As in this area proved to be harmful to humans. In accordance with the classification groups defined by the International Agency for Research on Cancer, the carcinogenic risks for As in the urban soils of the study are shown in Table 2. The RI value for As for children and adults was greater than 10^{-4}, which indicates that the carcinogenic risk is dangerously high in these soils. Therefore, this study showed that urban soils around the electronics areas had elevated arsenic concentrations. (Wu et al., 2018)
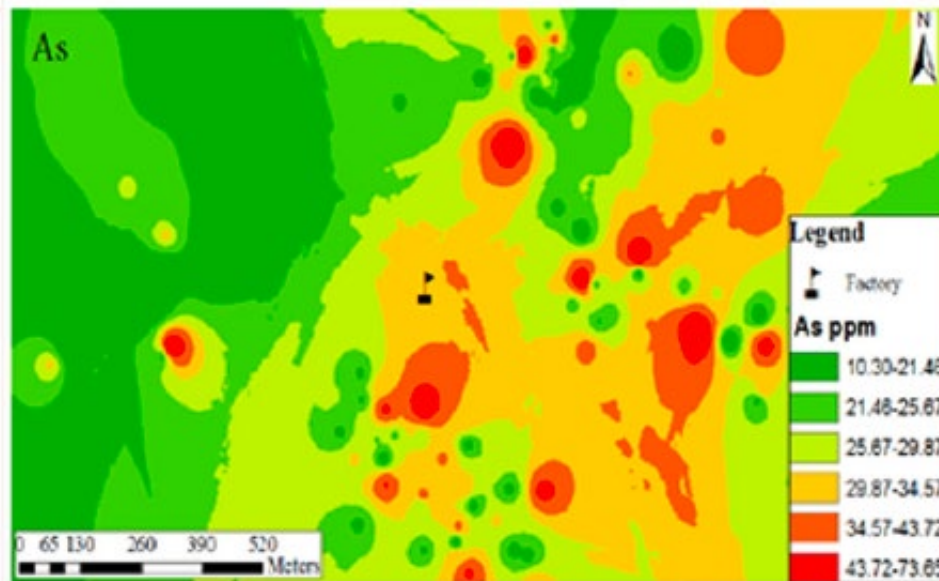
Figure 3: Spatial distribution map of Arsenic in urban soils around the electronic manufacturing. (Wu et al., 2018)

Metals	HQ$_{ing}$ (mean)		HQ$_{inh}$ (mean)		HQ$_{der}$ (mean)		Hazard index (HI)		Carcinogenic risk (RI)	
	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults
As	1.13E	1.52E-01	7.78E-05	3.49E-05	6.20E-02	1.62E-01	1.20E + 00	3.14E-01	1.71 E-03	2.34 E-04

Table 2: Health risk of Arsenic in the soils around electronics manufacturing facility. (Wu et al., 2018)

Research in Tacoma, Washington found elevated levels of arsenic in urine samples from residents living near a copper smelter. This information caused concern for the community because arsenic exposure at the smelter had been related to an increase risk of lung cancer. Inorganic arsenic specifically arsenic trioxide was the primary form of arsenic contamination in the community. The area of the study conducted was in parts of north Tacoma and Vashon and Maury Islands. A total of 121 households in the study area and 10 in the Bellingham comparison area were selected. Four hundred thirty-five individuals were included in the study out of the 121 households. The biological samples used to measure human exposure to arsenic consisted of urine, hair, and handwash. Environmental samples consisted of soil, ambient air, personal air, house dust, etc. After samples were analyzed, the major indicator of arsenic exposure in the study was arsenic in urine. Although As can be excreted in the feces, skin, hair, nails, and sweat, the major elimination route is the urinary system. For most personal samples, males had higher concentrations of arsenic than females. The two primary reservoirs of arsenic contamination in the community which was the smelter and the soil. Children in Ruston appeared to be getting arsenic contamination from contact with the soil, i.e. hand to mouth activities. (Polissar et al., 1990)

An Arsenic Chemical Plant located in Nandan County, China produced As which resulted in a large amount of waste residue. Due to lack of proper disposal and safe landfill, the waste water residues caused serious pollution to the surrounding environment of the chemical plant. The soil was divided into four soil layers: first layer (0-0.5 m), second layer (0.5-2 m), third layer (2-4 m), and fourth layer (4-6 m). The exposure of the local population was estimated by considering three different routes: dust ingestion, dermal contact with soil, and inhalation of soil particles. The study showed that the average contents of As were higher than the acceptable concentration value. The maximum concentration of As was 28,900 mg/kg which was 722.5 times higher than the acceptable guideline level, which results in high cancer risk for the community. The Arsenic concentration levels for each layer is shown below with the first layer having the most As. (J. Li et al., 2019)
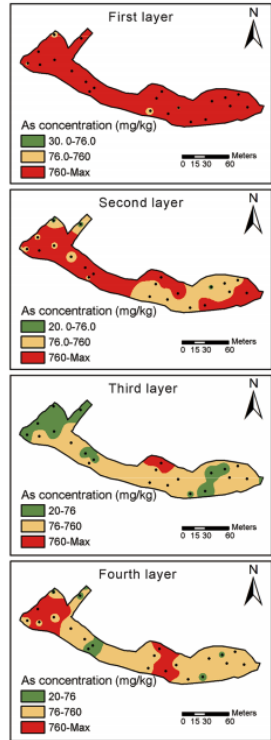
Figure 4: Spatial distribution of remediation area for As. (J. Li et al., 2019)

Also, research in Wilmington, Delaware determined high concentrations of As in the soil near tanning salons. In previous years, As compounds were used at various stages of the tanning process; such as As-based coloring agents, arsenate leather preservatives, and the hides were de-haired in large container of As solution. Soil samples were taken in Christiana Park which was once surrounded by industrial and commercial sites until the early 20th century. Two sample depths (0-20 cm, 20-40 cm) were taken at eight locations in the park depicted in Figure 5. The soil samples contained an average of 40 mg kg -1 at a depth of 0-20 cm below the surface, and 153 mg kg-1 As at a depth of 20-40 cm. The typical range of As in Delaware soils averages around 1-10 mg kg -1 As. Therefore, the averages at these two depths in Christiana Park exceeded the states average of As concentration in soil. In 2008, the remedial process was completed which consisted of installation of a one-foot clean protective cap on top of a geo-textile demarcation fabric across the entire site. (Landrot et al., 2012)
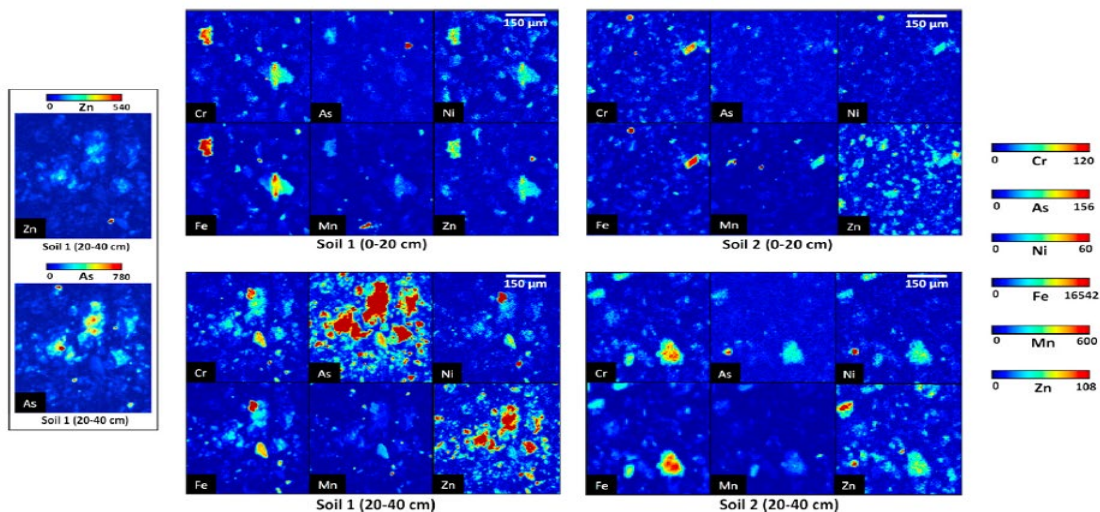

Figure 5: Spatial distribution of heavy metals at depths of 0-20 cm and 20-40 cm below the surface. (Landrot et al., 2012)

Conclusion

Heavy metals such as Cu, Zn, Pb, Ni, Co, Cr, and As have increased in Urban soils due to the anthropogenic activities. As has become a more concerning heavy metal because of its hazardous properties that adversely affects the environment and human health. As contamination from anthropogenic sources has been reported globally. The biochemistry of As in soil can be complex, and is mostly determined by the chemical speciation. The different valence states of As determine the toxicity of the element. Typically, As(III) is more toxic than As(V). Speciation is vital not only for understanding the biogeochemical cycling of As in different ecosystems, but also for designing safe disposal options.

Remediation of metal-contaminated sites, specifically Arsenic, involved physical, chemical, and biological approaches that may achieve with the partial or complete removal of As from soil. Physical remediation includes capping, soil mixing, soil washing, and solidification. Chemical Remediation has a high success rate in adsorption, immobilization, precipitation, and complexation reactions. Bioremediation is unique because it relies mainly on natural processes and does not require chemical amendments. Bioremediation techniques can be grouped into two categories: (i) Intrinsic bioremediation which the process to contain essential nutrients that are required to sustain microbial activity while degrading the targeted pollution, (ii) engineered bioremediation which accelerates the in situ microbial degradation rates to remove the contamination.

Research has been conducted on the hazards of As, speciation of As, and the remedial processes of As. However, further research is needed for the following:

- Research in relation to how the potential of contaminated urban soils impacts the geochemical trends of specific soil orders.
- Research on specific sources of As contamination result in specific As speciation.

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