



## METAL LEACHING FROM CHROMATED COPPER ARSENATE (CCA)-TREATED WOOD: IMPLICATIONS ON THE ENVIRONMENT

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**ABSTRACT:** *The use of chromated copper arsenate (CCA) treated wood is a common practice. In Ghana, (CCA)-treated woods are used often as utility poles. The siting of these utility poles in the environment may lead to serious health implications as the levels of arsenic, chromium and copper in the environment particularly, in their immediate surroundings become elevated as they are leached out. The objectives of this study were to estimate the levels of As, Cr and Cu in the treated wood, in the soils in the immediate surroundings of the wood and some soils far away from the treated wood products. A series of solvents were also tested for their ability to extract the metals from the treated wood. In all, 5 treated woods consisting of 2 freshly treated and 3 weathered, 2 untreated woods and 10 soil samples were analyzed for their levels of these metals. The wood samples were generated into ash, sawdust and smaller blocks. The levels of the metals in the treated wood samples were significantly higher than in the untreated samples. The average levels of As, Cr and Cu in the weathered wood ash is between (8201.1 mg/kg and 12802.6 mg/kg) and in the freshly treated wood ash between (3102.6 mg/kg and 4050.2 mg/kg). The results of the levels of the metals leached by the four different solvents tested showed the solvent effectiveness to leach out the metals in the order, Sea water < De-ionised water < SPLP < Rain. A particular finding of interest was that the efficiency of extract was also dependent on the leaching time. The Levels of the metals recovered after leaching for 5 days in all samples were highest followed by 3 day and 1 day. The levels of As, Cr and Cu were also found to be highest in soils around the in-service CCA treated utility poles with the maximum amount of 8.9 mg/kg for As, 47 mg/kg for Cr and 89.8 mg/kg for Cu.*

**KEYWORDS:** Metal Leaching, Chromated Copper Arsenate (CCA), Treated Wood, Environment

### INTRODUCTION

Chromate copper arsenate (CCA), is a common preservative, which has been used in the U.S to treat wood purposed for outdoor structures, for example, decks, fences, utility poles, and marine dock right from the early 1970s. Recently, CCA was subject of risk assessments by the U.S Environmental Protection Agency (EPA) and U. S. Consumer Product Safety Commission (CPSC) for potential exposures to children who contact CCA-treated playgrounds and home decks [1]. In response to these risk assessments, manufacturers of CCA began a voluntary transition from CCA to alternative wood preservatives, and as of January 1, 2004, new CCA-treated wood is no longer manufactured for residential uses in the U.S. Although CCA-treated wood has been phased- out for residential applications, many in-service CCA structures currently exist in the U.S. due to the long service life of this treated wood which varies from 10 to 40 years. Therefore, ongoing and future exposure to toxic metals from CCA treated wood remains a possibility. Large amount of the chemicals in



CCA-treated wood have been documented to be lost (i.e. depleted) during the long service lives of the product according to stake test. Studies have documented depletion rates ranging from an average 25% lost after 20 to 43 years of exposure in temperate Sweden which can potentially impact runoff, soils, and potentially groundwater [1].

The chemical, chromate copper arsenate (CCA), is used in the treatment of wood. It consists of hexavalent chromium, divalent copper and pentavalent arsenic. It is generally formulated to be leach-resistant when fixed to wood. Complete fixation of CCA to wood is defined by the reduction of hexavalent chromium to trivalent chromium resulting in the formation of insoluble complexes in the wood [2, 3]. The retention level or amount of CCA used depends on the particular application of the wood. Typical standard retention levels utilized by the wood preservative industry are 4.0, 6.4, 9.6, 12.8 and 40.0 kg/m<sup>3</sup> [4], where kg refers to the mass of CCA on an oxide basis and m<sup>3</sup> corresponds to the volume of wood. Low retention levels 4.0 and 6.4kg/m<sup>3</sup> are permissible for above ground applications. Wood treated to a higher retention, 9.6kg/m<sup>3</sup> is used for load bearing structures such as pilings and structural poles, while retention levels of 12.8 and 40.0kg/m<sup>3</sup> are used for foundations and saltwater applications. Although there are several applications of treated wood, their use as utility poles for the conveyance of cables is the most popular in Ghana. Treated wood as utility poles due to its inexpensive nature have replace the expensive concrete poles used previously.

In Ghana, the use of treated wood for various purposes has taken a new dimension. In the treated wood industry, chemical preservatives are added to manufactured wood products to prevent biological decay. Treated dimensional lumber, poles and plywood are used in construction of fences, decks, docks, utility poles and other wooden structures. Building contractors also utilize small amount of treated wood products in the construction of residential and commercial structures [2]. Arsenic, chromium and copper all present potential risks to human health and the environment when exposures occur at sufficiently high concentrations. Exposure routes of concern include direct human contact with the treated wood, human exposure to media impacted by preservatives migrating from the treated wood, and exposure of organisms to preservative compounds in the environment. Pathways of concern resulting from direct human contact with wood products include those resulting from touching the wood (e.g. dermal sorption, ingestion of dislodged chemicals from hand-to-mouth contact) and inhalation of wood particles during construction and maintenance activities [5,6,7].

Concerns over possible human health impacts from contact with CCA-treated wood have prompted the phasing out of CCA-treated wood for most residential uses in the US as at 2003 [8]. When environmental media such as groundwater, surface water or soil become contaminated by preservatives migrating from CCA-treated wood, human exposure may also result [9]. Although the arsenic, chromium and copper in CCA-treated wood are have low leachability over several decades, small amount of these toxic contaminants nonetheless do leach over time [10, 11, 12]. Preservative leaching from CCA-treated wood in the environment is an issue of concern with respect to both the wood product performance and possible impacts on human health and the environment [13, 14, 15].

### **Justification**

In Ghana, CCA-treated wood is mainly used as utility poles in conveying electricity, rail slippers and telecommunication cables. The use of CCA-treated wood as utility poles were



introduced into the country in the mid-1980's to replace the then concrete utility poles which were very expensive, had shorter life span and very cumbersome to erect. The life span of CCA-treated utility poles is between 25 to 40 years while the concrete utility poles last for about 25 years. Table 2.3 shows yearly distribution of CCA-treated utility poles in the Ghanaian environment. Volta River Authority, Ministry of Energy and some Telecommunication companies have been the sole agents in the distribution of these CCA treated poles. A statement from the facility manager at the ECG bounded warehouse alluded to the dependence on budget at hand for the level distribution of these poles in the environment. For example, in 2011, only 45,000 utility poles could be distributed throughout the country [20].

**Table 1.1 Yearly distribution of CCA treated utility poles by ECG.**

<b>YEAR</b>	<b>QUANTITY AT STOCK (LOCAL &amp; IMPORTED)</b>
<b>1985-2001</b>	ND
<b>2002</b>	14500
<b>2003</b>	15205
<b>2004</b>	16764
<b>2005</b>	17895
<b>2006</b>	20150
<b>2007</b>	22560
<b>2008</b>	25400
<b>2009</b>	29611
<b>2010</b>	37700
<b>2011</b>	45000
<b>TOTAL</b>	<b>244785</b>

Since the local industries involved in the production of treated utility poles cannot meet the local demands, ECG import treated utility poles to augment the local production. The facility manager at ECG bounded warehouse revealed that there is virtually no data covering the distribution of poles from 1985 to 2001. However, available data revealed an estimated number of 244785 poles distributed from 2001 to 2011. The treated utility poles come in two forms 11 and 9 meters for high tension and low voltage respectively.

They are erected anywhere viz: marshy areas, near water bodies, parks, playgrounds, farms and around residential facilities. Due to these wide spread uses, human exposure to this preservative is inevitable. Consequently, concerns over possible human health from exposures led to the phasing out of CCA treated wood from most residential areas in the US as at 2003. Likewise, Germany and Sweden banned the use of treated wood early 1970. In this vein, several studies have revealed that chromium, copper and arsenic leach from CCA-treated wood in the developed world particularly USA and the Western Europe. However, in Ghana, studies pertaining to the leaching of these toxic metals in the environment have not been explored. Thus the disposal of treated wood after serving their useful purposes is of great concern. Hence the purpose of this was to assess the possible leaching behavior of the Cr, Cu and As in the CCA treated wood.



Specific objectives are:

- To assess the presence and levels of Cr, Cu and As in CCA treated wood.
- To determine the levels of As, Cr and Cu in the soil around and 10 meters away from treated utility poles.
- To investigate the leaching ability of the preservative chemicals from CCA treated wood into the environment with respect to time, pH and leaching solutions.

In most nations around the world, manufactured wood products from many wood species such as teak, pine etc. normally require chemical preservative treatment if they are to be used in the environments where they may decay. The treatment involves impregnation of the wood with preservatives under pressure [15]. Often wood preservatives applied mostly are oil borne chemicals and water borne chemicals. The main water borne wood chemicals used in recent times all over the world is chromated copper arsenate (CCA). Chromated copper arsenate (CCA) preserved wood formed about 79% of the USA wood preservative market as at 1996.

These chemicals are used to treat outdoor structures like marine docks, utility poles, fences, decks, buildings or residential houses etc. Several studies confirm that large amount of chemicals impregnated are depleted as a results of the long period of exposure to the environment. A study conducted in Sweden confirms a depletion rate of 25% after an exposure period of between 20 to 43 years. Hawaii also recorded a depletion level of 22% after 44 years of exposure [16,17]. A study of the leachate levels conducted in Japan and Australia under field conditions in almost 12 months recorded concentrations of arsenic ranging from 0.1 to 8.4 mg/L [18,19].

Additionally, higher arsenic leachate levels have been recorded in parks with CCA treated decks

about 29mg/kg in Florida [21]. However, only few studies have discussed ground water contamination with these leachates. These studies indicate that leachates from the CCA treated wood can be potential contaminants in the environment [13,22 ,23].

### **The Rise and fall of CCA-Treated Wood**

The use of chemicals in the preservation of wood started as far back as 1880s. Some historic milestones are:

- **1880s:** United State- Creosote pressure-treated railroad ties
- **1911:** Commercially used as wood preservative- Copper Napthenate.
- **1926:** Celcure Company developed-Copper Chromate (CC) wood preservative
- **1933:** The technology of Chromated Copper Arsenate (CCA) was patented.
- **1933:** Marks the first time CCA treated **lumber** was sold in Europe.
- **1938:** CCA-A (the first CCA formulation) is introduced in the United States.



- **1955:** American Wood Preservers Institute (AWPI), a wood treatment industry group was established.
- **1968:** CCA-C, the most widely-used formulation for Chromated Copper Arsenate was introduced.
- **1968:** Toxicity of CCA first recorded. : report of a CCA-related worker injury occurred at Koppers, when workers fell ill after breathing CCA sawdust.
- **1972:** Dr. Ronald Hood publishes additional studies on the teratogenic effects of arsenic on fetal development in mice.
- **Mid-1970s:** Germany banned CCA-treated wood.
- **1978:** EPA began special review of toxicity of CCA
- **Mid-1980s:** Demand for CCA-treated lumber soared during the 5 years period of 1983-1988.
- **1993:** Sweden banned CCA lumber products.
- **1993:** U.S. EPA banned use of arsenic acid.
- **1994:** Demand for CCA lumber soared again, as housing started to rise by 13% in 1994.
- **1996:** Toxic arsenic levels detected in ash from wood co-generation facilities around Florida stirred controversy.
- **1999:** Arsenic was discovered in the soil at Gainesville, Florida area elementary school playground, spurring a big controversy. The playground was soon torn down and all contaminated soil was remediated.
- **March 2001:** St. Pettersburg Times released Special Report: “*The Poison in your Back Year*”. Gainesville Sun followed suit with Special Report: “*Wood Worries*”.
- **May 2001:** Environmental groups petition U.S. Consumer product Safety Commission to ban the use of CCA wood for playground equipment.
- **January 2002:** States, town and villages across the U.S. rally to ban CCA from their parks and playgrounds including the state of Massachusetts, cities of Denver and St. Louis, and even the tiny community of Healey, Alaska.
- **February 2002:** European Union considered banning CCA treated wood in its 15 member countries including Germany, Belgium, Luxembourg, France, Portugal, Spain, Italy, Greece, Austria, The United Kingdom, Ireland, Finland, Sweden, Denmark and the Netherlands.
- **February 12, 2002:** Timeline of 2 years set for voluntary phase out of CCA treated, agreement between EPA and industry stakeholders.



- **April 2002:** Canadian wood treaters and Canadian government agencies also agreed to a voluntary phase out period.
- **May 2002:** Toxic hexavalent chromium was shown to also leach from CCA wood under alkaline conditions.
- **September 2002:** Environmental Working Group (EWG) reports showed high levels of arsenic leaching out of pressure-treated wood in older decks, playsets and picnic tables.
- **December 2002:** Injuries from arsenic in CCA scraps found in landscaping mulch were reported.
- **January 7, 2003:** The European Union (EU) announced its ban on arsenic in wood preservatives such as CCA to take effect on June 30, 2004.
- **March 17, 2003:** EPA announced the finalization of the voluntary ban on residential uses of CCA to take effect on December 31, 2003.
- **January 1, 2004:** EPA's voluntary ban on manufacture of residential CCA Treated wood products in the U.S. took effect.
- **March 16, 2005:** Australia's Pesticides and veterinary Medicines Authority (PVMA) ruled that CCA treated timber will be phased out for use in play equipment [97].

### Classification of CCA

Chromated copper arsenate is a mixture of chromium, copper and arsenic oxides or salts, ( $\text{CrO}_3$ ,  $\text{CuO}$  and  $\text{As}_2\text{O}_5$ ). The arsenic and copper act as biocides while the chromium acts as a "fixing" agent to bind the metals to the wood. The percentage compositions of each CCA formulation also depend on the intended use of the wood products. However, some wood preservative industries permit other variations. The CCA fixation process refers to the chemical reactions that take place when hexavalent chromium [Cr (VI)] is reduced to trivalent chromium [Cr(III)] in the wood [23]. The chemical species occurring in the wood after fixation include  $\text{CuCrO}_4$ ,  $\text{CrAsO}_4$ ,  $\text{Cu(OH)CrAsO}_4$ ,  $\text{Cr(OH)}_3$  and a variety of metal complexes with lignin and cellulose [24, 25]. The bulk of the fixation process occur in a few days and the rate of chromium fixation depends on factors such as temperature, time and wood species [26, 27]. There are generally three different types of CCA: Type A, Type B and Type C, ( Table 1).

**Table 1. 2: Percentage composition of types of CCA [28].**

	Type A(%m/m)	Type B(%m/m)	Type C(%m/m)
$\text{CrO}_3$	65.5	35.3	47.5
$\text{CuO}$	18.1	19.6	18.5
$\text{As}_2\text{O}_5$	16.4	45.1	34.0





## **Types of Preservation**

Chemical preservatives used in the treatment of wood can be put into two (2) main groups; oil and water borne preservatives. In oil borne preservatives, oil or organic solvent are used as the carrier solution in the water-borne preservatives. Water borne preservatives normally consist of solutions of salt due to the presence of active ions [29]. Some examples of water-borne preservatives include alkaline copper quaternary (ACQ), copper boron azole (CBA), disodium octaborate tetrahydrate (DOT) and acid copper chromate (ACC) [30].

Examples of oil borne preservatives include creosote, coal tar, copper naphthenate, and copper-8-quinolinolate.

## **Functions of CCA.**

Chromated copper arsenate is a chemical preservative which renders wood durable by rendering the wood fibers useless as food source for fungi and termites. The mixture of stable metallic oxides which on contact with wood fibers form insoluble precipitates become fixed in the wood, and are expected not to migrate or evaporate. The arsenic and copper present in the preservative act as biocides with the chromium also acting as fixing agent to bind the metals to the wood [31].

## **Treatment Processes of Wood**

Wood preserving chemicals may be applied to wood in several ways. Pressure methods involve injecting chemicals into the wood in a pressure retort or cylinder. Non pressure methods include soaking, dipping, brushing and spraying. Specialized thermal and non-pressure diffusion processes can also be used for some types of application and products [32].

## **Leaching Test of CCA-Treated Wood**

The wood treatment industry and the scientific community utilize a variety of methods to evaluate preservative loss from CCA-treated wood products. One objective of such testing is to measure preservative depletion from CCA-treated wood products so that the effective service life of the product can be assessed [33]. A second objective is to measure the amount and rate of preservative leaching when the treated wood is exposed to water. This provides an assessment of potential contamination of water, soil and sediment and the resulting impacts to human health and the environment [28, 34, 35, 36]. Many investigators have employed several different testing protocols to evaluate preservative leaching from CCA-treated wood products including:

- Test in which the wood is exposed to the soil environment and preservative loss is measured over time [37, 38].
- Test in which small pieces of CCA-treated wood are leached with aqueous solutions and the preservative concentrations in the leachates are measured [39, 40].
- Test in which structures are leached with actual or stimulated rainfall and the resulting runoff is captured and analyzed [39].



Results of leaching studies are reported in several different ways, including the concentration of preservative component in the leachate (mg/L), the fraction of the original preservative leached (%) and in terms of leaching flux ( $\mu\text{g}/\text{cm}^2$  day). Since many different factors (e.g. wood type and preservative method, solution pH and ionic strength, leaching test liquid-to-solid ratio, specimen size, time of contact) impact the amount of arsenic, chromium and copper that leached from CCA-treated wood and because of the different reporting formats, care must be taken when comparing results from different studies. For example prior to the 1990s more of the leaching work began to focus on potential environmental impacts associated with preservative leaching in which CCA-treated wood was leached in a variety of different pH solutions [10]. Six 5-cm<sup>3</sup> blocks were submerged in 5 L of leaching solutions for 40 days with one experiment using a citric acid/sodium hydroxide solution to buffer the pH to 3.5, 4.5, 5.5, 7.0 and 8.5 and a second experiment adopted sulphuric acid to control pH (3.5, 4.5, and 5.5); the pH was adjusted daily. The relatively large fraction of preservative that leached prompted the researchers to conclude that leaching of CCA-treated wood in acid water may present an unacceptable environmental risk. This research received some media attention, especially as related to the possible impacts of acid rain on CCA-treated structures used in residential settings which spurred additional research into the leaching of CCA-treated wood with respect to environmental impacts.

Over the next decade, other CCA-treated wood leaching studies with specific focus on examining preservative leaching rate and the resulting potential environmental impacts were conducted. The majority of these studies focused on the impacts of metal leaching from CCA-treated wood on aquatic system [40] with American Wood Preservers Association (AWPA) publishing a new leaching protocol, E-11, that involved leaching 19-mm blocks in 300 cm<sup>3</sup> of deionized water for 14 days [5]. The water was replaced at specified intervals and the collected leachate was analyzed. In an analysis of preservative leaching from CCA-treated decks using the E-11, additional data were collected beyond the 14 days.

Other series of deck-boards were also subjected to rainfall for 300 days and measured the preservative leached by the rain [39]. In general, arsenic and copper leached more than chromium and leaching rates increase with a decrease in pH. The use of weak acids with a strong ability to complex or chelate metals (e.g. citric acid) increases the mass of metals leached above that expected to result from pH alone. As would be anticipated, the small wood specimens tested at the laboratory scale leach a greater amount of preservative relative to the larger wood products in actual use.

### **CCA-Treated Wood in Waste Stream**

Most of the studies discussed above dwelled on leaching during in-service application, i.e. leaching under environmental conditions where CCA-treated wood products are used (e.g. water bodies, terrestrial settings). Another area where the leaching of metals from CCA-treated wood poses potential environmental concern is disposal. CCA-treated wood enter the waste stream in several locations. New construction activities result in discarded scrap wood, sawdust and other debris. Demolition and renovation activities result in a large quantity of wood which often occurs in sizes and shapes the same as the original wood products. While CCA-treated wood products have a predicted in-service life of 20 to 25 years [41, 42] for lower retention treated wood (lumber, timber and fences), more recent surveys show the “actual” in-service life to be 9 years, 10 to 12 years and about 13 years, and that early retirement of the wood is attributed to aesthetics due to the effects of natural weathering [43,





44, 45]. For higher retention treated wood (utility poles and crossites), the “actual” in-service life is approximately 40 years and greater in some cases [41].

Disposal of CCA-treated wood is an issue to the solid waste managers because of the magnitude of the waste stream and the lack of viable recycling markets. A roughly estimated 140,000 m<sup>3</sup> of discarded CCA-treated wood were disposed during 2000 and that this amount was expected to increase to 900,000 m<sup>3</sup> by 2015 in the US [46]. In the US, the majority of discarded CCA-treated wood products are managed in landfills with construction and demolition (C&D) debris landfills that accept CCA-treated wood were not required to have linear systems. Leaching of preservatives from land filled CCA-treated wood poses a concern because of possible impact on leachate at lined landfills and groundwater at unlined facilities. Some CCA-treated wood is mixed with untreated wood and becomes part of the recovered wood mixture at C&D debris recycling facilities [47, 48].

The waste management profession has historically used leaching test to evaluate the risk of disposal of solid waste to the environment. Leaching tests are often a required component of solid and hazardous waste regulations. For example, in the US, the toxicity characteristics leaching procedure (TCLP) is performed to determine whether a solid waste is a toxicity characteristic (TC) hazardous waste. Unlike leaching tests designed to examine preservative leaching in aquatic and terrestrial environments data from the US solid waste regulatory leaching tests on CCA-treated wood have not been reported. Even though CCA-treated wood is no longer used for most US residential applications starting in 2004, the majority of CCA-treated woods ever sold remain in service hence disposal of this stock will be an issue for the coming decades.

### **Leaching and Analytical Procedure**

Two types of leaching procedures were performed: (1) batch leaching tests standardized by regulatory agencies and (2) modifications of standardized leaching experiment conducted to evaluate how several test variables impact leaching procedure results.

### **Regulatory Leaching Procedures**

Five regulatory-based leaching tests were performed. These were TCLP, SPLP, EPTOX, MEP and WET. In the TCLP, a buffer organic acid solution is used as an extraction fluid and this was designed to stimulate contamination leaching in a municipal solid waste (MSW) landfill environment. The acid used is acetic acid, one of the organic acids formed during the anaerobic decomposition of organic matter in MSW. The TCLP extraction fluid is prepared by adding 11.4 cm<sup>3</sup> of glacial acetic acid to 1 dm<sup>3</sup> of deionized water. 1N NaOH is then added to the mixture to maintain a pH of 4.93.

The EXTTOX a the predecessor of the TCLP requires the continual addition of acid to maintain a constant extraction pH. The method requires that the pH of the mixture be maintained at 5 by adding 0.5N acetic acid.

The SPLP is conducted in a similar fashion as the TCLP with the exception of the leaching fluid. The SPLP leaching fluid is a stimulated acid rain which is prepared by adding dilute sulphuric acid and nitric acid solution (60/40) to achieve a pH of 4.20.



The WET is used in a similar manner as the TCLP (determination of whether a solid waste is a hazardous waste). The WET leaching fluid is a buffered citric acid solution and was prepared by titrating a 0.2M citric acid solution with 4.0 N NaOH to a pH of 5.0.

The MEP is developed to estimate the potential long term leachability of contaminants from solid waste. This test employs an initial acetic acid extraction followed by sequential extractions with stimulated acid rain. The initial extraction fluid is the same as the EPTOX and the stimulated rainfall extraction fluid is similar to the SPLP [49].

### **Arsenic Contamination and Chemistry in the Environment**

Inorganic arsenic (As), largely arsenic trioxide ( $As_2O_3$ ), is a popular poison, which was used in earlier times as an efficient means of doing away with inconvenient spouses. Its widespread use as homicidal agent was stopped, however, from the 1830s when the forensic chemist Marsh, outlined a sensitive and reliable analytical method that was for the determination of As in food, wine and biological tissues [50, 51, 52]. Many epidemiological studies have clearly identified inorganic As as a human carcinogen, and its presence in drinking water in certain regions of the world threatens the health of millions of people. This contamination is widely regarded as the largest current calamity of chemical poisoning in the world [53]; and As together with fluorine (F), are the most dangerous inorganic pollutants detected in groundwater [54].

Arsenic is common trace metalloid, found in the atmosphere, soils and rocks, natural waters and organisms. It is found in variety of chemical forms throughout the environment and readily undergoes transformation by microbes, changes in geochemical conditions, and other environmental processes [55]. Naturally, As comes out into the environment by volcanic emissions, weathering reactions and biological activity. It also enters by a number of human activities. Waste materials generated by mining of sulphur ore bodies represent a significant anthropogenic source of environmental As contamination, besides manufacturing of semi-conductors, pigments, glass, metals and alloys, refining petroleum, combustion of fossil fuels and wastes, the use of arsenical pesticides, herbicides, and As as an additive to livestock feed and its continuous use for wood preservation. These works have left a profound legacy of As pollution around the world. Moreover, the combined human activity with natural reservoirs of As imposes significant human and animal health risks [53, 56, 57]. However, because of its usefulness and exploitation, As contamination is now widespread in the environment. Currently, about 60-100 million people are at risk of exposure to excessive levels of As globally, especially in India, Bangladesh, China, Vietnam, South America, and parts of Europe [54].

Thus among the various sources of As in the environment, drinking water is mostly the one which threatens and affects human health. The combination of high toxicity and widespread occurrence has created urgent need for effective monitoring and measurement of As in soils, surface waters and groundwater. The elevated levels of As in groundwater are usually associated with a natural mineralogical source. Those who depend on ground bore waters for drinking and domestic purposes could place themselves at risk. Increased incidence of prostate cancer in Victoria, Australia and in Utah, USA has been linked to drinking waters having high levels of As [53].



Because of the increased evidence for the chronic toxicological effects of As in drinking water, recommended and regulatory limits of many countries and authorities have reduced. The WHO guideline value for As in drinking water was provisionally reduced in 1993 from 50 to 10  $\mu\text{g L}^{-1}$ . The new value rests on the increasing awareness of the toxicity of As, especially its carcinogenicity, and the ability to quantify it [58]. In like manner, the EC and US-EPA have reduced As in drinking water from 50 to 10  $\mu\text{g L}^{-1}$ . Yet, developing nations, the most As affected operate presently at 50  $\mu\text{g L}^{-1}$  standard because of lack of financial support for scientific research to measure such lower concentrations. Accordingly, the need exists for As monitoring at sites supposedly contaminated because of the high toxicity and the widespread occurrence, such as landfills, facilities handling As containing wastes, and sites where As is found at toxic concentrations in groundwater likewise leaching of As from treated wood is a possible health concern as there exist the potential for soil and groundwater contamination. In cognizance of these, many studies had been carried out around the world, especially in most developed nations, not only in USA.

### **Groundwater Arsenic Problems**

Water drawn from unconsolidated/bedrock aquifers accounts for most of the municipal and private drinking water supply in most countries. The natural chemistry of groundwater relates to the geochemistry of the aquifer materials through which it flows and the residence time of the water in those aquifer materials. Now there is growing evidence that the source of As in groundwater is dominantly natural and originates from minerals in the rocks as reported in North and South America, Europe and Asia. Studies in parts of Australia, USA and Canada suggest geologic sources as indicated. Anthropogenic sources of As like treated lumber and manufacturing may contribute to groundwater contamination [59].

Bangladesh, in Asia was the first area in which health risks associated with As groundwater contamination noticed. An estimation of about 30-35 million people in the area were believed to have been exposed to high As levels which far exceeded the recommended guideline value. This calamity was one of the greatest environmental disasters, the worst case of mass poisoning of water in the world. The most common external manifestation of As poisoning was skin disorders including hyper/hypopigmentation changes and keratosis [53, 60].

West Bengal, India also saw catastrophic proportions of Arsenic contamination in groundwater. The presence of high inorganic As was linked to severe ailments (e.g. gastroenteritis, skin and liver cancer). Many inhabitants were exposed [61, 62]. The number of patients with arsenicosis in West Bengal (India) was over 200,000 [100].

Large areas of China also face(d) severe As exposure from groundwater contamination. Over 3 million people were or are estimated to be affected [63]. In Shanxi Province alone, an estimated 900,000 people are at risk of arsenocosis; and the belief is that many of the wells give water containing As concentration higher than 50  $\mu\text{g L}^{-1}$ , according to a recent report [53, 54].

Other nations where As concentrations occur above 50  $\mu\text{g L}^{-1}$  are Mexico, Chile, Hungary, Argentina, Romania, Taiwan, Vietnam and some parts of the USA, Nepal, Thailand, and Cambodia [53]. However, in Ghana, such studies are limited as such, As contamination of groundwater and its health implications have not been much investigated.



## Arsenic in the Environment

Fluxes of As in the environment originate via natural and anthropogenic sources. The ratio of natural and anthropogenic inputs is 60:40 and there is a general agreement that most anthropogenic inputs are from smelting operations and fossil fuel combustion [64]. **Natural Sources**

Arsenic (As) is ubiquitous in nature. It occurs in detectable concentrations in all soils and nearly all other environmental media. The occurrence of As in the earth's crust ranges 1.5-2.0 mg L<sup>-1</sup> (ppm). Arsenic ranks 20<sup>th</sup> in crustal abundance, ahead of molybdenum and is a major constituent of more than 245 minerals of which 60 % are arsenates, 20 % sulphides and sulphosalts, 10 % are oxides and 10 % comprise arsenide, native elements and metal alloys found in high concentrations in sulfide deposits as arsenides, sulphides, and sulpho-salts [63, 65]. Table 2.1, gives some examples of As containing minerals.

The geologic background of a particular soil determines its native As content. Soils with overlying sulphide ore deposits usually contain large amounts of As. Arsenic concentrations of the rocks depend on rock type, with sedimentary rock showing content ranging 0.3-500.0 mg L<sup>-1</sup> while igneous rock with higher content ranges 1.5-3.0 mg L<sup>-1</sup>. Natural processes affecting As mobility, therefore result in the introduction of As into aqueous phases are weathering of rocks, geo-chemical reactions, contact between As -bearing sediments and aquifers, volcanic emissions and atmospheric deposition of As into water bodies [69]. Aside its higher concentration in sulphide minerals, As occurs in geological materials such as shales, phosphorites, iron, cherts, limestone and manganese ores [53].

**Table 1.3. Few arsenic ores occurring in nature.**

Mineral	Composition
Niccolite	NiAs
Realgar	AsS
Orpiment	As <sub>2</sub> S <sub>3</sub>
Cobaltite	CoAsS
Arseno-Pyrite	FeAsS
Tennantite	(Cu,Fe) <sub>12</sub> As <sub>4</sub> S <sub>13</sub>
Enargite	Cu <sub>3</sub> AsS <sub>4</sub>
Arsenolite	As <sub>2</sub> O <sub>3</sub>
Claudetite	As <sub>2</sub> O <sub>3</sub>
Scorodite	FeAsO <sub>4</sub> .2H <sub>2</sub> O

## Anthropogenic Sources

Today, man's activities have resulted in the introduction of large quantities of As into the environment, through direct release, loss or waste. The annual world production of As has been increasing in the past 60 years. At present, the global production of As is approximately 75,000 to 100,000 metric tons year<sup>-1</sup>. Sweden is the world's largest producer of As, while the US consumes about 50 % of As produced worldwide [66].



Arsenic trioxide is a byproduct from the smelting of As containing ores of copper, iron, zinc, lead, gold, silver, manganese and tin. Therefore, the quantity of As produced relates to the level of production of these metals. Arsenic trioxide, also known as white As constitutes 97 % of As that enters product manufacturing. Combustion of fossil fuels and smelting of sulphur-containing ores both contribute significantly to the release of As (primarily  $As_2O_3$ ) into the atmosphere. Coal, fly ash, clays and shale usually exhibit high As concentrations. About 2.5 g of As is released into the atmosphere for every ton of coal burnt [53]. Arsenic released into the atmosphere is predominantly in particulate forms, and therefore, rapidly removed from the atmosphere via both wet and dry precipitations, and ultimately reaching surface and ground waters. Additionally, migration of As from discarded CCA-treated wood is another good source of As to the environment during its life service as well as when it is weathered. The possible environmental impacts upon disposal raise concern, most notably for As. When CCA-treated wood burned, As can be released to the air and soil and when it in landfill, As can leach into groundwater. Thus CCA-treated wood may pose risk to groundwater and soil [67].

### **Arsenic – Chemistry in the Environment**

Arsenic (atomic number 33), appears in Group V of the periodic table. It has an atomic weight of 74.92 g, and is one of the most widely distributed elements in the earth's crust and in the biosphere. It is steel-grey, brittle, crystalline metalloid with two main allotropic forms that are yellow and metallic grey. The latter is the stable form under ordinary conditions. However, it tarnishes in air, when heated, rapidly oxidizing to arsenious oxide ( $As_2O_3$ ) [53, 66].

Arsenic exists in four-oxidation states: -3, 0, +3 and +5. Elemental As ( $As^0$ ) occurs rarely in nature, formed by the reduction of As oxides, whereas traces of toxic arsines can be detected in gases emanating from anoxic environment [115]. Both arsines and methylarsines, which have an oxidation state of (-3) are unstable in air. Arsenic trioxide ( $As^{3+}$ ) is a product of smelting operations and is the raw material, used in the production of most arsenicals. Oxidation of  $As_2O_3$  leads to the formation of Aspentoxide ( $As^{5+}$ ).

Arsenic covalently bonds with most of the non-metals, metals, and forms stable organic compounds in its trivalent and pentavalent states [53].

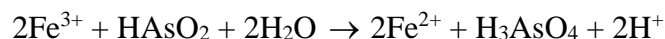
### **Environmental Biogeochemistry of Arsenic**

Once As is released into the environment (particularly soils and sediments) from natural or anthropogenic sources, abiotic and microbiological processes contribute to its transformation between inorganic and organic forms. The abiotic processes include oxidation, co-precipitation, surface complexation and reduction reactions of As. Arsenic also undergoes biotransformation once it gets inside the living cells. Both biotic and abiotic chemical processes of As are discussed below.

#### *Abiotic oxidation of arsenite ( $As^{3+}$ ) to arsenate ( $As^{5+}$ )*

This process occurs through the oxidation of  $As^{3+}$  by  $Mn^{4+}$  and  $Fe^{3+}$



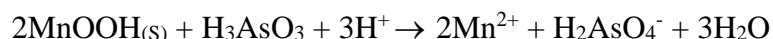


$\text{Mn}^{4+}$  and  $\text{Fe}^{3+}$  are very effective in the oxidation of  $\text{As}^{3+}$  to  $\text{As}^{5+}$  by electron transfer mechanism. In addition, the oxidation of arseno-pyrite ( $\text{FeAsS}$ ) by  $\text{Fe}^{3+}$  is responsible for the release of As into the groundwater in areas where waters are highly contaminated with As



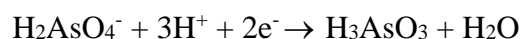
*Co-precipitation of  $\text{As}^{3+}$  to  $\text{As}^{5+}$*

$\text{As}^{3+}$  co-precipitation with Mn (III) oxide/Manganite



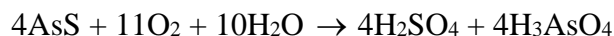
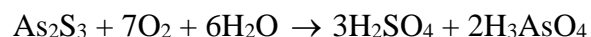
*Reduction of  $\text{As}^{5+}$  to  $\text{As}^{3+}$*

The formation of sulphides in reducing environments accompanies the reduction of  $\text{As}^{5+}$  to  $\text{As}^{3+}$ .



*Oxidation of arsenic-sulphide compounds*

The As-sulfide compounds can undergo oxidation-releasing arsenic into water bodies.



*Biotransformation of arsenic in the environment*

Many aquatic organisms are capable of accumulating As and may catalyze the oxidation of  $\text{As}^{3+}$  to  $\text{As}^{5+}$  while promoting the formation of methylarsines through biomethylation reaction [53, 68].



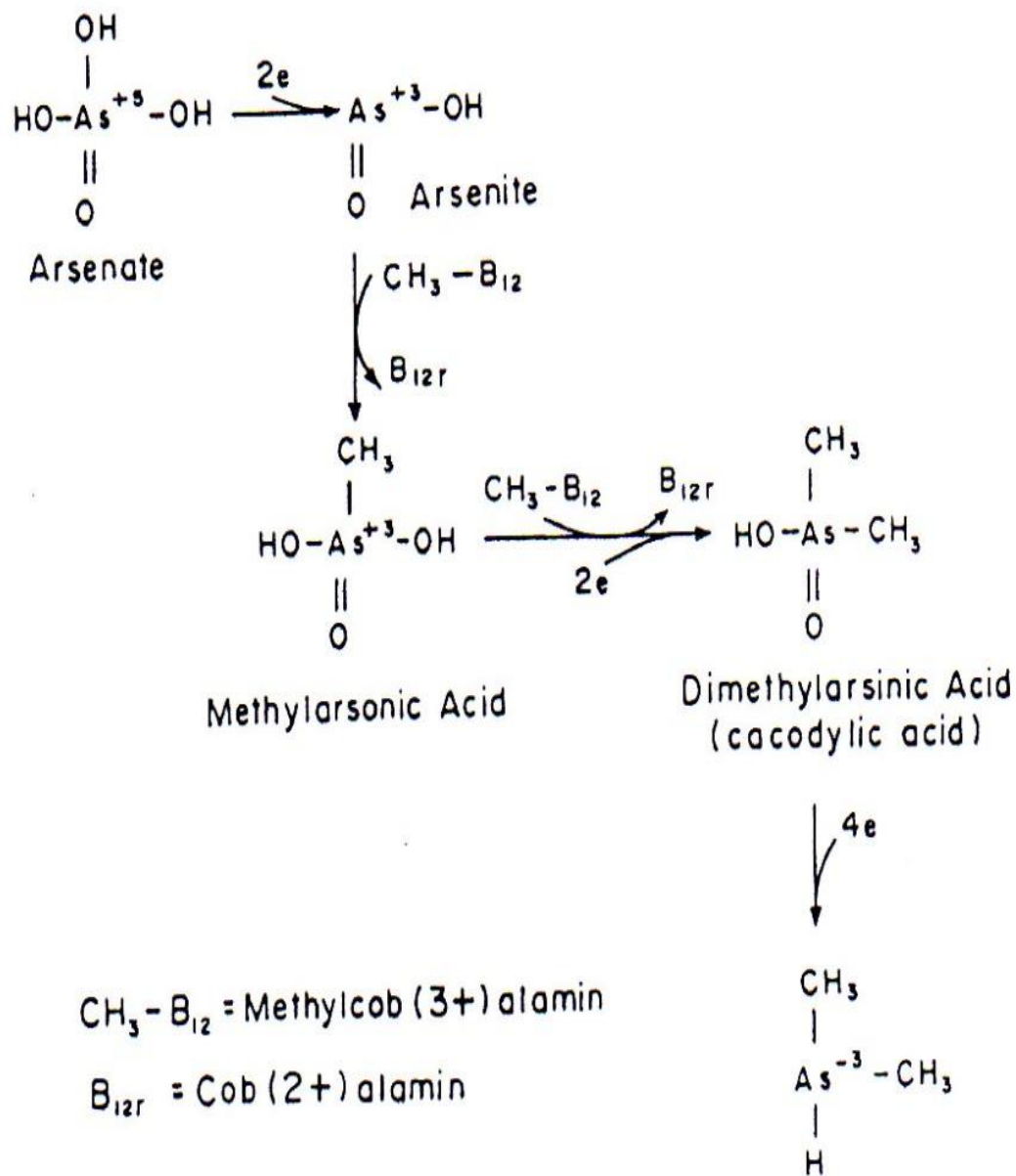


Fig 1.1 Biotransformation of arsenic in the environment [96].



## Biological Cycle of Arsenic

Arsenic like mercury, when it enters the environment undergoes transformation through the metabolic activities of microorganisms (bacteria and fungi). Fig. 2.1 shows the biochemical pathway leading to the formation of methylated As compounds. Inorganic arsenate is first reduced to arsenite, which is then methylated to form methylarsonic acid. Reductive methylation of methylarsonic acid results in the formation of dimethylarsinic acid (cacodylic acid). This acid is then reduced to form dimethylarsine. Methylarsonic acid never reduces in the absence of a methyl donor, which suggests a second methylation must occur before the compound can reduce to arsine. However, dimethylarsinic acid reduces rapidly to alkylarsine even in the absence of methyl donor (Fig. 2.1) [53, 71].

## Arsenic and Human Health

Arsenic is a human carcinogen. The major sources of As exposure are food, drinking water, soil and air; and it affects the important functional organs of human body. It interferes with the functioning of the lungs, genes, heart, kidneys, liver, brain, immune system and the reproductive system. The three most common biomarkers of As are As levels in hair, nails and blood. The US-EPA has classified As as a group-A human carcinogen. The various means by which human become exposed to As, are discussed below:

### Routes of exposures of AS

The main source of As exposure is food, but this channel contributes little to the overall risk associated with the metal exposure because dietary As includes primarily organic forms which are relatively non-toxic.

Majority of harmful As exposure comes from drinking water from wells drilled through As bearing rocks. Drinking water primarily contains inorganic As in the forms,  $As^{3+}$  and  $As^{5+}$ . Arsenite tends to be more toxic in human than  $As^{5+}$ . This is because it binds to sulphhydryl groups in enzyme systems essential for metabolism, which inhibit their action. It also affects respiration by binding to the vicinal thiols in pyruvate dehydrogenase and 2-oxo-glutarate dehydrogenase. In recent times, As is believed to interact with glucocorticoid receptor. Arsenate on the other hand is a molecular analog of phosphate and inhibits oxidative phosphorylation. This affects cellular energy production, thus short-circuiting man's life energy [69, 70].

Chronic As exposure via drinking water has adverse health effects on human, from skin and internal cancers of the bladder, kidney, liver, lung, colon, uterus, prostate and stomach. Other examples are diabetes mellitus and vascular, reproductive, developmental and neurological effects [62, 71].

The non-cancer effects also arise from both chronic and acute exposure. Among those symptoms linked with acute exposure are abdominal pain, vomiting, diarrhoea, muscular weakness and cramping, pain to the extremis, erythematous skin eruptions and swelling of eyelids, feet and hands. A progressive deterioration in the motor and sensory responses may also result, finally leading to shocks and death. Non-cancer effect of chronic As poisoning includes anemia, headache, confusion, hypertension, diabetes, atherosclerosis and a variety of skin lesion.



Arsenic is known to exist primarily in inorganic forms, but monomethylarsic acid (MMA) and dimethylarsic acid (DMA) have also been found in some soil extracts [72]. Soil and waterborne As does not readily permeate the skin. Soil can be a key source of exposure in the young children who show significant hand-to-mouth activity.

Human exposure is on more sporadic basis through a hodgepodge of human activities, such as burning of fossil fuels, waste incineration, smelting of ores, pesticide and herbicide use, coal burning, semiconductor production, and other manufacturing processes. The public impact of these exposures is largely unknown as the epidemiologic focus has been on exposure via drinking water.

Exposure could also be through direct inhalation of arsine, the most toxic compounds of all arsenicals. It is detectable in gases emanating from landfills, anaerobic waste water treatment facilities and in headspace samples collected from a hot spring environment [73].

### ***Copper Contamination and Chemistry in the Environment***

Copper (Cu) with atomic number 29 appears in group 1B of the transition elements of the periodic table and has atomic mass of 63.546 amu. It occurs in four oxidation states  $\text{Cu}^0$ ,  $\text{Cu}^{+1}$ ,  $\text{Cu}^{+2}$  and  $\text{Cu}^{+3}$  with  $\text{Cu}^{+2}$  being the most common [74]. Cu has two isotopes the most abundant being  $^{63}\text{Cu}$  and the other one being  $^{65}\text{Cu}$ . Cu is reddish in colour in its metal state with a bright metallic luster, is malleable and ductile, and is a good conductor of heat and electricity with boiling point of 2567 °C, melting point of 1083.4 °C and specific gravity of 8.96  $\text{gcm}^{-3}$  at temperature of 20 °C. Copper is ranked 26<sup>th</sup> in abundance in the lithosphere [75]. Cu is found in many minerals [76].

**Table 1.5.** Major copper ores occurring in nature

<b>Mineral</b>	<b>Composition</b>
Chalcopyrite	$\text{CuFeS}_2$
Chalcocite	$\text{Cu}_2\text{S}$
Bornite	$\text{Cu}_5\text{FeS}_4$
Tetrahedrite	$(\text{CuFe})_{12}\text{Sb}_4\text{S}_{13}$
Cuprite	$\text{Cu}_2\text{O}$
Malachite	$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$
Azurite	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
Bonchantite	$\text{Cu}_4\text{SO}_4(\text{OH})_6$
Antlerite	$\text{Cu}_3\text{SO}_4(\text{OH})_4$



### ***Atmosphere***

Both anthropogenic and natural sources contribute to the presence of Cu in the atmosphere. Copper mining, metal smelters, waste incineration, agricultural and industrial application and combustions are various ways in which Cu is introduced into the atmosphere. Natural sources may include forest fires and volcanic particulates. The forms of Cu released from combustion and high temperature sources are generally assumed to exist as oxides (CuO and Cu<sub>2</sub>O) but also as elemental Cu (vapour) and as Cu adsorbed onto sub-micron particulates. Sulphation may also be an important transformation process as metallic oxides age [77, 78].

### ***Water and sediment***

Copper occurs in aquatic system predominately in the more stable Cu<sup>+2</sup> state. Cu<sup>+1</sup> is unstable over the range of pH normally encountered in aerated surface waters and readily oxidizes to the Cu<sup>+2</sup> state [78, 79]. Cu may associate with water to form the free aquo-cupric ion [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>+2</sup> [80]. In natural water very little free hydrated copper is present because it readily complexes with both inorganic and organic ligands and or may adsorb onto clays, sediments and organic particulates. Factors that may influence the adsorption of Cu include pH, Cu concentrations, competing cations and the adsorbents' properties

Desorption of Cu may also occur particularly in the presence of high concentration of competing cations such as Ca<sup>+2</sup> and Mn<sup>+2</sup> [81]. The ion Cu<sup>+2</sup> can complex with OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> in water to form Cu(OH)<sup>+</sup> and Cu(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>.

Because of this complexing with CO<sub>3</sub><sup>2-</sup> the bioavailability of Cu decreases with increasing water hardness. In surface water Cu<sup>+2</sup> will form complexes with wide range of organic compound such as humic and fulvic acids and in fresh river water 76% to 99% of Cu can occur as organic complexes [81]. Under anaerobic conditions in reduced environment Cu will be present as cuprous oxide, metallic copper and copper sulphate.

### ***Soil***

The major physical and chemical processes that affect the transport and distribution of copper and its soil complexes in soil are adsorption, aqueous-phase solubility, leaching and lateral movement

### ***Adsorption and mobility***

Cu is strongly adsorbed to soil particles and therefore has very little mobility relative to the other trace metals and as a result of this limited mobility applied Cu tends to accumulate in soil and eventually ends up in one of the six pools [75].

- Dissolved as soluble ions or as inorganic as well as organic complexes in soil solution
- Adsorbed onto exchange site of Mn, Fe and Al oxides and hydroxides
- Adsorbed onto exchange site on complexes with organic matter
- Adsorbed on the clay-humus colloidal complexes
- Fixed in the crystal lattice structure of soil minerals or
- Occluded in the stable organic complexes in humus.



Factors that may influence the distribution of Cu in each of the pool are pH, cation exchange capacity CEC of the soil, organic matter content of the soil, amount and type of clay, presence of oxides of Mn, Fe and Al and the reduction-oxidation potential of the soil [85, 86]. In general, Cu solubility decreases as pH increases which was proved later that, the capacity of soil to absorb Cu increased with increasing pH with a maximum holding capacity of neutral to slightly alkaline conditions pH 6.7- 7.8[84, 85]. Furthermore, soils with alkaline conditions tend to favour precipitation of Cu, thus Cu is more mobile under acidic than alkaline conditions [84].

### ***Aqueous-Phase Solubility***

Cu is insoluble in hot and cold water, however, Cu in minerals tend to be more soluble than the native Cu element [83]. In solution Cu exists as divalent  $\text{Cu}^{+2}$  or as one of the stable complexes of ions over a range of pH soil may contain several other forms of Cu including  $\text{CuSO}_4$ ,  $\text{CuCl}_2$ ,  $\text{CuCO}_3$ ,  $\text{Cu(OH)}_2$ . While in the soil solution Cu and its complex species are subjected to ion exchange. Solubility and mobility of Cu may be increased by the presence of dissolved organic matter and surfactants in the soil or in sewage sludge applied to soil. As a result of competition for the available exchange site between the various cations in the soil solution  $\text{H}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ , the speciation of Cu depends strongly on the chemical composition of the water phase and the particles [86].

### ***Leaching and Lateral Movement***

Copper is one of the least mobile trace elements because of its ability to specifically adsorb to soil particles and therefore applied or deposited Cu will persist in soil for a long time because it is strongly adsorbed to organic matter, oxides of Fe, Al and Mn and clay minerals [85]. Significant leaching of Cu in the soil profile can occur as a result of changes in the pH, organic matter and soil texture. Decrease in pH increases Cu solubility thereby increasing its mobility. Leaching of Cu however, occurs only during a prolonged artificial rainfall with a pH of 2.8. Copper was reported to start to chelate at pH below 4.7 and begin to desorb at pH 3.0. Therefore acidic rainfall will not result in significant leaching of Cu from organic soil unless the pH of the rainfall decreases to level below 3.0 [84].

### ***Copper and human health***

Copper is required in the formation of hemoglobin, red blood cells as well as bones, while it helps with the formation of elastin as well as collagen - making it necessary for wound healing. A lack of copper may also lead to increased blood fat levels. It is also necessary for the manufacture of the neurotransmitter noradrenaline as well as for the pigmentation of hair. On other hand, toxic levels will lead to diarrhea, vomiting, liver damage as well as discoloration of the skin and hair, while mild excesses will result in fatigue, irritability, depression and loss of concentration and learning disabilities [87].

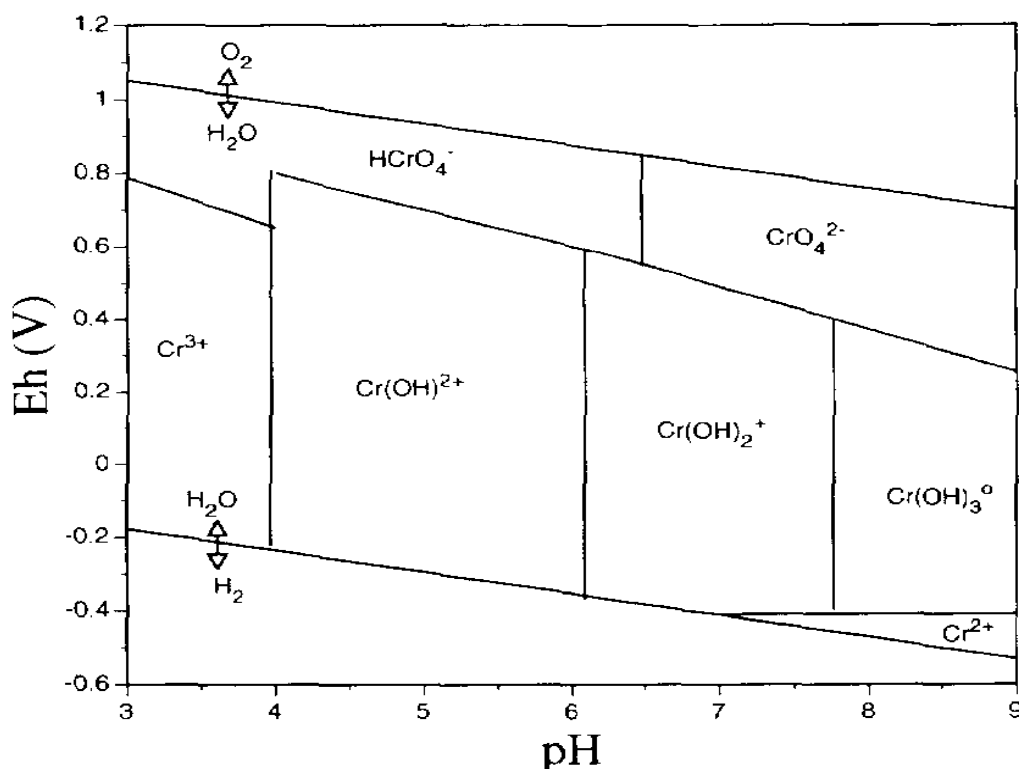
### ***Chromium in the Environment***

Chromium (Cr) with atomic number of 24 and atomic mass of 51.9961 amu is one of the world's most strategic and critical materials having a wide range of uses in the metals and chemical industries. Cr alloys enhance metal resistance to impact, corrosion, and oxidation. Cr is used in stainless steel and non-iron alloy production for plating metals, development of pigments, leather processing, and production of catalysts, surface treatments, and in

refractories. Cr is solid with shiny and silvery in colour as well as hard and brittle at room temperature, generally react with halogen gas such as fluorine at high temperature of 400°C and pressure of 200 to 300 atm. Cr occurs in the atmosphere as chromite ( $\text{FeCr}_2\text{O}_4$ ) with boiling point between 2672 °C – 2945.15 °C, melting point 1857 °C – 2130.15 °C and density of  $7.19\text{gcm}^{-3}$  at 293K. Cr has four naturally occurring isotopes  $^{50}\text{Cr}$ ,  $^{52}\text{Cr}$ ,  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$ . The oxidation states of Cr ranges from -2 to +6 and the most stable oxidation state is +3. Cr(VI) is not as stable as Cr(III) because it is a strong oxidizing agent, fast reacting and likely to form complexes.

### *Chemical State of Cr in the Environment*

Chromium is the tenth most abundant element in the earth mantle and its elevated soil and water concentrations result principally from industrial waste or spills. Although, Cr(III) is not significantly hazardous in itself, the potential oxidation to Cr(VI) can makes it risk rather than that of Cr(VI) form. Cr(VI) is commonly very mobile in soil and water because it forms anionic species. Although Cr(VI) is therefore not appreciably retained by the negatively charged colloid in soil, it is adsorbed on many hydrous oxides. In addition to the possibility of immobilizing Cr(VI), this species can be reduced to Cr(III) which alleviates the hazard imposed by Cr(VI) and the possibility of oxidation of Cr(III) back to Cr(VI) must be considered. Organic matter (both soluble and insoluble) and Fe(II) and sulphide are capable of reducing Cr(VI) as Cr(III) poses little hazard to biological activities Cr(VI) is very toxic to living matter.



**Fig 1.4 Phase diagram depicting the thermodynamic stability of aqueous Cr species over a range of Eh and pH values in surface environment [86, 88].**





The formation of Cr(III) hydrolysis products at such a low pH has important implications on the sorption and solubility of its ions, hence Cr (III) retention on soil minerals should be appreciable under most pH values encountered. Under oxidized conditions Cr(VI) is often the thermodynamically most stable oxidation state of Cr solely based on the redox potential. Both the chromate  $\text{CrO}_4^{2-}$  and dichromate  $\text{Cr}_2\text{O}_7^{2-}$  with the protonated chromate species  $\text{HCrO}_4^-$  are potentially formed in the surface environment. All the Cr(VI) species will be anionic thus exhibiting a much greater mobility and bioavailability than Cr(III) in soil.

### ***Retention of Cr(VI)***

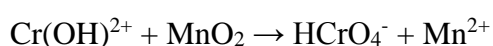
Reactions that immobilize Cr(VI) do not alter its toxicity but they do however decrease the risk imposed by the ions and the environmental risk of sorbed Cr(VI) is then dependent on the sorbent stability. Cr(VI) does not form an inner sphere complex on Fe hydrous oxide and similarly it is expected that Cr(VI) also forms an inner sphere complex on Al hydrous oxide. Therefore, precipitation of the Fe or Al hydrous oxides in situ may provide a means to diminish the risk imposed by Cr in Cr(VI) contaminated sites. In soils with low levels of Al and Fe hydrous oxides, one should be aware that there may be a very low capacity for Cr(VI) sorption.

Hydrous oxides of Fe and Al often are present in significant levels in surface environment, hence they commonly have a net positive charge and potential chemical affinity for Cr(VI) [89].

### ***Reduction and Oxidation of Cr(VI)***

Reactions that reduce Cr(VI) to Cr(III) are of great importance since the hazard of this element will be decreased. Various species in soil and water have the capacity to reduce Cr(VI); organic material, sulphides and ferrous iron. One may expect that under reducing conditions Cr(VI) would directly transform to Cr(III) but this however is not always the case. Kinetic limitations based on electron symmetry constraints in the electron transfer process stabilized the existing Cr oxidation state (either Cr(III) or Cr(VI)) unless a suitable redox couple directly complexes with Cr species. The toxicity of Cr(VI) makes it useful for controlling biological activities in a system where microbial contamination may be detrimental. In soil Cr(VI) may oxidize and itself be reduced by both living tissues as well as residual organic matter [90]. Soil high in organic matter have proven to be effective in reducing added Cr(VI) regardless of the soil pH while less degraded organic matter such as cow manure have a more limited influence of Cr(VI) [91]. Reduction of Cr(VI) by organic matter results in Cr(III) and an organic product and although reduction of Cr(VI) is environmentally beneficial, in the presence of soluble organic chelating agent there is a high probability of forming a soluble Cr(III) complex. These organic complexes may be very stable and thus eventually complex with Mn oxide which may lead to the reoccurrence of Cr(VI) in the soil and water a most unfortunate consequence [92].

Most oxidation of Cr(III) to Cr(VI) represent a significant environmental hazard since a rather innocuous species is transformed into toxic one. Mn oxide has proven to be the only naturally occurring oxidant of Cr(III).





Various factors are possible which could limit the oxidation process such as the alteration of the  $\text{MnO}_2$  surface by retention of the reaction products or reactants. Reaction products were eliminated as the source of oxidation inhibition and direct microscopic and spectroscopic evidence revealed that the cause of inhibition was a  $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$  surface precipitation on the  $\text{MnO}_2$  [93].

### ***Exposure Pathway***

For some a significant health concern is the possible adverse effect of human ingestion of Cr(VI) in drinking contaminated groundwater or surface water. This is still being debated within the scientific community. Dermal contact through bathing or washing in Cr(VI)-contaminated water is another exposure pathway. Chromate ( $\text{CrO}_4^{2-}$ ) is a mineral containing the chromate ion,  $\text{Cr}_4^{2-}$ .

An example of chromate is potassium chromate,  $\text{K}_2\text{CrO}_4$ . Chromates can enter the bloodstream through breaks in the skin.  $\text{CrO}_4^{2-}$  blood poisoning occurs when  $\text{CrO}_4^{2-}$  destroys red corpuscles. Inhalation is also an important human exposure pathway; however, it is less likely to be associated with exposure to Cr(VI)-contaminated soils and groundwater and more likely associated with industrial processes such as welding, cutting, heating of Cr alloys, and work related practices. For dermal exposure, chromated copper arsenate (CCA) pressure-treated

lumber is ubiquitous in residential areas. This green-colored pressure treated lumber is used for building residential decks, picnic tables, swing sets, and other play structure [94].

### ***Chromium and human health***

Chromium is an essential nutrient required for normal sugar and fat metabolism and works primarily by potentiating the action of insulin but an elevated amount can lead to certain illness such as lung cancer through airborne contamination, irritation or damage to the nose, throat, lung, eye and skin. These illnesses associated with Cr are noticed by symptoms such as sneezing, coughing, itchy and burning sensation.

Though these heavy metals are essential for biological activities in small quantity, elevated amounts of these metals may lead to chronic toxicity. Many illnesses have been associated with the exposure to these metals. As enumerated above, these ailments may include damaged or reduced central nervous and mental function; lower energy level; damage to lungs, kidney, liver and other important organs [95].

### ***Analytical methods for As, Cu and Cr Determination***

Arsenic (As) in environmental media (water and soil) can be determined in the laboratory using the following fixed laboratory assays. They are, the Atomic Absorption Spectroscopy (AAS), Atomic Fluorescence Spectroscopy (AFS), Graphite Furnace Atomic Absorption (GFAA), Hydride Generation Atomic Absorption Spectroscopy (HGAAS), Inductively Coupled Plasma-Emission Spectrometry (ICP-AES), and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). These instruments accurately measure As in environmental sample to parts per billion (ppb) concentrations i.e.  $\mu\text{g L}^{-1}$  and  $\mu\text{g Kg}^{-1}$  for water and solid samples respectively [66]. Before As is determined with any of these instruments, pretreatment with acidic extraction or acidic oxidation digestion of the sample is required. The significance of

pretreatment is that all As species is converted into the inorganic form for easier detection and measurement. These laboratory assays measure As accurately but they are expensive to operate and maintain.

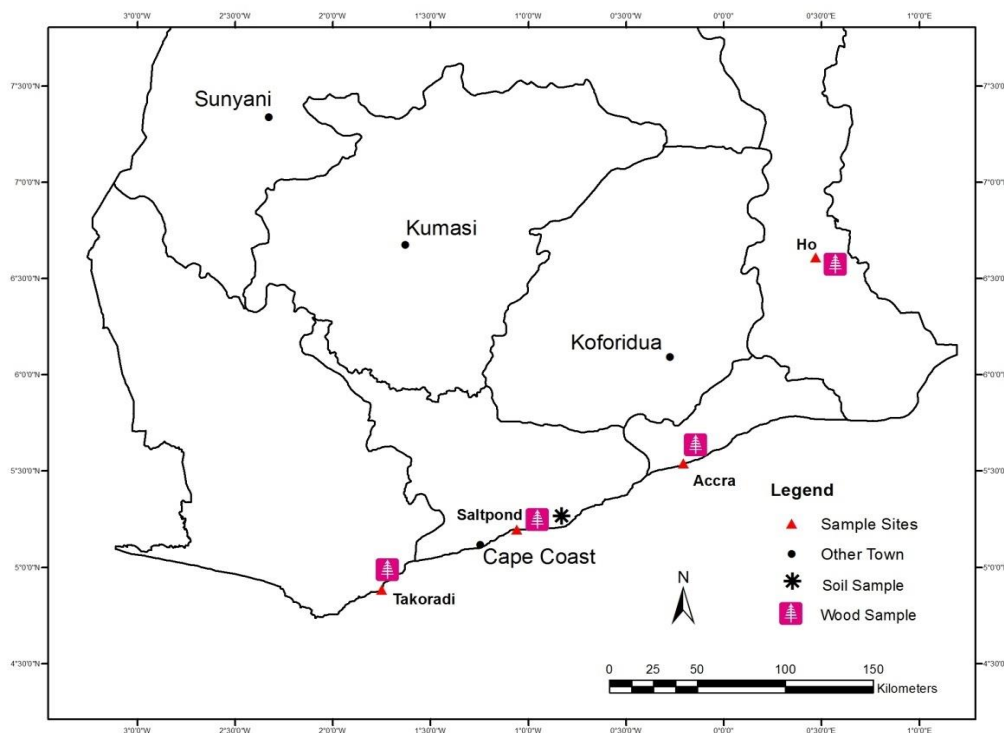
### *Portable x-ray fluorescence*

Another effective technology for detecting As in the field is the use of X-ray fluorescence. It directly measures soil samples for example, soil without requiring aqueous extractions. This technology involves radiation of environmental samples with X-ray or gamma rays. For As detection, a sealed  $Cd^{109}$  radioisotope source is often used. After the sample irradiation, the sample atom may absorb a photon, dislodging an electron from the inner shell of the atom. In this process, known as the photoelectric effect, an electron that cascades in from outer electron shells fills the resulting vacancy. This rearrangement of electron results in emission of X-rays characteristic of each atom, termed X-ray fluorescence (XRF). This combination uses a specific energy photon for the photoelectric effect while precisely measuring the energy of the XRF photon emitted by the sample to allow for an accurate identification of the elements in the sample. Presently, there are portable XRF devices to measure As in groundwater down to  $50 \mu g L^{-1}$  [55].

## METHODOLOGY

### Study Area

The study area is the southern part of Ghana where most of these CCA-treated utility poles manufacturing companies are located.



**Fig. 3.1** Map showing the sampling areas (southern Ghana)

## Materials and Methods

New polypropylene containers were obtained and used. The polypropylene containers were rinsed with de-ionized water and immersed in warm soap bath for 48 hours. The containers were later rinsed with de-ionized water and then immersed in 10% HNO<sub>3</sub> solution at room temperature for another 48 hours. Containers were rinsed with de-ionized water and then immersed in 50% HNO<sub>3</sub> bath for 24 hours. The containers were further rinsed with de-ionized water containing 1% high purity HCl. They were later capped and placed overnight in a clean oven at 60°C. The containers were then removed from the oven and allowed to cool. The acidified water was discarded and the oven drying repeated. Containers were rinsed three times with de-ionized water and then filled with de-ionized water acidified with high purity HCl. The containers were tightly capped and double bagged in re-sealable polyethylene bags and stored. All glassware and other apparatus such as crucibles used in this project were also pre-cleaned in the same way as described above. Reagent blanks and reference material were incorporated in the digestion procedure.

## Sample Collection

Both wood and soil samples were collected. Soil samples were collected from different environments (Fig. 3.2-6). Treated and untreated dimensionless lumber were obtained from sale agents of the CCA-treated wood companies in Ghana.



**Fig 3.2 Some finished CCA treated poles packed in the sun ready to be transported across the nation.**





**Fig 3.3 CCA treated poles sited around residential facilities**



**Fig 3.4 CCA utility poles erected on school compound.**



**Fig 3.5 CCA utility poles sited about 100 meters from the beach**



**Fig 3.6 CCA utility pole erected in backyard okra garden**





Dimensionless weathered treated woods were gathered from out of service CCA-treated utility poles left in the environment from Accra in the Greater Accra region and Saltpond in the Central region. Imported CCA -treated utility poles from Chile was also obtained from the Electricity Company of Ghana, Saltpond sub-station.

**Table 3.1: Statistics of CCA Wood Samples**

<b>Location</b>	<b>Treated (New)</b>	<b>Treated (Weathered)</b>	<b>Untreated</b>
<b>Takoradi</b>	1	0	1
<b>Ho</b>	1	0	1
<b>Accra</b>	0	1	0
<b>Saltpond</b>	0	1	0
<b>Chile (Foreign)</b>	0	1	0
<b>Total</b>	<b>2</b>	<b>3</b>	<b>2</b>

Soil samples were collected from five identified locations within Saltpond district viz: residential houses, school playground, beach, sales point and backyard garden. The soil samples were collected at distances of 50 meters apart in between in-service CCA-treated utility poles in duplicates. All soil samples were collected with plastic spoon into zip lock polyethylene bags tightly closed and stored in refrigerator until analysis.

### **Chemicals and Reagents**

Analytical grade reagents were used. Digestion of wood, wood ash and soil samples were performed using 68% HNO<sub>3</sub> and 63% HClO<sub>4</sub>. De-ionized water was also used for all the analytical work. Synthetic Precipitation Leaching Procedure (SPLP) solution was also prepared using 98% H<sub>2</sub>SO<sub>4</sub> and 68% HNO<sub>3</sub>.

### **Sample Preparation**

Sawdust and block samples were generated by cutting and drilling dimensionless lumber with electronic hand drill and cutter, collected into re-sealable polyethylene bags and closed. These were stored at room temperature in the laboratory till analysis. For newly treated wood samples, analytical portions were obtained from dimensionless lumber at three different regions top, mid-way and bottom respectively.

### **Ash Generation**

Ash samples were generated from sawdust from the various wood samples by combustion in a laboratory furnace. The sawdust samples were weighed into pre-cleaned labeled crucibles and placed in the furnace. The temperature of the furnace and allowed to ash at 600°C for 3 hours.

### **Digestion of sawdust**

Approximately 1g of sawdust generated from wood samples was carefully weighed into a pre- cleaned conical flasks. A solution mixture of HNO<sub>3</sub> and HClO<sub>4</sub> (1:1) was prepared. 20 cm<sup>3</sup> of the solution mixture was added to 1g each of the sawdust and heated on hot plate until mixture went colourless for 6 hours. The digestates was allowed to cool and made up to 50



cm<sup>3</sup> with deionized water.. The resultant mixtures were carefully filtered into pre-cleaned polypropylene containers using the Whatman no. 2 filter papers. Samples were then analyzed for As, Cr and Cu with ICP-MS at Tema Oil Refinery kept in the refrigerator before analysis [98].

### ***Laboratory Batch Leaching Experiment of Wood samples***

Several batch leaching experiments were conducted on a set of five wood samples. The wood samples were generated into smaller blocks of dimension 10 mm x10 mm x40 mm.

Approximately 5g of each sample was leached in 100ml of the leaching solutions to obtain a solid to liquid ratio of 1:20.

Each sample was leached in four (4) different solutions of different pH values (sea water, pH=8.22, rain water pH=5.40, SPLP mixture pH=5.60 and de-ionized water pH= 6.10) in glass containers which were covered, allowed to leach for a total of seven days running. Samples of the leachate were taken from each container after 24, 72 and 120 hours respectively. The samples were carefully filtered and two drops of concentrated HNO<sub>3</sub> was added to preserve till analysis. All leaching procedures were carried out at room temperature. Blanks consisting of the various leaching solutions were used as a quality assurance in the entire laboratory batch leaching procedure.

### ***Digestion of Soil Samples***

Approximately 1g of dry soil samples were carefully weighed into pre-cleaned conical flasks. A solution mixture of 69% HNO<sub>3</sub> and 63% HClO<sub>4</sub> (1:1) was prepared. 20 cm<sup>3</sup> of the solution mixture was added to 1g each of the soil samples and digested and analyzed as describe in 3.6.2.

### ***Quality Control and Quality Assurance***

A number of quality control measures were employed in order to obtain accurate and reproducible results in the analysis from the initial sampling process to the final analysis of the heavy metals using the ICP-MS instrument. Strict precautions were taken to minimize cross contamination during handling and preparation of the samples. Reagent blanks and reference material were analyzed to ascertain the accuracy and reliability of the measurements. Samples were also analyzed in duplicate to increase the reliability of the results.

## **RESULTS AND DISCUSSION**

### **Levels of Arsenic, Chromium and Copper in CCA Treated Wood**

Chromated copper arsenate (CCA) treatment process is used to preserve wood used for utility poles by impregnating the wood with an aqueous solution containing CrO<sub>3</sub>, CuO and As<sub>2</sub>O<sub>5</sub>. The amount of CCA added to the wood, the retention value, is a function of the intended use of the wood. CCA-treated wood used for above ground purposes require at least 4.0kg of CCA/m<sup>3</sup> of the wood (115). Upon impregnation, the wood treatment preservatives undergo a chemical reaction with the wood in which the preservatives elements become bound or fixed



to the wood fibres (115). In this study, the levels of CCA components in treated wood were assessed from different locations. The levels found in the different states of the wood were apparently, Table 4.1. Newly treated

**Table 4.1 Levels of As, Cr and Cu (mg/kg) in CCA treated and untreated wood.**

<b>Sample Location</b>	<b>As</b>	<b>Cr</b>	<b>Cu</b>
<b>Takoradi (New)</b>	2450.2	890.2	430.6
<b>Ho (New)</b>	1902.6	480.3	350.1
<b>Accra (Wt)</b>	2081.0	103.7	98.4
<b>Saltpond (Wt)</b>	350.6	210.0	100.2
<b>Chile (Wt)</b>	878.0	400.7	216.4
<b>Takoradi (Unt)</b>	21.6	4.4	ND
<b>Ho (Unt)</b>	11.4	2.1	ND

*New = Freshly treated, Wt = Weathered treated, Unt = Untreated*

wood obtained from Takoradi contained the elevated levels of the three metals with As being the highest. This is indication of the CCA preservative loading by the different manufacturers. In the case of weathered CCA wood samples arsenic leached the most among the other two metals. Thus, since the weathered CCA wood samples have been exposed to harsh environmental conditions for a very long time, it was not surprising that much less levels of the heavy metals in CCA preservative chemicals was leached. Unlike the weathered wood samples, freshly prepared wood showed a much greater tendency to leach more arsenic than the other heavy metals present. Moreover, since the treatment procedure leaves behind a layer of CCA residue on the surface of the freshly treated wood, the general view was that CCA losses are higher soon after installation and attenuate with time.[151,152,153]. However as CCA treated wood ages deterioration allows once fixed arsenic, chromium and copper to be readily released or leached. This was true with the weathered wood sample from Saltpond which contained lower values of As, Cr and Cu. The weathered wood from Accra also showed lower values of Cr (103.7 mg/kg) and Cu (98.4 mg/kg). Likewise the imported wood which had weathered in the environment for sometime also gave higher values. On the whole, untreated wood had the lowest metallic content indicative of no addition of CCA.

### **Levels of Arsenic, Chromium and Copper in Laboratory Batch Leaching Experiment**

Blocks of CCA treated wood samples were leached in four different solvents: sea water, rain water, deionized water and synthetic precipitation leaching procedure (SPLP) solution. It has been shown that arsenic in CCA treated wood leach more than copper in leaching test at more neutral pH conditions where water is used as the leaching solvent or solution [35, 36]. On the whole, among the leaching solutions, rain water and SPLP leached greater concentrations of all the heavy metals present in the CCA treated wood. The SPLP solution had the same pH since this solution was employed to mimic the natural rain, Tables 4.2-4.4, (Figures 4.1 -4.4, Appendix I, II). The leaching behavior of the different solutions could be explained by several factors discussed below:



**Table 4.2 Levels of As, Cr and Cu (mg/kg) leached from CCA treated wood blocks using different leaching solutions after 1 day (24 hours).**

Sample location	Leaching Solution	As	Cr	Cu
	<b>RAIN (pH=5.40)</b>	0.0288	ND	ND
<b>Takoradi (New)</b>		150.8	100.2	80.0
<b>Ho (New)</b>		120.8	90.5	50.6
<b>Accra (Wt)</b>		30.4	25.2	11.4
<b>S'pond (Wt)</b>		20.8	15.7	4.7
<b>Chile (Wt)</b>		40.3	33.5	14.3
	<b>DEIONIZED (pH=6.10)</b>	ND	ND	ND
<b>Takoradi (New)</b>		130.4	95.0	49.0
<b>Ho (New)</b>		100.2	70.5	27.9
<b>Accra (Wt)</b>		28.3	18.4	9.6
<b>S'pond (Wt)</b>		15.6	38.9	2.6
<b>Chile (Wt)</b>		34.7	20.3	8.6
	<b>SEA (pH=8.22)</b>	0.0362	ND	ND
<b>Takoraadi (New)</b>		60.0	30.2	18.2
<b>Ho (New)</b>		30.0	21.3	15.8
<b>Accra (Wt)</b>		10.6	6.1	4.4
<b>S'pond (Wt)</b>		8.6	5.4	2.2
<b>Chile (Wt)</b>		20.9	10.5	11.5

Sample location	Leaching Solution	As	Cr	Cu
	<b>SPLP (pH=5.60)</b>	0.0148	0.0092	ND
<b>Takoradi (New)</b>		140.4	90.6	70.1
<b>Ho (New)</b>		100.4	80.3	39.3
<b>Accra (Wt)</b>		28.1	20.3	11.1
<b>S'pond (Wt)</b>		18.4	11.0	34.4
<b>Chile (Wt)</b>		37.1	26.2	12.8

**Table 4.3: Levels of As, Cr and Cu (mg/kg) leached from CCA treated wood blocks using different leaching solutions after 3 day (72 hours).**

Sample Location	Leaching Solution	As	Cr	Cu
	<b>RAIN(pH=5.40)</b>	ND	ND	0.0069
<b>Takoradi (New)</b>		289.0	175.1	100.0
<b>Ho (New)</b>		202.5	160.0	82.9
<b>Accra (Wt)</b>		46.8	32.0	24.4
<b>S'pond (Wt)</b>		35.8	28.6	11.2
<b>Chile (Wt)</b>		58.4	49.0	29.3
	<b>DEIONIZED(pH=6.10)</b>	<b>ND</b>	<b>ND</b>	<b>0.0295</b>
<b>Takoradi (New)</b>		198.4	156.2	88.2
<b>Ho (New)</b>		181.4	140.4	53.9
<b>Accra (Wt)</b>		36.7	29.4	18.9
<b>S'pond (Wt)</b>		22.6	20.6	8.6
<b>Chile (Wt)</b>		58.0	39.3	24.4



	<b>SEA (pH=8.22)</b>	<b>ND</b>	<b>ND</b>	<b>0.0110</b>
<b>Takoradi (New)</b>		79.5	47.8	38.7
<b>Ho (New)</b>		52.7	39.1	28.5
<b>Accra (Wt)</b>		19.2	10.0	10.0
<b>S'pond (Wt)</b>		15.9	17.5	5.2
<b>Chile (Wt)</b>		32.3	22.5	18.5

<b>Sample Location</b>	<b>Leaching Solution</b>	<b>As</b>	<b>Cr</b>	<b>Cu</b>
	<b>SPLP(pH=5.60)</b>	ND	ND	0.0061
<b>Takoradi (New)</b>		200.1	160.1	91.0
<b>Ho (New)</b>		180.9	142.7	68.7
<b>Accra (Wt)</b>		42.7	30.1	21.0
<b>S'pond (Wt)</b>		31.6	21.3	10.0
<b>Chile (Wt)</b>		65.1	42.2	26.7

**Table 4.4 Levels of As, Cr and Cu (mg/kg) leached from CCA treated wood blocks using different leaching solutions after 5 day (120 hours)**

<b>Sample Location</b>	<b>Leaching Solution</b>	<b>As</b>	<b>Cr</b>	<b>Cu</b>
	<b>RAIN (pH=5.40)</b>	ND	ND	0.0156
<b>Takoradi (New)</b>		481.3	256.8	130.2
<b>Ho (New)</b>		400.9	208.1	95.3
<b>Accra (Wt) (New)</b>		79.8	69.6	39.4
<b>S'pond (Wt)</b>		68.3	51.8	19.5
<b>Chile (Wt)</b>		91.0	81.1	38.8
	<b>DEIONIZED(pH=6.10)</b>	ND	ND	0.0179
<b>Takoradi (New)</b>		278.2	190.1	106.5
<b>Ho (New)</b>		226.8	168.4	82.8
<b>Accra (Wt)</b>		48.2	39.1	38.0
<b>S'pond (Wt)</b>		39.3	41.5	20.9
<b>Chile (Wt)</b>		78.7	62.4	45.2
	<b>SEA(pH=8.22)</b>	<b>ND</b>	<b>ND</b>	<b>0.1230</b>
<b>Takoradi New)</b>		110.0	83.9	52.5
<b>Ho (New)</b>		88.4	71.0	42.7
<b>Accra (Wt)</b>		40.0	25.1	15.4
<b>S'pond (Wt)</b>		32.8	20.8	12.7
<b>Chile (Wt)</b>		64.0	40.9	22.3



Sample Location	Leaching Solution	As	Cr	Cu
	<b>SPLP (pH=5.60)</b>	ND	ND	0.0110
<b>Takoradi (New)</b>		301.2	209.6	112.1
<b>Ho (New)</b>		277.7	193.0	89.3
<b>Accra (Wt)</b>		59.2	50.1	36.4
<b>S'pond (Wt)</b>		48.0	43.0	21.1
<b>Chile (Wt)</b>		79.3	71.3	41.9

### Impact of pH

The impact of pH on metal leaching was examined from the pH values of 5.40 to 8.22 for the four different leaching solutions respectively. Higher concentrations of metals were leached at low pH values and low concentration at high pH values, Table 4.2 – 4.4, (Figures 4.1-4.4, Appendix I, II).

Elevated levels of arsenic were leached by both rain water and SPLP solution in the sample from Takoradi. Rain water (pH=5.40) leached 150.8 mg/kg of arsenic whereas 140.4 mg/kg of arsenic was obtained with SPLP (pH=5.60) after 24 hours. The least level of 60.0 mg/kg was observed with the sea water (pH=8.22). Surprisingly, the levels and distribution of the three metals have similar leaching pattern, As>Cr>Cu. Leached metal concentration was highest at low pH values as observed elsewhere [14]. Further, comparing levels of metals in leaching solutions for different locations, As, Cr and Cu were very high in all the samples from Takoradi and Ho. This was expected as the treated wood used was new unlike the weathered ones. The highest concentration of arsenic in weathered CCA wood samples was recorded in the foreign sample from Chile. Similar trend was observed for both chromium and copper. For example, 91.0 mg/kg of arsenic was leached by rain water, 79.3 mg/kg by SPLP, and 78.7 mg/kg by deionized water and 64.0 mg/kg by sea water from weathered CCA wood sample from Chile after 120 hours.

### Impact of Contact Time

Comparing Tables 4.2- 4.5, (Figure 4.1-4.4, Appendix I, II) it was observed that the concentrations of arsenic, chromium and copper used in CCA preservative chemicals increased as the number of contact times (days) increased. Similar to the pH, higher levels of arsenic were recorded with respect to the chromium and copper. The maximum concentration of arsenic after five days of experimentation was 481.3 mg/kg compared to 256.0 mg/kg for chromium and 130.2 mg/kg for copper, for the rain water solution. The least concentration of arsenic leached by rain water after 24 hours was 20.8 mg/kg which was almost three times the concentration of arsenic of a leached after five days of experimentation.

Furthermore, the highest concentrations of both chromium and copper were also achieved after five days with sample from Takoradi leaching more of all the three metals present in CCA treated wood. Also weathered CCA treated wood samples showed some potential of leaching heavy metals present with concentrations of arsenic being the higher than chromium and copper after five days of leaching. Looking at Tables 4.2 - 4.5, foreign weathered CCA wood sample leached 58.4 mg/kg as against 46.8 mg/kg from the Accra sample and 35.8 mg/kg leached from Saltpond representing their highest arsenic concentrations using rain water after five days.





Overall, the difference between the concentrations of arsenic and chromium in all the leachates generated after the days of experiment could be attributed to the effective fixation of chromium in the CCA treated wood which in tend makes it very difficult for chromium to be released from the treated wood.

### Impact of Leaching Solution

The type of leaching solution may also play a part in the ability of the heavy metals present in CCA treated wood to leach. The highest concentrations of all the three heavy metals were leached by rain water. From Table 4.4, the highest concentration was 481.3 mg/kg As, 250.8 mg/kg for Cr and 130.2 mg/kg for Cu were achieved when rain water was employed as the leaching solution. The lowest concentrations were also achieved when sea water was used, 32.8 mg/kg for arsenic, 20.8 mg/kg for chromium and 12.7 mg/kg for copper respectively for sea water leaching solution, (Figure 4.1-4.4, Appendix I, II).

**Table 4.5. Levels of As, Cr and Cu (mg/kg) with Organic Matter Content and pH in Soil Samples around and 50 meters away from CCA-Treated Utility Poles.**

	AROUND					AWAY				
	As	Cr	Cu	OM %	pH	As	Cr	Cu	OM	pH
<b>Residential</b>	7.7	23.6	84.6	1.89	7.80	6.5	22.1	77.2	1.81	7.10
<b>School</b>	7.6	47.8	89.8	1.71	7.40	7.3	30.4	80.5	1.82	7.22
<b>Beach</b>	2.3	2.2	12.1	1.43	8.73	1.2	1.2	10.6	1.55	8.97
<b>Sale Point</b>	8.3	39.1	43.5	1.88	7.00	7.5	35.5	39.8	1.73	6.91
<b>Farmland</b>	8.9	37.6	54.4	1.90	6.20	7.5	33.6	50.2	1.86	6.10
<b>Control Site</b>	0.01	0.10	0.02	1.66	5.88	0.01	ND	ND	1.56	5.58

*OM is Organic Matter Content*

### Levels of Arsenic, Chromium and Copper in Soil

To study the effect and impact of leachate from the immediate environment of in-service CCA treated wood, soil samples were collected. The study showed that soils around and away from the poles was all rich in the metals understudy, indicating that the treated woods undergo leaching via rain because the control had no or low levels of the elements.

In all the various study sites, the As levels were very low near the poles however as one moves away from the poles the level decreased likewise Cu and Cr. This shows clearly that leachates from the treated wood impacts on the levels of the contaminants putting humans at risk especially children who are the likely candidates in such places. Overall, residential and school playgrounds were noted for higher levels of all the three elements studied, suggesting possibility of human exposure. The lowest levels were observed at the beach corroborating the findings made on the poor ability of sea water to leach metals from the poles.

Organic matter content and pH levels of the soil samples showed no observable trend. The levels were very low in all the study sites as such cogent conclusions could not be drawn with respect to the As, Cr, and Cu levels in both vicinities closest and away from the poles.



## CONCLUSION AND RECOMMENDATIONS

The following conclusions are made from this research investigation:

1. All the treated wood samples from the different locations contained higher of As, Cr, and Cu with As being the highest.
2. The various leaching solutions showed variable potential in leaching As, Cr and Cu from the treated wood samples. It was observed that pH had paramount effect on the level of the metals leached from the wood samples. The higher the pH of the leaching solution the higher the levels of metals leached.
3. Of all the types of leaching solutions studied in the experiment, rain water recorded significant levels of metals leached followed by SPLP with sea water showing the poorest leacheability.
4. Organic matter content however, did not show any observable trend with regards the content of soil samples taken in the immediate vicinity of the treated poles and away from the poles.

### Recommendations

1. The different uses of the treated wood must be examined to know how much Cr As, and Cu are released into the environment.
2. In studies involving the leacheability of different simulated solutions with time, enough time must be allowed for a complete removal of leachates so as to evaluate the optimum time of leachate removal.
3. It is also recommended that studies on CCA treated wood should be conducted periodically to inform future policies as regards the regulation status of the treated wood

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