



Sudan University for Science and Technology

College of Graduate Studies



Determination of Mercury Concentration in Soil and Water Samples from Gold Mining Areas in North and East Sudan

تحديد تركيز الزئبق في عينات من التربة والمياه بمناطق تعدين الذهب في شمال وشرق السودان

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of
Master of Science in Chemistry

By

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إستهلال

قال تعالى:

(اقْرَأْ بِاسْمِ رَبِّكَ الَّذِي خَلَقَ (1) خَلَقَ الْإِنْسَانَ مِنْ عَلَقٍ (2) اقْرَأْ وَرَبُّكَ الْأَكْرَمُ (3) الَّذِي عَلَّمَ بِالْقَلَمِ

(4) عَلَّمَ الْإِنْسَانَ مَا لَمْ يَعْلَمْ (5)

سورة القلم الآية (1-5)

Dedication

I dedicate this work to the soul of my mother, my father, and my wife.

Acknowledgements

Firstly my unlimited praise and thanks to Allah Almighty, who created me and gave the power and support to finish my research.

I would like to thank my research supervisor, Professor Mohammed Adam Abbo for his continuous support, patience, motivation, and immense knowledge. His guidance helped me through the time of research and writing of this thesis. I could not have imagined having a better supervisor and mentor for my study.

I would also like to thank my dear comrade Bakry Basheer for his effort, assistance and moral support to complete this research.

Abstract

The main objective of this research is to determine the concentrations of mercury in soil and water samples from the mining areas in the north and east of Sudan to assess the pollutant risk of mercury on the environment, thus contributing to find the optimal treatment methods for the presence and accumulation of mercury in the environment.

Seven soil samples were collected from the mining areas of the Nile State, northern Sudan, three soil samples and three rainwater samples were collected from mining areas east of Atbara River, eastern Sudan.

The samples were analyzed by thermal decomposition, amalgamation, and atomic absorption spectrophotometry.

Comparing the result of soil samples with Canadian Council of Ministers of the Environment (CCME) guidelines for residential and agricultural limit it is found that average concentration of mercury in soil ($22.52\mu\text{g/g}$) was 3.5 times the permissible limit.

For water sample average concentrations of mercury was ($0.2742\ \mu\text{g/L}$) that value was approximately twice the permissible limit for cleaning water and within the permissible limit for drinking water according to the Environmental Protection Agency(EPA) recommendation.

The ratios that were reached, compared to the permissible limits globally, are catastrophic and predict the occurrence of severe and destructive consequences for the environment.

المستخلص

الهدف من البحث معرفه تراكيز عنصر الزئبق في تربة ومياه مناطق التعدين شمال وشرق السودان لتقييم التلوث بالزئبق وخطورة ذلك علي البيئة وبالتالي الإسهام في إيجاد طرق المعالجة المثلى لخفض تركيز الزئبق وتراكمه في البيئة والتربة .

تم جمع عدد سبع عينات تربة من مناطق التعدين بولاية نهر النيل شمالي السودان وتلاثة عينات تربة ومثلها عينات مياه أمطار من مناطق تعدين شرق نهر عطبرة شرقي السودان .

تم تحليل العينات باستخدام تقنية التفكك الحراري المملغم ومطيافية الإمتصاص الذري.

بمقارنة نتائج التربة مع القواعد الإرشادية لحدود الزئبق المسموح بها في التربة السكنية والزراعية المعتمدة بواسطة مجلس وزارة البيئة الكندية، كان متوسط تراكيز الزئبق (22.52 مايكروجرام/جرام) أعلى بـ 3.5 مرة من الحدود المسموح بها.

بالنسبة لعينات المياه كان متوسط تراكيز الزئبق (0.2742 مايكروجرام/لتر) تصل إلى ما يقارب ضعف الحد المسموح به للماء النظيف وداخل الحد المسموح به لمياه الشرب حسب توصية وكالة حماية البيئة.

النسب التي تم التوصل اليها مقارنة بالحدود المسموح بها عالميا كارثية وتنبئ بحدوث عواقب وخيمة ومدمرة للبيئة.

List of Abbreviations

CCME	Canadian Council of Ministers of the Environment
EPA	Environmental Protection Agency
FDA	Food and Drug Administration
NIOSH	National Institute for Occupational Safety and Health
AOAC	Association of Official Analytical Chemists
APHA	American Public Health Association
CVAAS	Cold Vapor Atomic Absorption Spectroscopy
CVAFS	Cold Vapor Atomic Fluorescence Spectroscopy
ICP MS	Inductively Coupled Plasma Mass Spectrometry
ICP AES	Inductively Coupled Plasma Atomic Emission Spectrometry
MIP AES	Microwave-Induced Plasma Atomic Emission Spectrometry
GC/AFS	Gas Chromatography Atomic Fluorescence Spectroscopy
HPLC/ UV	High Performance Liquid Chromatography Ultraviolet detection
HPLC/ECD	High Performance Liquid Chromatography Electrochemical Detection
CNT	Carbon Nano Tubes
DMA	Direct Mercury Analyzer
ASGM	Artisanal and small-scale gold mining
CRM	Certified Reference Material
RfD	Reference Dose
UNEP	United Nations Environment Program

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Chapter One

Introduction and Literature review

1. Introduction and Literature Review

1.1 Introduction

1.1.1 Mercury

The heavy metal mercury has been used for centuries both as a medicine and a poison and is currently used for many commercial purposes. Recently, attention has been refocused on this metal due to concern of environmental exposure. Some particular sources of exposure to mercury that have been publicized include ingestion of contaminated seafood, administration of vaccines to infants, use in dental amalgams, and inclusion in folk remedies and rituals. The chemistry, toxic kinetics, mechanism of action, sources of risk and exposure, regulatory actions, clinical manifestations of acute and chronic exposure, treatment, and laboratory testing for mercury will be reviewed and discussed*.

Physicochemical properties of mercury

Mercury extraction is easy; it has an almost unique appearance, it readily displaces gold from its ores and it forms amalgams with many other metals, these properties caused the alchemists to regard it as one of the "fundamental" substances. It occurs chiefly as cinnabar, the red sulphide HgS, from which it is readily, extracted either by roasting (to give the metal and sulphur dioxide) or by heating with calcium oxide; the metal distils off and can be purified by vacuum distillation.

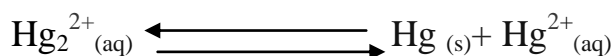
Mercury has a large relative atomic mass, but, like zinc and cadmium, the metal bonds are not strong. These two factors, together, may account for the very low melting point and boiling point of mercury. The low boiling point means that mercury has an appreciable vapor pressure at room temperature; 1m³ of air in equilibrium with the metal contains 14mg of vapor, which is highly toxic.

* Larry, et al, 2002

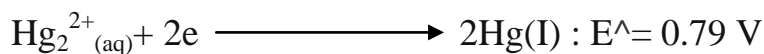
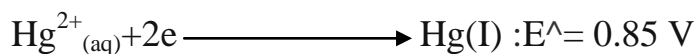
Exposure of mercury metal to any reagent which produces volatile mercury compounds which enhances its toxicity. The metal is slowly oxidised by air at its boiling point, to give red mercury (II) oxide; it is attacked by the halogens (Which cannot therefore be collected over mercury) and by nitric acid.

Compounds of mercury

The chemistry of mercury compounds is complicated by the equilibrium



The relevant redox potentials are:



Hence mercury is a poor reducing agent; it is unlikely to be attacked by acids unless these have oxidising properties (for example nitric acid), or unless the acid anion has the power to form complexes with one or both mercury cations Hg^{+2} or HgF^{+} , so altering the E° values.

Nitric acid attacks mercury, oxidizing it to $\text{Hg}^{2+}(\text{aq})$ when the acid is concentrated and in excess, and to $\text{Hg}^{2+}(\text{aq})$ when mercury is in excess and the acid dilute.

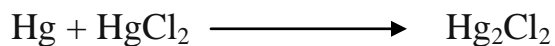
Hydriodic acid $\text{HI}(\text{aq})$ reacts with mercury, mercury(II) to form iodocomplexes.

Oxidation State (1+)

The mercury (I) ion has the structure so that each mercury atom is losing one electron and sharing one electron, i.e. is using two valency electrons. The existence of Hg^{+} has been established by experiments in solution and by X-ray diffraction analysis of crystals of mercury (I) chloride, Hg_2Cl_2 where mercury ions are in pairs with adjacent chloride ions.

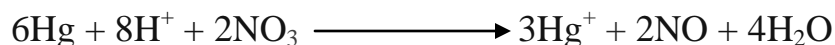
The ion $\text{Hg}^{1+}(\text{aq})$ tends to disproportionate, especially if the concentration of $\text{Hg}^{2+}(\text{aq})$ is reduced, for example by precipitation or complex formation. However, the equilibrium can be moved to the left using excess of mercury, or by avoiding

aqueous solution. Thus, heating a mixture of mercury and solid mercury(II) chloride gives mercury(I) chloride, which sublimes off:



The product, commonly called calomel, is a white solid, insoluble in water; in its reactions (as expected) it shows a tendency to produce mercury(II) and mercury. Thus under the action of light, the substance darkens because mercury is formed. Addition of aqueous ammonia produces $\text{H}_2\text{N-Hg-Hg-Cl}$, but this also darkens on standing, giving $\text{H}_2\text{N-Hg-Cl}$ and a black deposit of mercury.

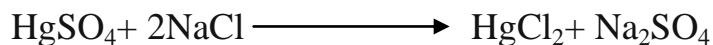
Mercury (I) ions can be produced in solution by dissolving excess mercury in dilute nitric acid:



From the acid solution white hydrated mercury(I) nitrate $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ can be crystallised out; this contains the ion $[\text{H}_2\text{O-Hg-Hg-H}_2\text{O}]^{2+}$ which is acidic (due to hydrolysis) in aqueous solution. Addition of chloride ion precipitates mercury(I) chloride.

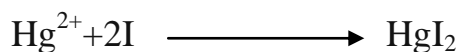
Oxidation state (2+)

Mercury(II) oxide, HgO , occurs in both yellow and red forms; the yellow form is precipitated by addition of hydroxide ion to a solution containing mercury(II) ions, and becomes red on heating. Mercury(II) oxide loses oxygen on heating. Mercury(II) chloride is obtained by dissolving mercury(II) oxide in hydrochloric acid; the white solid is obtained as a sublimate by heating mercury(II) sulphate and solid sodium chloride:



The aqueous solution has a low conductivity, indicating that mercury (II) chloride dissolves, essentially, as Cl-Hg-Cl molecules and these linear molecules are found in the solid and vapor. A solution of mercury(II) chloride is readily reduced, by

tin(II) chloride, to give first white insoluble mercury(I)chloride and then a black metallic deposit of mercury. Mercury(II) iodide, HgI_2 is either red or yellow, is precipitated(yellow, turning red) by adding the stoichiometric amount of iodide ion to a solution containing mercury(II):



Mercury (II) sulphide, HgS , again appears in two forms, red (found naturally as cinnabar) and black, as precipitated by hydrogen sulphide from a solution containing Hg(II) ions.

Mercury Complexes

Mercury (I) forms few complexes, one example is the linear $[\text{H}_2\text{O}-\text{Hg}-\text{Hg}-\text{H}_2\text{O}]^{+2}$ found in the mercury(I) nitrate dehydrate. In contrast, mercury(II) forms a wide variety of complexes, with some peculiarities: (a) octahedral complexes are rare, (b) complexes with nitrogen as the donor atom are common, (c) complexes are more readily formed with iodine than with other halogen ligands. Mercury(II) halides, HgX_2 can be regarded as neutral, 2- coordinate linear complexes $\text{X}-\text{Hg}-\text{X}$. X is readily replaced; addition of ammonia to a solution of mercury(II) chloride gives a white precipitate $\text{NH}_2-\text{Hg}-\text{Cl}$; in the presence of concentrated ammonium chloride, the same reagents yield the diamminomercury (II) cation, $[\text{NH}_3-\text{Hg}-\text{NH}_3]^{2+}$, which precipitates as $[\text{Hg}(\text{NH}_3)_2]\text{Cl}_2$. In presence of excess chloride ion, mercury(II) chloride gives complexes $[\text{HgCl}_3]^{1-}$ and $[\text{HgCl}_4]^{2-}$, but the corresponding iodo complex $[\text{HgI}_4]^{2-}$, from mercury(II) iodide and excess iodide, is more stable. (It is rare for iodo-complexes to form at all and very rare to find them with stabilities greater than those of chloro-complexes.) In both solid HgI_2 and the complex $[\text{HgI}_4]^{2-}$ mercury is tetrahedrally 4-co-ordinated. The $[\text{HgI}_4]^{2-}$ ion has a characteristic reaction with ammonia-a trace produces a yellow color and more ammonia gives a brown precipitate. (An alkaline solution containing $[\text{HgI}_4]^{2-}$ ions

is therefore used as a test for ammonia; Messier's reagent.) Insoluble salts of the anion $[\text{HgI}_4]^{2-}$ are known, $\text{Cu}_2[\text{HgI}_4](\text{red})^*$.

1.1.2 Toxicology and health effects of Mercury

Mercury is considered as a global contaminant because it can undergo long-range transport in the atmosphere, while it is also persistent in the environment, accumulating in the food web and poisoning severe adverse effects on both humans and ecosystem health. All forms of Hg are toxic, with methyl mercury (MeHg), a neurotoxin, being the form of particular concern because of its ability to bioaccumulate and biomagnify. Acute Mercury exposure can produce permanent damage to the nervous system; in addition, Mercury can affect the lungs, kidneys, brain, and/or skin and cause adverse effects^{**}.

Long-term exposure to low levels of inorganic mercury appears to be the kidneys. Short-term exposure to higher levels of any form of mercury can result in damage to the brain, kidneys, and fetuses. Mercury has not been found to be carcinogenic. However, there are significant differences in the toxicity of the major forms of mercury. Mercury has been found to have a deleterious effects a wide range of human systems including the respiratory, cardiovascular, a hematologic, immune, and reproductive systems. The bioaccumulation of mercury in various forms contributes in large measure to its toxicity^{***}.

1.1.3 Exposure to Mercury

As mercury cycles through various forms and media, its bioavailability and toxicity change through both biological and chemical reactions. Because mercury is found throughout the environment, everyone is exposed to low levels of mercury.

* Chambers and Holliday, 1975

** Fitzgerald, et al, 2003

*** Alan, et al, 1996

Dental amalgams are themselves about half mercury and it is known that mercury in the breath of persons with mercury amalgam fillings is higher than those without. However, health effects of dental amalgams are unknown.

Mercury emanating from amalgams is, at least initially, entirely in inorganic forms, which are not readily accumulated by the body as compared to methyl mercury.

Other principal means of human mercury exposure are through the use of skin care products and, particularly, through the consumption of methyl mercury contaminated fish. The three pathways of exposure are then inhalation, absorption, and ingestion*.

1.1.4 Mercury as an environment pollutant

Mercury contamination in environment is a major concern because of its toxicity and bio-accumulative ability. Physicochemical properties of soils determine mercury mobilization from soils to water resources and been transferred through aquatic food webs to humans. The effects of land use may change the soil properties and increase the potential anthropogenic mobilization of mercury from soil to groundwater.

The quality of soil and water resources in two Sekotong's gold mining villages in Lombok, Indonesia, and the nearby river, named Merebekriver, has been assessed based on the compliance standard of mercury concentrations and other physicochemical properties set by US.EPA.

The data shows, mercury concentrations of soils in two villages were 0.029, 0.180 (mg/kg) and mercury concentrations on ground water in two villages were 0.049, 0.325 (ppb).

A high mercury contamination was found in all sampling locations of the river, but still meet the compliance. The high mercury level at the sampling locations nearby

* Alan, et al, 1996

the both villages shows human activity contributes to an increased mercury level in river water*.

1.1.5 Sources of Mercury pollution

Mercury, which occurs as a result of both natural and anthropogenic sources in our environment

Natural Sources

It can occur naturally in a variety of valence states and conjugations, such as Hg^0 (elemental mercury), Hg^{+2} (dissolved in rainwater, or as the ore cinnabar, HgS), and as an organometal such as methyl mercury (CH_3Hg) and $(\text{CH}_3)_2\text{Hg}$. Moreover, through natural chemical and biological reactions, mercury changes form among these species, becoming alternately more or less soluble in water, more or less toxic, and more or less biologically available.

Mercury is initially released into the biosphere through volcanic activity, it is present in the earth's crust at a concentration of 0.5 ppm. Mercury typically forms the sulfide (HgS) because of the prevalence of sulfides in volcanic gases. In this fashion it is found naturally in deposits as the red sulfide ore, cinnabar. It is commercially mined as this form. Volcanic sources emit an estimated global total of 60,000 kg of mercury per year.

Biomass, particularly trees and brush, accumulate and harbor a substantial fraction of the biosphere's mercury. When forest fires heat these fuels to temperatures well above the boiling point of mercury (357°C), mercury may be released to the atmosphere as either Hg^{2+} or the decomposed Hg^0 . The Hg^0 released may be oxidized in the atmosphere over time to Hg^{2+} which is also quite soluble in water and so dissolves in the moisture in the air when released in this fashion.

* Doni, et al, 2015

Forest fires and rains are responsible for the transport and deposition of mercury over much of the world's surface, regardless of its source.

Mercury is, also, a component of seawater and is released naturally through the evaporation of elemental mercury from the ocean's surface. Both elemental and ionic mercury are soluble in water, although elemental mercury to a much smaller degree. As less soluble elemental mercury evaporates, the equilibrium reaction is pulled towards more elemental mercury, which then releases more elemental mercury from the ocean's surface.

Anthropogenic Sources

Mercury is used in a broad array of more than 2000 manufacturing industries and products. The watershed of the San Francisco Estuary contains tremendous amounts of mining-related, bulk mercury contamination. Historically, mercury was mined intensively in the Coast range and transported across the Central Valley for use in Sierra Nevada placer gold mining operations. Virtually all of the quicksilver used in these operations was ultimately lost into Sierran watersheds. It has been estimated that, in river drainages of the Mother Lode region alone, approximately 7600 tons of refined quicksilver was inadvertently deposited in conjunction with, Gold Rush era, mining.

Coal is known to contain mercury as a result of testing done upon the flue gas emitted from power plant stacks. The quantity released by burning coal is estimated to be on the order of 3000 tons per year globally, about the same amount released through all industrial processes.

During the burning of coal, mercury is initially decomposed to elemental mercury and then, as the flue gas cools and exits the plant, the majority of mercury is quickly oxidized, probably catalytically, due to the presence of other metals in the gas, to its water-soluble, ionic form(Hg^{2+}).

Crude petroleum is known to contain small but measurable amounts of mercury. Approximately 16 to 18 million barrels (672 to 756 million gallons) of crude oil are consumed daily in the United States. At an average concentration of 0.41 ppm mercury and an average density for crude oil of 6.9 lbs per gallon, the minimum total amount of mercury vaporized daily is therefore 1901 lbs. This value represents an annual discharge of 347 tons of mercury nationwide, assuming that all of the oil is combusted.

Elemental mercury is employed as the electrode in the electrochemical production of chlorine gas and caustic soda (sodium hydroxide). Near most paper and pulp facilities which employ this technology to bleach the paper product white, the sediment is contaminated with high concentrations of mercury*.

Standards and limits

There are many rules and references for the permissible limits of mercury in soil and water that have been approved by international and/or regional organizations and agencies as shown in (Table 1.1) to protect the environment and humans from the damage caused by mercury.

Table 1.1 Environmental and Occupational Exposure Limits of Mercury in water.^{**}

Defined Limit	Delegating Body/Document	Threshold Exposure Limit
Ambient Water Quality Criteria	Clean Water Act (EPA)	144 ng/L (ppt)
Drinking Water Maximum	EPA	≤ 2 µg/L (ppb)
Food Products (fish and seed grain)	FDA EPA (proposed recommendation)	≤ 1 mg/kg (ppm) CH ₃ Hg ≤ 0.01 mg/kg

* Alan, et al, 1996

**Larry, et al, 2002

Canadian council of ministers of the environment (CCME)^{*} was published in 1999 soil quality guidelines for mercury for protection of environmental and human health (Table 1.2)

1.2 Soil quality (CCME) guidelines for mercury (mg/kg)

No	Land use	CCME Limit (mg/kg)
1.	Agricultural	6.6
2.	Residential/ parkland	6.6
3.	Industrial	50

1.1.6 Methods of analysis and determination

Many of the analytical methods used for environmental samples are the methods approved by federal agencies and organizations such as EPA and the National Institute for Occupational Safety and Health (NIOSH). Other methods that are approved by groups such as the Association of Official Analytical Chemists (AOAC) and the American Public Health Association (APHA). Additionally, analytical methods are included that modify previously used methods to obtain lower detection limits, and/or to improve accuracy and precision.

Mercury levels have been determined in numerous environmental matrices, including air, water (surface water, drinking water, groundwater, sea water, and industrial effluents), soils and sediments, fish and shellfish, foods, pharmaceuticals, and pesticides. The sample preparation varies with the complexity of the matrix, but most complex samples require decomposition of the matrix and reduction of mercury to its elemental form^{**}.

Both CVAAS and CVAFS have been used to monitor air and suspended

* Canadian Council of Ministers of the Environment, 1999

** Horvat, 1996

particulates in air for mercury. Both methods are sensitive, accurate, and precise, although slightly greater sensitivity was reported with AFS (low ppt) than with AAS (mid ppt); When AAS or AFS was combined with gas chromatography (GC), the different mercury species (inorganic mercury, dimethyl mercury, diethyl mercury, and methyl mercury chloride) present in the air could be separated. A colorimetric method, based on the formation of a colored complex formed in the presence of mercury, has been used as a quick and simple field test that can detect mercury present at the mid-ppb level.

Numerous methods, including CVAAS, inductively coupled plasma (ICP) MS, ICP atomic emission spectrometry (AES), microwave-induced plasma (MIP) AES, GC/AFS, high-performance liquid chromatography (HPLC)/UV, HPLC/ECD, and spectrophotometry, have been used to determine mercury levels in aqueous media*.

1.1.7 Treatment of Mercury pollution

Removal technologies such as adsorption, desorption, oxidation and reduction used. The major aim of these technologies is to separate mercury from the contaminated media or transform toxic mercury species into less toxic ones. The most widely adopted immobilization techniques are stabilization and containment, which prevent mercury migration by chemical complexation or physical trapping, respectively.

Adsorption and desorption

The adsorbents usually possess high surface area as well as high porosity and the formation of chelates is the major sorption mechanism synthesized thioether-functionalized covalent triazinenanospheres to adsorb Hg^{+2} and Hg^0 from water. Excellent adsorption capability was observed (1253 and 813 mg/g for Hg^{+2} and Hg^0), respectively utilized silica-coated magnetic nanoparticles to extract Hg (II)

* Beckert, et al, 1990

from wastewater, and the adsorption of mercury ions onto the imine (C-NH-) groups on the surface of nanoparticles was discovered.

Stabilization and containment

Stabilization approaches immobilize mercury in contaminated sites through chemical complexation to decrease solubility in order to minimize exposure of mercury to the environment.

During the chemical stabilization process, sulfur-containing reagents such as elemental sulfur, pyrite (FeS_2) or thiosulfate are commonly used to react with Hg^0 in contaminated soil to form HgS , which is very insoluble.

Low-permeability physical barriers (e.g. slurry walls, caps or grout curtains) are installed around the contaminated soil to isolate and contain the soil, and thus prevent the migration of mercury to the surrounding environment.

Nanomaterials

Nanomaterials are gaining more and more attention in mercury remediation of soil, water and flue gas, owing to their high adsorption capacity, small dimension and other unique electrical, mechanical and chemical properties.

A range of nanomaterials have been used for Hg remediation. They can be divided into three types: nanoparticles, nanosheets and nanocomposites. Among these types, nanosheets are less frequently used than nanoparticles and nanocomposites, while MoS_2 nanosheets can achieve a high adsorption capacity of both $\text{Hg}(0)$.

There are several major types of nanoparticles and nanocomposites. Carbon-based nanomaterials such as carbon nanotubes (CNT) are gaining much interest, and in order to improve their interactivity, amine or thiol groups are introduced through chemical functionalization. ferric oxide (Fe_3O_4) nanoparticles are another emerging material for Hg remediation. They possess some outstanding properties, such as ease of recovery, super paramagnetism and large surface area.

Biochar:

Biochar is a solid and stable high-carbon material produced through thermal decomposition of organic material (biomass such as wood, manure or leaves) in the absence of oxygen or under oxygen-limited conditions at relatively low temperatures (< 700 C).

Biochar is recognized as a functional material for in situ remediation of mercury contaminated sites due to its advantageous properties (e.g., easy operation, little environmental degradation and high adsorption efficiency) and has also received considerable attention for the remediation of contamination by other metals* .

Methyl mercury:

The dominant route of exposure to methyl mercury is through the ingestion of fish. Most fish, both freshwater and saltwater, contain methyl mercury. Methyl mercury can be absorbed through the skin and the lungs as well.

Once absorbed into the circulation, methyl mercury enters erythrocytes where more than 90% will be found bound to hemoglobin. Lesser amounts will be bound to plasma proteins. About 10% of the burden of methyl mercury is found in the brain where it slowly undergoes demethylation to an inorganic mercuric form. Methyl mercury readily crosses the placenta to the fetus, where deposition within the developing fetal brain can occur. In the brain, methyl mercury causes focal necrosis of neurons and destruction of glial cells and is toxic to the cerebral and cerebellar cortex. In 1953 and 1960, the toxicity of methyl mercury was recognized worldwide following epidemics of mercury poisoning in the Japanese inhabitants of Minamata and Niigata Bays due to consumption of fish caught in the region. Waste containing mercuric chloride had been released into the bays and

became concentrated in the fish after conversion to methyl mercury by plankton. The subsequent birth of infants suffering from degenerative neurological disorders,

* Liuwei, et al, 2020

Blindness, and deafness even though the mothers exhibited only mild symptoms demonstrates the increased susceptibility of the fetus to methyl mercury exposure. Acute alkyl mercury poisoning is often referred to as Minamata disease. The largest epidemic, methyl mercury poisoning occurred in Iraq in 1971 to 1972 when more than 500 people died and more than 6000 were hospitalized due to ingestion of bread made from seed grain treated with fungicide containing methyl mercury. A daily intake of more than 0.3 mg

Methyl mercury produces chronic mercury poisoning in the average 70 kg adult. This level of consumption is consistent with steady-state mercury concentrations of 0.2 mg/L in blood, 60 mg/kg in hair, and an approximate total body burden of 25 mg* .

1.2 Literature Review

World-wide, large quantities of liquid mercury are used to extract sedimentary gold from river bed soil by forming an amalgam which is then heated to evaporate Mercury, leaving pure gold. An estimated 130 or more tons of mercury are released per year in the Amazon basin.

In 2000 Toxic Exposure Surveillance System report of the American Association of Poison Control Centers documented 4,186 exposures to mercury in the United States. Of these, 980 were in children younger than 6 years with the majority of exposures in persons older than 19 years. Only 1, a gold miner, died due to an accidental exposure while attempting to extract gold with poor ventilation.

In most situations, the primary route of exposure to mercury for the general public is via the consumption of fish** .

An artisanal gold mining region located in North of Atbara (Dar-Mali locality), River Nile State, Sudan has been studied with the aim to evaluate the soil

* Alpers, et al, 2005** Litovitz, et al, 2000

Contamination with mercury and twenty soil samples were collected from different sites around gold mining area.

Microwave digestion oven model (CEM Mars 5) was used to digest soil samples and Mercury concentration was determined by ICP mass Spectrometer (Perkin Elmer 350D).

This study revealed that high concentrations were obtained at mining zones particularly inside gold extraction basins (2.62 mg kg⁻¹ soil), and the minimum concentrations were found at Nile River terrace (0.10 mg kg⁻¹ soil). Generally, Mercury concentration in the study area were rated as to following sequences; Inside gold extraction basins > Outside gold extraction basins > around gold mining zones>Nile Valley University(Instructional farm)> Inside residential zones> Nile Valley University(Agricultural college), > Recent Nile River terrace* .

In the other study to assess the mercury (Hg) exposure level of gold miners in Butana mining area, in Eastern, Sudan.

A total of 20 hair samples and 20 nails samples were collected from 10 sites in Butana mining area, Random sampling was adopted.

Hair samples were taken from occipital region of the head, and the Samples of nails were cut using clean stainless steel scissors.

All samples were packed in clean, sealable bags and transferred to the laboratory for analysis.

Total Mercury in Hair and nail samples were determined using US EPA Method 7473 and a direct mercury analyzer(DMA-80; Milestone Inc.,Shelton, CT, USA). The method is based thermal decomposition, amalgamation, and AAS.

* Mushtaha, et al, 2018

Average of mercury concentration levels in hair samples of gold miners were between 3.02 mg/kg to 8.34 mg/kg, while in nail samples were between 2.53 mg/kg to 7.26 mg/kg.

The research indicates that gold miners and local population in the study area had high exposure to mercury vapors because the miners burn gold-mercury amalgams to vaporized mercury and recover the gold*.

Artisanal and small-scale gold mining (ASGM) is one of the largest sources of mercury (Hg) pollution. The population of gold miners in the studied three villages was 1300 households (25.77% from a total of 5044 households) in Indonesia. (ASGM) involves both men and women employed as miners and gold amalgam processors, respectively.

The results showed an average T-Hg in men of 3.27 ± 2.89 ppm, and women of 5.91 ± 4.69 ppm. The level of T-Hg in the respondents was associated with distance to the ball mills and not related to distance to the mine site**.

To enhance gold recovery from hydraulic mining, hundreds of pounds of liquid mercury (several 76-lb flasks) were added to riffles and troughs in a typical sluice. Some remobilized placer sediments, especially the coarser material, remain close to their source in ravines that drained the hydraulic mines. Mercury use in sluices varied from 0.1 to 0.36 lb per square foot. A typical sluice had an area of several thousand square feet; several hundred lb of mercury were added during initial start-up, after which several additional 76-lb flasks were added weekly to monthly throughout the operating season (generally 6 to 8 months, depending on water availability). During the late 1800s, under the best operating conditions, sluices lost about 10 percent of the added mercury per year, but under average conditions,

* Israa, et al, 2019

** Alfonsus, et al, 2020

The annual loss was about 25 percent. Assuming a 10 to 30 percent annual loss rate, a typical sluice likely lost several hundred pounds of mercury during the operating season^{*}. From the 1860s through the early 1900s, hundreds of hydraulic placer-gold mines were operated in California, especially in the northern Sierra Nevada. The total amount of mercury released into the environment from placer mining operations throughout California has been estimated at 10,000,000 lb, of which probably 80 to 90 percent was in the Sierra Nevada^{**}.

Historical records indicate that about 3,000,000 lb of mercury were lost at hard rock mines, where gold ore was crushed watersheds since 1999. Fish from reservoirs and streams in the Bear-Yuba watersheds have bioaccumulated sufficient mercury to pose a risk to human health^{***}.

Food and Drug Administration (FDA) advisory limit for methyl mercury in commercial fish is 1 ppm (1 µg/g). By comparison concentrations of 10 to 30 ppm were present in fish during the Minamata epidemic. The United States has placed restrictions on commercial fisheries prohibiting the sale of fish having a total mercury content of greater than 0.5 µg/g. This limitation can be difficult to maintain in contaminated areas. Generally, marine levels of mercury range from undetectable to 5.0 µg/g (average 0.2 to 0.5 µg/g) but contaminated freshwaters have been as high as 40 µg/g^{****}

* Hunerlach, et al, 1999

** Churchill, 2000

*** Kuwabara, et al, 2003

**** Yess, 1993

In 2001, the FDA issued an advisory to pregnant women and women of childbearing age who may become pregnant regarding the potential hazard of consuming fish that might have high levels of methyl mercury. Among the fish included in the warning were shark, swordfish, king mackerel, and tilefish. These fish tend to contain high in methyl mercury content not only due to feeding on smaller fish, but also because they live longer and accumulate high concentrations of mercury in their tissues. Once released into the ocean environment, mercury is sequestered by plankton and other microorganisms and converted to methyl mercury. When fish consume these organisms, methyl mercury accumulates in the fish without harm. Unfortunately, humans and other species that consume the fish are not as lucky. The National Research Council has estimated that annually 60000 newborns are at risk of mercury poisoning. The Environmental Protection Agency (EPA) has established a reference dose (RfD) of 0.1 $\mu\text{g}/\text{kg}$ body weight/day for methyl mercury. The EPA defines a reference dose as an estimate of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. The RfD for methyl mercury was originally established based on data from the Iraq epidemic and was re-evaluated using epidemiological longitudinal developmental studies in the Seychelles Islands, the Faroe Islands, and New Island. The National Academy of Sciences report to Congress in July 2000 determined that the EPA's RfD for methyl mercury (0.1 $\mu\text{g}/\text{kg}/\text{day}$) is a scientifically justifiable level for the protection of public health, and that the Faroe Islands study is the most appropriate study for deriving RfD*.

Human exposure has raised such concern that 128 countries have signed a global treaty, The Minamata Convention on Mercury, which entered into force in August 2017.

* National Academy of Sciences, 2002

This treaty has the explicit objectives to reduce Mercury emissions and protect human health and the environment. Major highlights of the Minamata Convention include a ban on new Mercury mines, phase-out of existing operations, and removal of Mercury from a number of products and processes, including the regulation of artisanal and small-scale gold mining. The convention also entails control measures for Mercury emissions to air and the release to land and water as well as for interim storage of Mercury and its disposal once it becomes waste. Mercury derived from both natural and anthropogenic sources enters the global Mercury cycle Fig (1.1) and is ultimately wet or dry deposition into either aquatic or terrestrial ecosystems. Notably, Mercury is very persistent in soils, lakes and oceans^[18] and its mobility depends on the chemical speciation, which is a function of several soil parameters and their interactions.

Although soil has a natural capacity to attenuate heavy metals through various mechanisms, concentrations exceeding the attenuation capacity will inevitably lead to soil contamination. Mercury contamination in soil derives mainly from Hg mining and metallurgy, gold mines and Zn/Pb smelters, chemicals production facilities involved in the production of chlor-alkali, chloroethylene and acetaldehyde, landfills, military installations and wood/forestry impregnation sites*.

Subsurface sediments and soils contaminated with mercury present unique challenges for remediation.

* Wang, et al, 2012

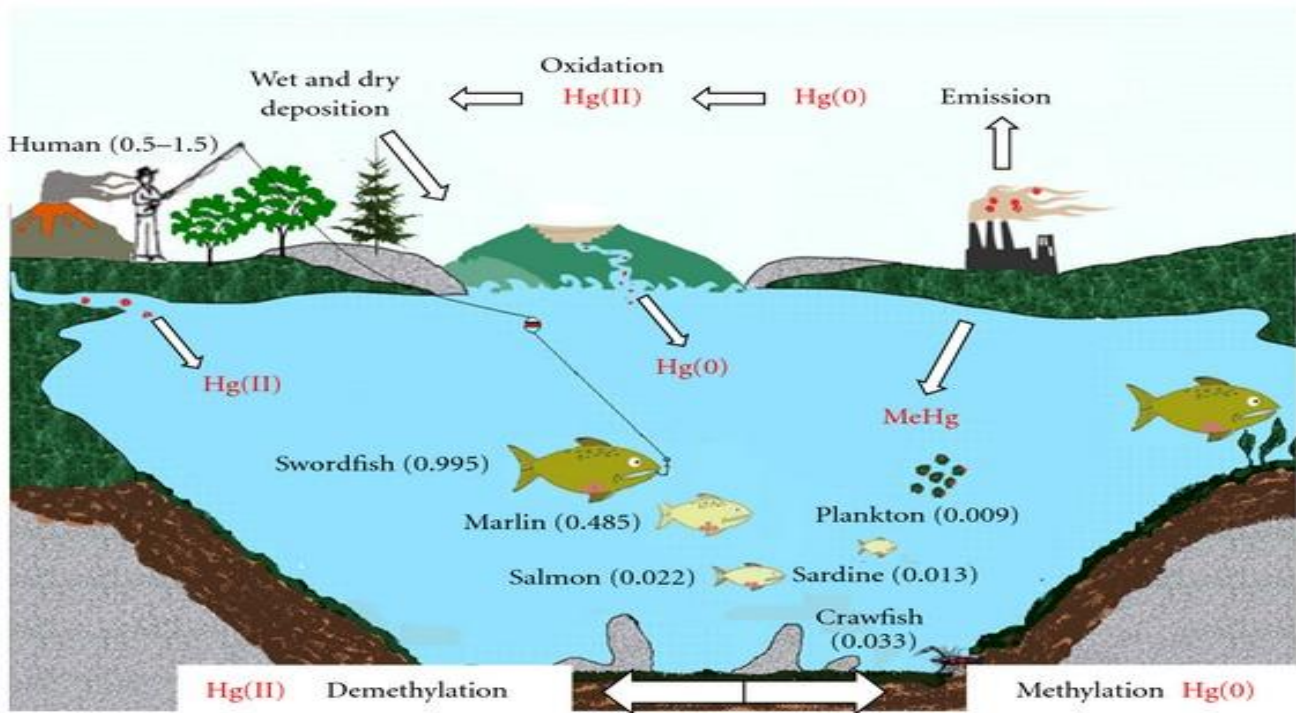


Figure 1.1 Mercury cycle in the ecosystem including MeHg generation in aquatic Environment*

*Roos, et al, 2012

1.3 Objectives

The main objective of this research is to:

1. Determine of mercury concentration in soil and water sample using DMA technique in mining areas of northern and eastern Sudan.
2. To investigation the optimal remediation of Mercury environmental contamination.

Chapter Tow
The Materials and Methods

2. Materials and methods

2.1 Study Areas



The study area is located around mining areas in Abuhamad locality (gabqaba, almaqal, alobeidiya, alfaraqa and nuraya), River Nile state, Northern Sudan; and from the east of Atbara River, Kasala State.

2.2 Materials

A total of ten soil samples and three rain water samples were collected from 6 sites in mining areas in North and East Sudan (east of Atbara River), random sampling was adopted.

Seven soil samples were collected from (gabqaba, almaqal, alobeidiya, alfaraqa and nuraya) northern Sudan, when three soil samples were collected from east of Atbara River.

Water Samples were collected from rainwater hole near the mining area east of Atbara River, all samples were packed in clean, sealable bags and transferred to the laboratory for analysis.

2.3 Instrumentation

(DMA-80) direct mercury analyzer

Principle of operation

The sample introduction device consists of a motorized support equipped with a metal or metal alloy sample boat.

Once the sample is either manually or automatically dispensed into the sample boat, the boat is mechanically introduced automatically into a quartz decomposition tube.

The decomposition tube is heated by two, independently, programmable furnaces the decomposition and catalyst furnaces, and each furnace is capable of maintaining a temperature of at least 750 C. The samples are first dried and then thermally decomposed in an oxygen rich furnace, releasing mercury vapor.

Mercury and other combustion products are released from the sample and they are carried to the catalyst section of the furnace, where nitrogen and sulfur oxides, as well as halogens and other interfering compounds, are eliminated.

Mercury vapor is transported, by oxygen, over the amalgamator that traps the mercury.

Mercury is selectively trapped, in a separate furnace, through gold amalgamation. The amalgamation furnace is heated and mercury is rapidly released. The mercury vapor flown via the carrier gas in to a unique block with tri-cell arrangement, positioned along the optical path of the spectrophotometer, where it is Quantitatively measured by atomic absorption at 253,65nm.

The flow path through the spectrometer and cuvettes is maintained at approximately 120 C, by a heating unit, to prevent condensation and minimize carry-over effects.

A mercury vapor lamp is used as the light source.

The detector is connected to a computer for data acquisition and analysis.

2.4 Methods

The standard solutions of mercury were prepared by serial dilution from known Standard stock solutions of 1000mg/L. A calibration curve was prepared and then the analysis of the samples for the mercury was performed.

Total Mercury in the soil and water samples were determined using US EPA Method 7473 and a direct mercury analyzer (DMA-80; Milestone Inc., Shelton, CT, USA).

The method is based on thermal decomposition, amalgamation, and AAS.

Sample (0.003 g) of soil samples and (0.5ml) of water samples were weighed onto nickel boat, the boat was placed into an auto sampler which sequentially inserts them into the combustion tube of the instrument.

There, the samples were heated with oxygen flowing over them at 200 ml min⁻¹, the decomposition and combustion products were swept through a catalyst tube where oxidation was completed, and nitrogen and sulfur oxides and halogens were trapped.

The remaining gases, including Hg⁰, were carried to a gold amalgamator which selectively traps Hg. Later, the gold trap was rapidly heated releasing Hg vapor into the spectrophotometer.

Absorbance, measured at 253.7 nm, is a function of mercury concentration. The parameters of DMA-80 direct mercury analyzer were adjusted according to the manufacturer's recommendation.

Chapter Three
Results and Discussion

3. Result and Discussion

Table 3.1 the sequence of calibration curve standard solution and absorbance

Table 3.1 Cell (0) Absorption response of Mercury standard solutions

No.	Hg (ng)	Absorbance (A)
1.	0.0000	0.0250
2.	0.0000	0.0132
3.	0.5000	0.0886
4.	1.0000	0.1583
5.	1.5000	0.2409
6.	2.0000	0.3143
7.	2.5000	0.3703
8.	5.0000	0.5908
9.	10.0000	0.9558
10.	15.0000	1.2097

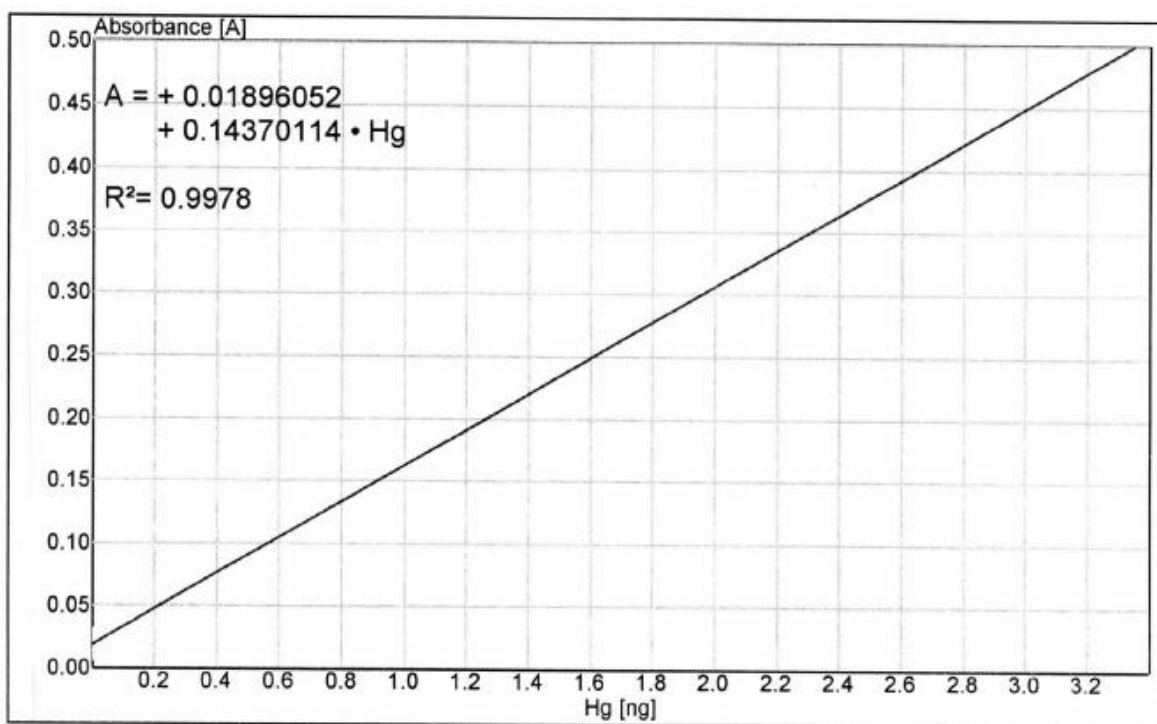


Figure 3.1 Calibration curve (cell 0)

Table 3.2 Cell (1) Absorption response of Mercury standard solutions

No.	Hg (ng)	Absorbance (A)
1.	0.0000	0.0090
2.	0.0000	0.0050
3.	0.5000	0.0325
4.	1.0000	0.0595
5.	1.5000	0.0916
6.	2.0000	0.1208
7.	2.5000	0.1446
8.	5.0000	0.2450
9.	10.0000	0.4582
10.	15.0000	0.7014

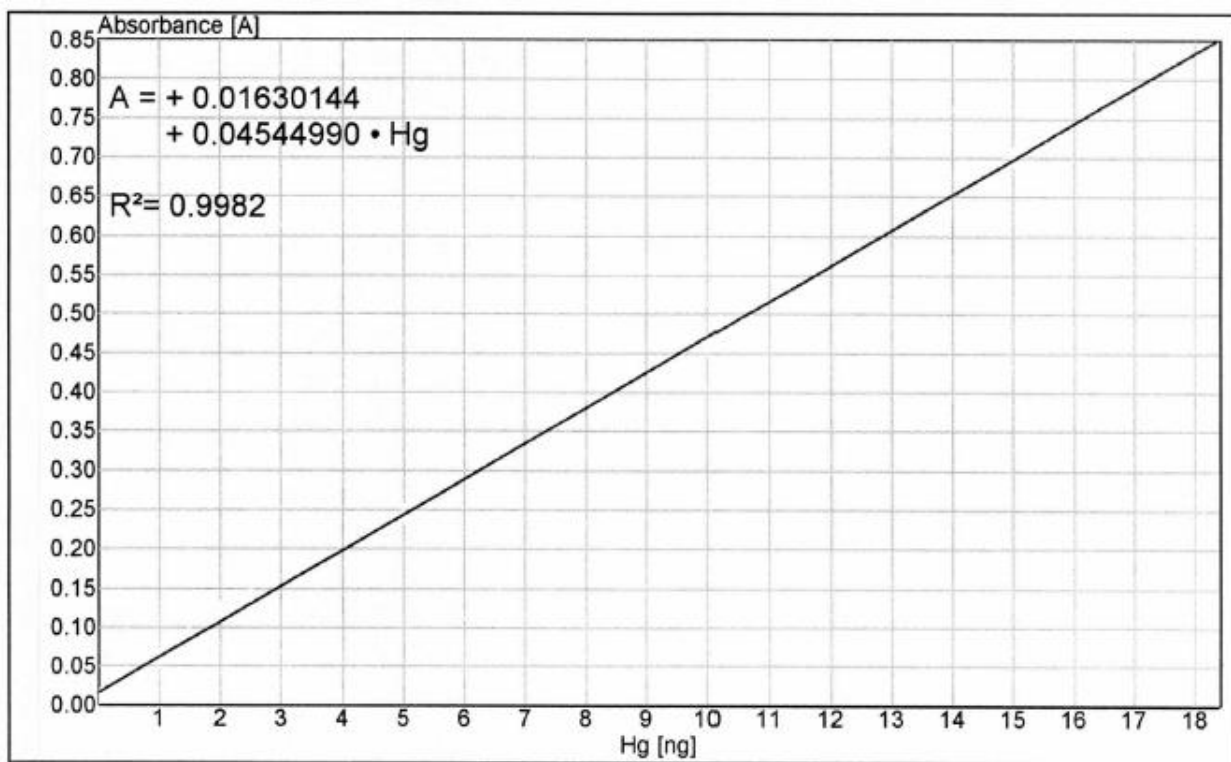


Figure 3.2 Calibration curve (cell 1)

3.1 Soil Sample Results

Table 3.3 shows result of 10 soil samples collected from the study areas

Table 3.1 Mercury Concentration ($\mu\text{g/g}$)

No	Name of sample Area	Hg ($\mu\text{g/g}$)
1.	Gabqaba	22.9257
2.	Almaqal	31.5909
3.	Alfaraqa (A)	18.9575
4.	Alfaraqa (B)	3.6740
5.	Alobeidiya (A)	35.7944
6.	Alobeidiya (B)	16.0783
7.	Nuraya	31.2931
8.	east of atabara river (A)	25.1224
9.	east of atabara river (B)	19.3714
10.	east of atabara river (C)	20.4103
11.	Mean	22.5218
12.	Standard deviation	9.226281

All the results of soil tests showed the presence of mercury element in different concentrations (Table 3.3), figures 3.3 and 3.4 shown the response of absorbance against the time (s) of mercury passing through tri cell. The highest concentration (Fig 3.3) was found at 35.7944 $\mu\text{g/g}$ in alobaidiya- A, the lowest concentration at 3.674 $\mu\text{g/g}$ (Fig 3.4) was found in alfarqa-B, and the average concentrations in soil in the mining areas was 22.5218 $\mu\text{g/g}$ and standard deviation is 9.226.

Results were explained in Fig 3.5 (bar graph) and Fig 3.6 (Pi diagram) to show values of Mercury concentrations and its percentage distribution.

Compared to a study conducted on soil in mining areas in North of Atbara (Dar-Mali locality), River Nile State, Sudan, it was found that the average concentration of mercury was 1.36 ppm, the concentration of Mercury In soil under study which is approximately 16 times of compared study.

According to a similar study conducted in Kenya^{*}, the concentration of mercury

* Yess, 1993

Was 1920 ppm which is equivalent to 85 times the concentration that was reached. According to CCME residential and agricultural limit all samples result consider above of permissible limit except Alfaraga (B) sample, and it's within CCME industrial limit.

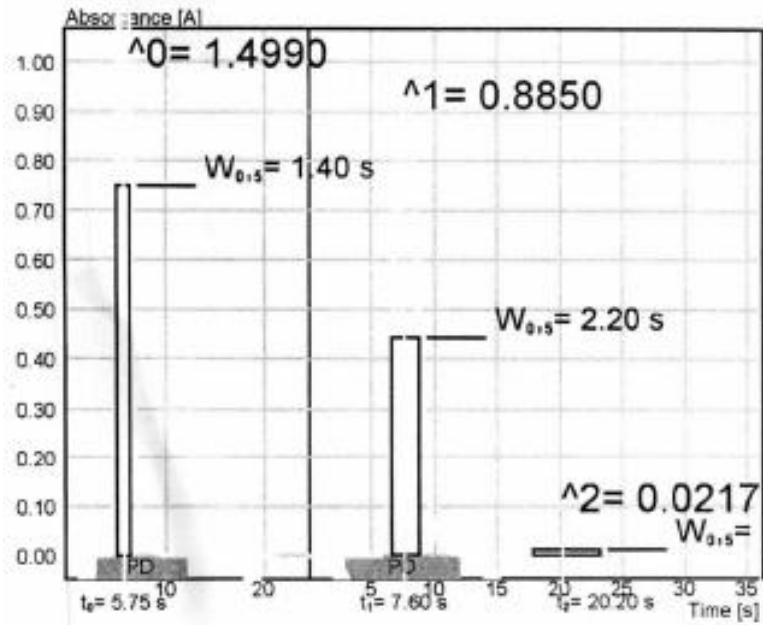


Figure 3.3 signal curve -Alobeidiya (A)

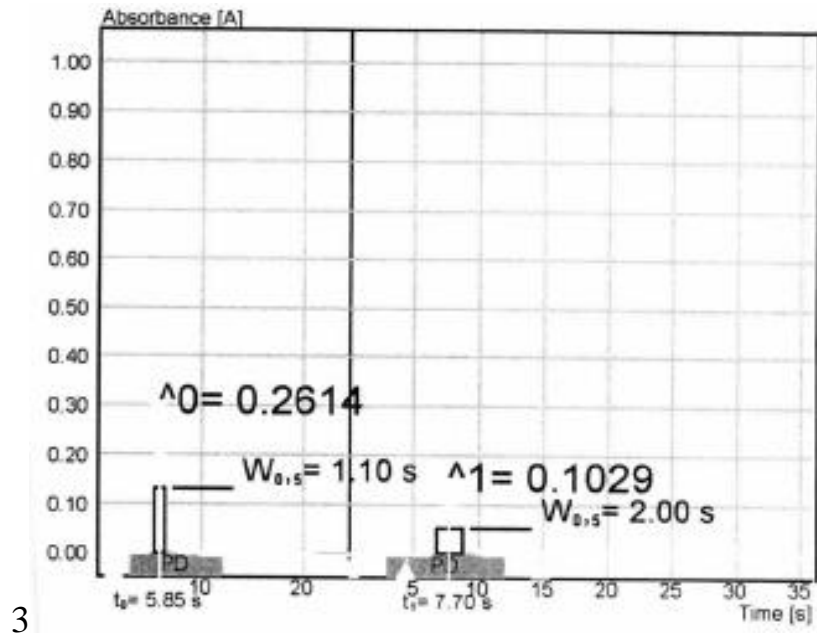


Figure 3.4 signal curve- Alfaraga (B)

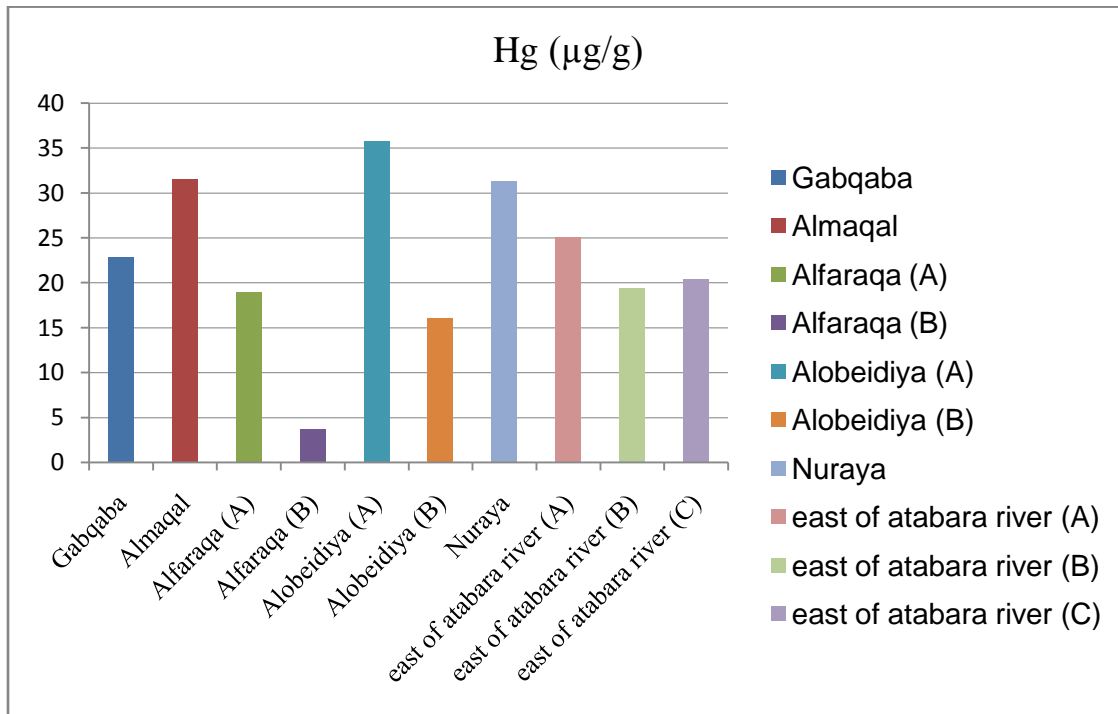


Figure 3.5 soil result diagram

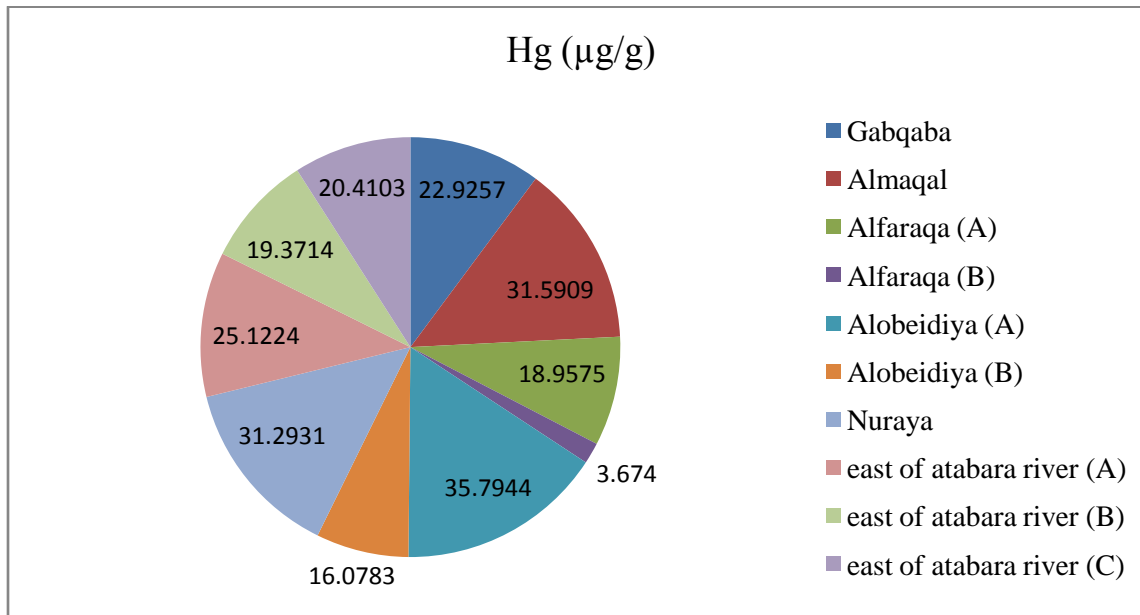


Figure 3.6 soil result pi diagram

3.2 Rain Water Sample Results

Table 3.4 shows result of 3 water samples collected from the study area

Table 3.2water sample result

No	Name of sample Area	Hg ($\mu\text{g/L}$)
1.	east of atabara river (A)	0.0915
2.	east of atabara river (B)	0.4946
3.	east of atabara river (C)	0.2365
4.	Mean	0.2742
5.	Standard deviation	0.204177

All the results of rainwater test near the mining area east of Atbara river showed the presence of mercury in different concentrations (table 3.4), the highest concentration (Fig 3.7) 0.4946 $\mu\text{g/L}$ was found in sample B, the lowest concentrations 0.0915 $\mu\text{g/L}$ was found in sample A, The percentages of mercury concentrations have been shown in Fig3.8 (Pi diagram)and the average concentration of mercury was 0.2742 $\mu\text{g/L}$ and standard deviation is 0.2042.

It was found that there are high concentrations (0.2742 $\mu\text{g/L}$) up to approximately twice permissible limit for cleaning water and within permissible limit for drinking water according to the EPA recommendation (144 ng/L, $\leq 2 \mu\text{g/L}$) respectively.

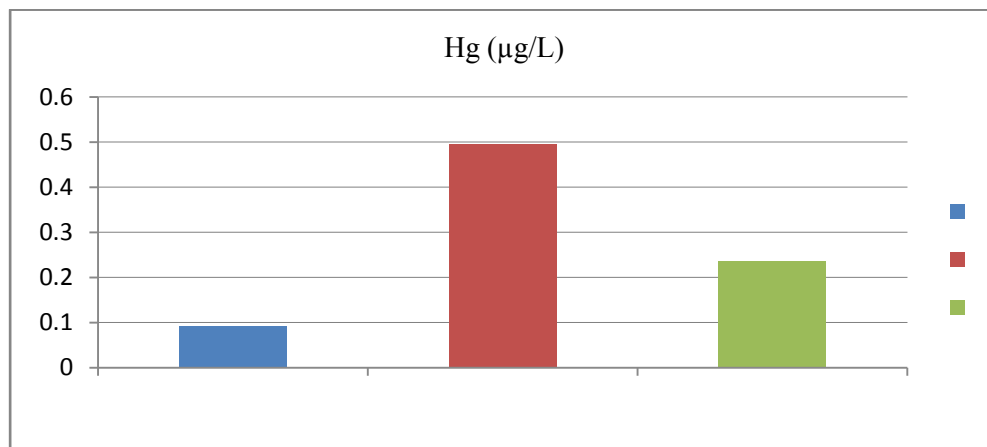


Figure 3.7water result diagram

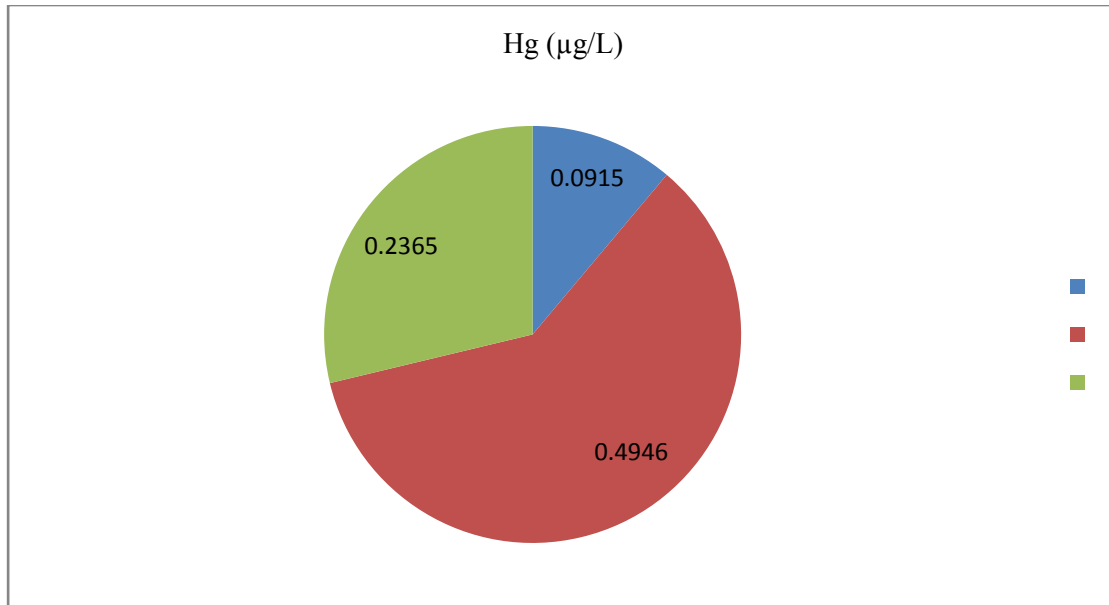


Figure 3.8 water result pi diagram

3.4 Conclusions

As a result of Mercury random use in gold mining, there are high concentrations up to approximately twice the permissible limit for cleaning water and within permissible limit for drinking water according to the EPA recommendation.

By comparing the result of soil samples with CCME guidelines the concentration is up to 3.5 times of the permissible limit for residential and agricultural limit.

Results obtained are catastrophic and predict the occurrence of severe and destructive consequences for the environment when compared to permissible limits.

3.5 Recommendations

- It is recommended that further studies should be conducted to cover and survey all mining areas in Sudan.
- Review mining policies in Sudan, and obligate mining entities to scientific controls for the use of mercury to ensure that it does not leak into the environment.

- Precipitation in those areas works to transfer mercury from the soil and the environment surrounding the mining areas to rivers and groundwater, it is necessary to measure mercury concentrations along the course of the Nile and take samples from fish.
- Soil samples result showed that areas under study are not suitable for any agricultural or residential activities, while they can be used as an industrial area only.
- It is necessary to investigate the concentration of mercury in humans (blood, hair, nails) and animals (dairy, meat) as well as plants in the mining areas.

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