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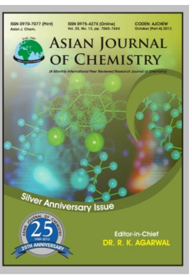

Arsenic Contamination: Africa the Missing Gap

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Arsenic is becoming a major challenge around the world due to its effect on human health. The World Health Organization set the standard for arsenic as 10 μg/L but most country do not adhere to this but rather still work with old standard of 50 μg/L. A lot of research has been carried out in different part of the world to determine the level of contamination. Europe has been able to reduce the effect of arsenic to the extent that it is almost non existence. Other continents are also trying to reduce the effect of arsenic and this can be seen from the number of research that has been reported. However, Africa is behind in this regard and not much data can be obtained on arsenic pollution or contamination. There is therefore a need for a thorough monitoring of arsenic in Africa so as to have a true picture of the level of arsenic contamination in Africa.

Key Words: Arsenic, Africa, Contamination, Pollution, Human health.

INTRODUCTION

Arsenic is a metalloid that shows many metallic properties and co-exists with other metals such as iron, copper, nickel, zinc, *etc.* as sulphides or oxides in nature[1]. It is ubiquitous and ranked 20th in natural abundance of the earth's crust, 14th in seawater and 12th in the human body[2]. Its concentration in most rock material ranges from 0.5 to 2.5 mg/Kg, though higher concentrations are found in finer grained argillaceous sediments and phosphorites[3]. Arsenic is mobilized by natural weathering reactions, biological activity, geochemical reactions, volcanic emissions and other anthropogenic activities[3]. The anthropogenic activities include processing of varieties of ores like Cu, Au, Ni, Pb and Zn, ingredients of many insecticides and herbicides, cotton and wool processing, arsenic based wood preservative, feed additives in various metal alloys and in mining, seepages from hazardous waste sites, power generation by the burning of arsenic contaminated coal or wood with arsenic based preservative and semiconductor and glass manufacturing units[1]. Soil erosion and leaching contribute to 612×10^8 and 2380×10^8 g/year of arsenic in dissolved and suspended forms in the oceans, respectively[4]. Most environmental arsenic problems are the result of mobilization under natural conditions[5].

Arsenic occurrence: Arsenic naturally occurs in over 200 different mineral forms of which approximately 60 % are arsenates, 20 % sulphides and sulphosalts; the remaining 20 % includes arsenides, arsenites, oxides, silicates and elemental As. As^0 and As^{3-} are rare in aquatic environments[2]. Organic arsenic species available in contaminated surface and ground water are monomethylarsenate (MMA) and dimethylarsenate (DMA)[1]. The most abundant arsenic ore minerals are arsenopyrite (FeAsS) and arsenianpyrite [$Fe(S,As)_2$]. Other arsenic-bearing sulphides in mineralized areas include realgar (AsS) and orpiment (As_2S_3). Arsenic is also present at high concentrations in the more common sulphide minerals, the most abundant of which is pyrite (FeS_2). Concentration in pyrite, chalcopyrite, galena and marcasite can be variable but potentially reach several weights. High concentration of arsenic can also be found in oxide minerals and hydrous metal oxides, especially when formed as weathering products of primary sulphide minerals. Iron sulphides and oxides constitute the most important sources of arsenic to underground water.

Arsenic concentration in various minerals ranges from less than 1 mg/kg as in the case of gypsum/anhydrite to 276,000 mg/kg in the case of marcasite. Table-1 shows the different arsenic concentrations found in minerals.

In soil, groundwater and aquatic environments of many parts of the world inorganic arsenic is often found in two oxidation states as arsenate [As(V)] and arsenite [As(III)][7-10]. High concentration of arsenic has also been found in some geothermal fluids. Geothermal systems are found in diverse

TABLE-1
ARSENIC CONCENTRATION IN VARIOUS MINERALS

Mineral	Arsenic concentration range (mg/kg)
Sulphide minerals	
Pyrite	100-120,000
Pyrrhotite	5-100
Marcasite	20-276,000
Galena	5-10,000
Sphalerite	5-17,000
Chalcopyrite	10-5,000
Oxide minerals	
Haematite	up to 29,000
Iron (III) oxyhydroxide	up to 76,000
Magnetite	2.7-41
Maghemite	up to 186,000
Silicate minerals	
Quartz	0.4-1.3
Feldspar	< 0.1-2.1
Biotite	1.4
Amphibole	1.1-2.3
Olivine	0.08-0.17
Pyroxene	0.05-0.8
Carbonate minerals	
Calcite	1-8
Dolomite	< 3
Siderite	< 3
Sulphate minerals	
Gypsum/anhydrite	< 1-6
Barite	< 1-12
Jarosite	34-1000
Others	
Apatite	< 1-1000
Halite	< 3-30
Fluorite	< 2

Adapted from: Smedley[6]

tectonic settings including active plate margins, continental and oceanic hot spots and within plate rift zones[11]. Geothermal brines from the Wairakei geothermal field in New Zealand have arsenic concentration up to 3800 µg/L[12]. Concentrations in the range < 0.03-10 µg/L were found in geothermal water from Iceland[13] and < 10-70 µ/L in geothermal water from Hawaii[11]. The reasons for the differences in arsenic concentrations in geothermal fluids between these tectonic settings are not fully understood.

High arsenic geothermal water often associated with a characteristic suite of other trace constituents such as Li, B, F, Hg, Sb, Se, Th and H_2S. Positive correlations with chlorine and salinity have also been reported[11]. Recently it has become increasingly apparent that some of the most extensive and serious groundwater arsenic problems occur not in areas influenced by metalliferous mineralization or geothermal activity, but in seemingly ordinary sedimentary aquifers. An important discovery of recent years has been that the sediments composing these aquifers do not tend to contain unusually high arsenic concentrations. Average concentration of arsenic in soils and sediments are in the approximate range of 5-10 mg/Kg. Arsenic also occurs in most igneous rocks (0.1-15.6 ppm), sedimentary rocks (0.9-42 ppm) and metamorphic rocks (5-10 ppm). It dissolves through a range of pH conditions which may lead to significant dissolution where high concentrations are present in rock[14]. Arsenic has also been found to exist in different concentrations in environmental media such as; air, rain, river, lakes, soil, seawater, *etc*. Table-2 shows the concentration of arsenic in different environmental media.

TABLE-2
ARSENIC CONCENTRATIONS IN ENVIRONMENTAL MEDIA

Environmental media	Arsenic concentration range
Air (ng/m^3)	1.5-53
Rain from unpolluted ocean air (µg/L)	0.019
Rain from terrestrial air (µg/L)	0.46
Rivers (µg/L)	0.20-264
Lakes (µg/L)	0.38-1,000
Ground (well) water (µg/L)	< 1 and > 1,000
Seawater (µg/L)	0.15-6.0
Soil (mg/kg)	0.1-1,000
Stream/river sediment (mg/kg)	5.0-4,000
Lake sediment (mg/kg)	2.0-300
Igneous rock (mg/kg)	0.3-113
Metamorphic rock (mg/kg)	0.0143
Sedimentary rock (mg/kg)	0.1-490
Biota-green algae (mg/kg)	0.5-5.0
Biota-brown algae (mg/kg)	30

Adapted from Ning, 2002[15]

Several cycles have been proposed by different scientists over the years, but Langdon *et al.*[16] were able to summarize all in a cycle as shown in Fig. 1. The cycle was able to capture all forms in which arsenic occurs in the environment.

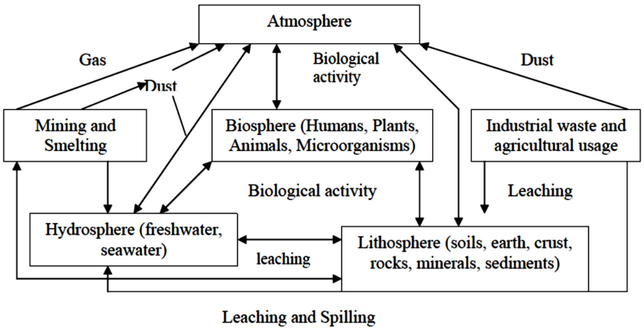

Fig. 1. Global arsenic cycle (Langdon *et al.*[16])

Chemistry of arsenic: Arsenic is a silver grey crystalline solid with atomic number 33, atomic weight 74.9, specific gravity 5.73, boiling point 613 ºC and a vapour pressure of 1 mmHg at 372 ºC. It melts at 817 ºC (28 atm) but it ordinarily sublimes at 616 ºC[3]. Arsenic exists in the -3, 0, +3 and +5 oxidation states. Environmental forms include arsenious acids (H_3AsO_3, $H_3AsO_3^{2-}$), arsenic acids (H_3AsO_4, $H_3AsO_4^{-}$, $H_3AsO_4^{2-}$), arsenites, arsenates, methylarsenic acid, dimethylarsinic acid, arsine, *etc*. Arsenic(III) is a hard acid and preferentially complexes with oxides and nitrogen. Conversely, As(V) behaves like a soft acid, forming complexes with sulphides. Inorganic forms of arsenic most often exist in water supplies. Arsenic is uniquely sensitive to mobilization (pH 6.5-8.5) and under both oxidizing and reducing conditions among heavy metalloids. Two forms of arsenic are common in natural waters: arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}), referred to as As(III) and As(V) respectively. Pentavalent (+5) or arsenate species are AsO_4^{3-}, $HAsO_4^{2-}$, $H_2AsO_4^{-}$ while trivalent (+3) arsenates include $As(OH)_3$, $As(OH)_4^{-}$, AsO_2OH^{2-} and AsO_3^{3-}.

Pentavalent species predominate and are stable in oxygen rich aerobic environments. Trivalent arsenites predominate in moderately reducing anaerobic environments such as groundwater[3].

Uses of arsenic: Arsenic has been used mainly as poison due to its potency[2,15]. This is mainly because white arsenic is odorless and tasteless and is also widely available. There are many uses of arsenic besides being the poison of choice for many murders. Arsenic is highly toxic in nature; caution is advised in the use of arsenic. It is used in different fields like medicine, military and other commercial uses. Arsenic is primarily used as wood preservative called chromate copper arsenate (CCA)[17,18]. Arsenic in its inorganic form is used for the production of pressure treated wood. In wood preservation, chromate copper arsenate is injected into the cellular structure of the wood. Pressure-treated wood is used for commercial, industrial and residential applications including decking, highway noise barriers, playground equipment, retaining walls, signposts, landscaping and utility poles. The benefit of using chromate copper arsenate pressure-treated wood is its resistance to rotting and insect attack which increases the wood's life to a great extent.

One of the most important uses of arsenic is as a doping agent in solid state devices such as transistors. Doping is the process in which an impurity such as arsenic is added to a semiconductor to increase its conductivity[18]. Arsenic is also used in the tanning industry as preservatives. It is widely used as a weed killer and it is often sprayed from small aircrafts over the fields to destroy any kind of infestation. It is also used as pesticide and in the manufacture of glass[17]. However, due to the growing popularity of organic pesticides, the amount of arsenic used for agricultural purposes has drastically decreased.

Another use of arsenic is as an anti-friction additive in ball bearings and to harden lead. Arsenic is also used for manufacturing germanium-arsenide-selenide specialty optical materials. Indium-gallium-arsenide was formerly used for short wave infrared technology. There are many arsenic uses in the field of medicine. The peasants in Austria consume large quantities of arsenic because they believe it is good for softness and cleanliness of the skin, gives plumpness to the figure, beauty and freshness to the complexion[2]. Use of arsenic was mostly for the treatment of syphilis, before penicillin was discovered. Fowler's solution, which was discovered in 1786, contains 1 % potassium arsenite and was used in the treatment of various diseases. Some other arsenic solutions that were recommended for the treatment of malaria, rheumatism, arthritis and tuberculosis are arsenic trioxide or Donovan's solution and arsenic trichloride or de Valagin's solution. Arsenic trioxide is used for the treatment of leukemia and it is also used for curing psoriasis[18].

Health implication of arsenic: Human exposure to arsenic can occur through ingestion, inhalation or skin adsorption. However, ingestion is the predominant form of arsenic intake. High doses of arsenic can cause acute toxic effects including gastrointestinal symptoms (poor appetite, vomiting, diarrhoea, etc.), disturbance of the functioning of cardiovascular and nervous system (*e.g.*, muscle cramps, heart complains) or death[19, 20]. Organs that are usually affected by arsenic are the liver, kidney, gastrointestinal tract, circulatory system, other sensitive tissues and the heart[10].

The first visible symptoms caused by exposure to low arsenic concentrations in drinking water are abnormal black-brown skin pigmentation known as *melanosis* and hardening of palms and soles known as *keratosis*. If the arsenic intake continues, skin de-pigmentation develops resulting in white spots that look like raindrops and is medically described as *leukomelanosis*. Arsenic may attack internal organs without causing any visible external symptoms, making arsenic poisoning difficult to diagnose. Elevated concentrations in hair, nails, urine and blood can be an indicator of human exposure to arsenic before visible external symptoms[21].

The symptoms and signs that arsenic causes appear to differ between individuals, population groups and geographic areas. Thus, there is no universal definition of the disease caused by arsenic. This complicates the assessment of the burden on health of arsenic. Similarly, there is no method to identify those cases of internal cancer that were caused by arsenic from cancers induced by other factors. The World Health Organization (WHO) guideline value for arsenic in drinking water was reduced from 50 μg/L to a provisional value of 10 μg/L in 1993. Most western countries adopted this limit in their current drinking water standards. On the other hand, many affected countries still operate the 50 μg/L standard due to lack of adequate testing facilities[22].

Apart from water, other potential sources of exposure of arsenic to human are food, soil and air. However, arsenic is found in seemingly innocuous places, which includes; wooden structures such as playground equipment, boat docks, patio decks, gazebos, walkways, fences, picnic tables, *etc*. The source of arsenic found in these structures is chromate copper arsenate, a wood preservative and pesticide that has been used for more than 60 years to protect wood from fungi, dry rot, mould and termites. It has been found out that children are likely to be poisoned by arsenic from this source[23].

Arsenic in agriculture: Arsenic concentration in soil is usually elevated relative to its occurrence in rocks. The lowest concentrations are from soils derived from granites and the highest in soils formed from sulphide ore deposits[24]. Higher levels of arsenic are also associated with alluvial soil, soil with a high organic content and groundwater affected by geothermal activity. Arsenic is liberated from rocks via the weathering process, during which it may be mobilised as salts of arsenic and arsenous acid. Concentration and liberation in soils may be influenced by the adsorption of arsenic onto secondary Fe, Al and Mn oxides, as well as clay minerals and organic matter[25,26]. The roasting of coal and sulphide ore releases arsenic trioxide into the atmosphere, which reacts with alkaline earth oxides to form arsenates, which are subsequently deposited in the soil. Arsenates of Fe and Al are the dominant phases in acidic soils and are less soluble than the Ca variety present in calcareous soil.

Anthropogenic activities also contribute to an increase in arsenic concentration in soil. These activities include the use of pesticides, insecticides, cattle and sheep dips. The state government of Australia built several sheep and cattle dip between the 1920s and 1980s to control tick[10]. Moremedi and Okonkwo[27] also reported that the use of arsenic to control ticks in cattle farms in South Africa leads to soil pollution in these areas, even though arsenic use has been stopped since the 1960s, the concentration is still very high in the soil around these cattle farms. Water soluble preservatives such as chromate copper arsenate and other arsenic based chemicals used as wood preservatives in the past have led to a wide spread of arsenic contamination in soils around wood preservation facilities. Also, during the manufacturing of these pesticides and herbicides, the release of waste may contaminate soil and water systems[28].

In addition, arsenic accumulation in the soil is taken up by plants and is then entrenched in mammalian/insectivore food chain[10]. The amount of arsenic in a plant is almost solely dependent on the amount of arsenic it is exposed to. Its concentration varies from less than 0.01 to about 5 µg/g dry weight basis[2]. It has been reported in Bangladesh that rice, grains, grass, mustard and amaranthus plants are contaminated with arsenic because the water used for irrigation is highly contaminated with arsenic. Paddy rice, the main staple food of Bangladesh, is also contaminated with As. High levels of arsenic have also been found in groundwater in other areas in Southeast Asia including China, Vietnam and Thailand, where rice is also a staple food. However, it is still not clear whether the arsenic in rice is in the form that is bioavailable[29]. It has also been reported that rice yield decreases by 10 % at a concentration of 25 mg/kg arsenic in soil. A green house study also revealed that the yield of a local rice reduced when irrigated with water having arsenic concentration ranging from 0.2 to 8 mg/L. The accumulation of arsenic in rice field soil and its introduction into the food chain through uptake by rice plant is becoming a major concern[28].

Level of arsenic and health effect in the world: Arsenic in drinking water is a global problem affecting countries in all the five continents. The most serious damage to health has taken place in Bangladesh and West Bengal, India. The World Health Organization estimated in 2001 that about 130 million people worldwide are exposed to arsenic concentrations above 50 µg/L (WHO, 2001). Affected countries include Bangladesh (> 30 million exposed people), India (40 million), China (1.5 million) and the United States (2.5 million). Arsenic in drinking water supply in Europe has never really been a matter of interest as most countries rarely exceed the standard of 10 µg/L. However, Hungary, Serbia, Croatia, Greece, Italy and Spain have reported high concentration of arsenic and special treatment steps are required to reduce the concentration to an acceptable level[30].

The problem of arsenic-contaminated water sources is, however, not confined to these countries, as illustrated by the map (Fig. 2).

The first case of a large-scale health problem caused by naturally-occurring arsenic to be identified and recorded was in Taiwan in 1968. Chile's contamination case became recognized as such in the seventies. In the eighties, the problems in West Bengal, India, as well as in Ghana, Mexico and several other countries were documented. The largest contamination case to date is clearly Bangladesh. In the early nineties patients from western districts in Bangladesh started to cross the border to visit hospitals in Calcutta, but it was not until 1995 before official exploration of the problem was initiated. After 1997 the number of studies and initiatives rapidly grew leading to

Fig. 2. Summary of the world distribution of documented problems with arsenic in groundwater (> 50 µg/L) and the environment (Ref. 5)

the discovery that most of the country should be considered at serious risk[31].

Worst hit by the effect of arsenic is Bangladesh and west Bengal in India both in the Asia continent. The crisis in Bangladesh and West Bengal highlights the health problems associated with arsenic poisoning. Skin problems such as keratosis, pigmentation and de-pigmentation and skin cancer are widespread. Patients who have been exposed for a longer period of time have developed internal organ problems such as cancer and many more have died. Nine districts in West Bengal, India and 42 districts in Bangladesh have arsenic levels in groundwater above the World Health Organization maximum permissible limit of 50 μg/L. The area and population of the 42 districts in Bangladesh and the 9 districts in West Bengal are 92,106 km^2 and 79.9 million and 38,865 km^2 and 42.7 million, respectively. Table-3 shows documented problems of arsenic in groundwater, countries affected and the approximate number of people at the risk.

Arsenic outbreaks: Smedley [6] reported that high arsenic concentration was found in three boreholes in a village in central Burkina Faso. He also reported that high concentration of arsenic in groundwater was also found in the northern part of the country but that more extensive testing programmes are ongoing. The high concentration of arsenic in these areas has resulted into skin disorder such as melanosis, keratosis and skin tumours. Hossain[29] reported that about 25 million people of 2000 villages in 178 arsenic-affected blocks of Bangladesh are at risk of arsenic poisoning and 3695 (20.6 %) out of 17896

TABLE-3
ARSENIC, COUNTRIES AFFECTED, NUMBER OF PEOPLE AT RISK, SPATIAL DISTRIBUTION AND NATURE OF CONTAMINATION (Ref.[32])

Country/Region	Number of people at risk	Spatial distribution and nature of the contamination
Taiwan South west and north east coastal Zones	200,000	Rural and small townships depending on well water of which many are contaminated at medium to high levels, some up to 1,800 μg/L
China Inner Mongolia Shaanxi, Xinjiang	600,000 1,100,000	Dispersed incidence of low and medium and occasionally high concentrations in wells. Some regions (*e.g.* Baotou, I-M): high incidence of contaminated wells at high concentration
USA >50 μg/L (esp. in Western part) >25 μg/L	200,000 2,500,000	Origin of As varies. As occurs primarily in groundwater and in some rivers (California) fed by geothermal sources. In mid-west and eastern plains low concentrations and disperse incidence.
Mexico Lagunera Region: towns of Torreón, Matamoros, Viesca, Francisco, Madero, San Pedro, Tlahualilo, Gomez Palacio, Mapimi, Lerdo, Nazas and Ceballos (Coahuila and Durango States)	400,000	An enclosed basin with primarily calcareous formations, As was first found in the east corner of the aquifer, but dissipated to other sides probably under suction of groundwater pumping. Low to medium concentrations in a large number of wells in the affected zone.
Chile Loa and Salado regions (north Chile): cities of Antofagasta, Colama, Chuquicamato, Salar de Atacama; Arica Province	400,000	Associated with quaternary volcanism in the sparsely populated and arid Central Andean Cordilleras. Many rivers and lakes contaminated by thermal springs or dissolution of salts. Many enclosed basins with evaporative lakes (*salares).* In some regions contaminated shallow wells. Low to high concentrations with sometimes well above 1,000 μg/L in river water (Ch: Loa R.). In north-western Argentinean plains also in sedimentary soils.
Argentina Salta Province: Puna and Chaco Salteño regions	200,000	
Bolivia Southern Altiplano (Dept. Potosí)	50,000	
Greece Thessaloniki	150,000	In particular aquifers. Hydrothermal origin. Low to high concentration.
Hungary	400,000	Mostly artesian wells in peaty and sedimentary soils. Low to medium concentrations.
Ghana Obuasi	100,000	Some shallow wells and streams contain low to medium concentrations. Gold mining and possibly some arsenopyrite oxidation.
India West Bengal State (suspected occurrence in Bihar, Gangetic and Brahmaputra plains)	In 8 Districts, out of total population of 40 million, 5 million "live close to contaminated well"	West Bengal: Out of 17 Districts, 8 have affected wells in various zones. Within these zones half of wells (medium depth) contain As at low to medium levels. Origin not conclusively established but not likely due to arsenopyrite oxidation.
Bangladesh In most Districts	80-90 million people live in affected Districts, of which 20-30 million "live close to contaminated well"	Low to high concentration in groundwater wells of 5-150 m deep. Some areas have 80-100 % of wells contaminated, others much less; across the affected Districts 30-40 % of wells affected (>50?g/L). Aquifers appear reductive alkaline environment, with As displaced from clay adsorption sites by cations such as phosphate
Vietnam Red River delta region, including Hanoi	As confirmed in some wells. Number of people affected unknown.	Preliminary testing in Hanoi and Red River districts has indicated a significant As problem in shallow tubewells used for drinking water. There are an estimated 150,000 shallow tubewells used for drinking in these regions.

people examined are suffering from arsenicosis. He also reported that another random survey in 95 villages of 6973 people showed that 2309 people (33.1 %) were found with arsenical skin lesions.

Arsenic in Africa: Based on current knowledge, Africa is the least affected continent and this is due to the limited research work that has been done on As. However, some cases of arsenic contamination of ground water and soil have been reported in different parts of Africa. The following countries have documented reported cases; Burkina Faso, Ghana, South Africa, Botswana, Ethiopia and Nigeria.

In Burkina Faso, the concentration of arsenic ranges from < 0.5 to 1630 µg/L. The high arsenic ground waters observed derive from zones of gold mineralization in Birimian (Lower Proterozoic) volcano-sedimentary rocks, the gold occurring in vein structures along with quartz and altered sulphide minerals (pyrite, chalcopyrite, arsenopyrite)[33].

In Ghana, arsenic concentrations in groundwater from two areas in Ghana, the Obuasi area in the Ashanti region and the Bolgatanga area of the Upper East region vary from < 1 - 64 µg/L and < 1 - 141 µg/L, respectively. Sulphide minerals such as arsenopyrite and pyrite are present in the Birimian basement rocks of both areas and this forms the dominant arsenic sources[34].

Reimann *et al.*[35] reported that out of 138 wells where samples were taken in the Ethiopia area of the East African Rift Valley 9 (6.5 %) showed arsenic concentration higher than 10 µg/L. It was concluded that arsenic was not a major problem in the area drinking water.

In Botswana, six of the twenty wells used for the analysis of arsenic showed a concentration > 10 µg/L, the recommended limit by WHO[36].

In southern Nigeria, the range of arsenic concentration in ground water was 0.4-6.88 µg/L[37]. Afolabi *et al.*[38] also recorded arsenic concentration in 12 wells. They reported that the concentration of arsenic was greater than the recommendation of the WHO. The high concentration was suspected to be as a result of the activities from mechanic and panel beaters workshops.

In South Africa, severe arsenic poisoning has been reported in Northern Cape and Limpopo province where concentration is said to be as high as 1000 µg/L[14]. Another source of arsenic to groundwater and the soil in South Africa is the use of chromated-copper-arsenate in the preservation of timber. The arsenic actually protects the timber from wood-destroying insects. Improper disposal of waste from timber plants however contaminates the soil and water systems around the plants[39].

Conclusion

Arsenic is a slow poison and it kills gradually, sometimes it is not even suspected as the cause of death in humans. A lot of research has been done around the world to reduce its effects on human health but Africa is still behind in this regard. The World Health Organization will need to beam its light on Africa in this regard and assist with finance and expertise to be able to get accurate information on the spread of arsenic. The search light should cover countries where petroleum is refined and explore, countries where there are lot of mountains and countries where arsenic is used as pesticides and herbicides in the agricultural sector. If this could be achieved, then a true picture of arsenic in Africa will be recorded.

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