KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI

COLLEGE OF SCIENCE

DEPARTMENT OF CHEMISTRY

SORPTION OF INORGANIC MERCURY ON SOILS FROM ANKOBRA BASIN IN THE
SOUTH - WESTERN PART OF GHANA

BY

AZANU DAVID, BSc (HONS)

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DECLARATION

I hereby declare that this submission is my own work towards the MSc and that, to the best of my knowledge, it contains no material previously published by another person or material which has been accepted for the award of any other degree of this University except where due acknowledgment has been made in the text.

David Azanu ……………………….. …………………

(PG 2848708) Signature Date

Certified by:

Dr. R. B. Voegborlo ………………………… …………………

Supervisor Signature Date

Certified by:

Dr. J. A. M. Awudza ……………..………… ……………….

Head of Department Signature Date

DEDICATION

I dedicate this work to the Comforter.

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ABSTRACT

Understanding the adsorption of mercury on soil from aqueous solution is necessary for tracing the fate of mercury in the environment. The fate of mercury in the soil is important not only to assess surface and groundwater quality, but also to understand mercury fluxes at the soil/air and water/air interfaces. The most important chemical retention mechanisms are sorption processes and precipitation. This study was undertaken to predict the fate of mercury emitted from artisanal gold mining activities within the Ankobra basin. Total mercury (THg) concentrations were determined in soils close to River Ankobra and its major tributaries in the south-western part of Ghana by Cold Vapour Atomic Absorption Spectrophotometry. Some soil characteristic such as pH, particle size distribution and organic matter were also determined. THg content of the soils ranged from 0.051µg/g to 0.366µg/g with an average of 0.15µg/g, which were below the permissible level of THg for soils (200µg/g) set by US EPA. THg correlated positively (r = 0.57) with the organic matter content of the soil. This indicates increasing Hg concentration with increasing organic matter content. Sorption of Hg (II) onto seven (7) different soils from the A-horizon indicated that the soils had an L - type isotherm and the distribution coefficient (K_d) ranged from 41.4 µg/g to 182.2 µg/g. The Freundlich model showed a better fit followed by Langmuir model and Linear model because most of the regression coefficients were close to one. The best fitness of Freundlich model to the other models could be attributed to the heterogeneous surface energies and exponential distribution of active sites which are characteristic of such soils. All the soils had adsorption intensity (n) lower than one, indicating that the soils could be good sorbents for Hg (II). This suggests that the fate of Hg and its availability in soil for runoff and leaching could be low for soils with such characteristics.

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LIST OF ABBREVIATIONS

- AD- Alzheimer's Disease

- ALS- Amyotrophic Lateral Sclerosis

- ATSDR- Agency for Toxic Substances and Disease Registry

- CEC- Cation Exchange Capacity

- CNS- Central Nervous System

- CVRWQCB- Central Valley Regional Water Quality Control Board

- IARC- International Agency for Research on Cancer

- MS - Multiple Sclerosis

- PD- Parkinson's Disease

- RPD - Redox Potential Discontinuity

- SRB- Sulfur- Reducing Bacteria

- THg- Total Mercury

- UNIDO – United Nations Industrial Development Organization

- U.S. EPA – United States Environmental Protection Agency

- WHO- World Health Organization

CHAPTER ONE

1. INTRODUCTION

Human activities such as mining and associated smelting, burning of fossil fuels, and industrial uses of mercury (Hg) in paints, batteries, medicine, and dentistry have significantly increased the global reservoir of atmospheric mercury since the beginning of the industrialized period (Fitzgerald *et al*., 1998). This Hg is widely distributed via atmospheric processes, and deposition from the atmosphere into terrestrial and aquatic systems, even those in remote areas, and has led to the recognition of Hg as a global pollutant (Jackson, 1997; Fitzgerald *et al*., 1998). Point sources are important in delivering Hg to aquatic systems, but atmospheric Hg deposition, either directly to the aquatic system or indirectly via deposition to terrestrial watersheds and its subsequent transport, is also significant (Fitzgerald *et al*., 1998; Schroeder and Munthe, 1998).

High concentrations of mercury have been found in sediments and fish in the vicinity of small-scale mining activities using amalgamation as their main technique. The concentration in most fish fillets in these areas exceeds the recommendations of the United States Food and Drug Agency (Babut *et al*., 2003). A major concern about the increasing background concentration of mercury in the environment is that any inorganic form (less toxic) can be converted into organic mercury, especially methyl - mercury, one of the most toxic compounds known to humans. Fish, far from obvious sources of Hg emissions, have been found to have Hg levels of concern to human health (U.S. EPA, 1997). Mercury contamination of the environment from gold mining using Hg in the amalgamation step has already been postulated as one of the worst environmental problems (Melamed and Villas Boas, 1998).

It has been estimated that, 5 tonnes of mercury is released from small-scale mining operations in Ghana each year (Hilson, 2001). Ghana has not paid the needed attention to Hg contamination due to artisanal gold mining activities. Moreover, there are no dependable data to assess the extent of Hg contamination in the various environmental compartments. Literature available on Hg pollution in Ghana deals with survey data on some of the rivers draining the south-western gold belt. Adimado and Baah (2002) have studied Hg concentrations in human blood, urine, hair, nail and fish from Ankobra and Tano river basins in south-western Ghana. Bannerman *et al.* (2003) reported that there was Hg and arsenic (As) contamination in sediment and water in the gold mining regions of the Ankobra river basin. Bonzongo *et al.,* (2003) also examined the extent of Hg contamination in water, sediment and soil from artisanal gold mining-impacted Ghanaian watersheds. Brief studies have also been carried out on Hg in water, sediments and soils of some rivers near Dunkwa-on-Offin (Golow and Mingle, 2003; Golow and Adzei, 2002). In addition, Amonoo-Niezer *et al.* (1996) investigated Hg and Arsenic pollution in soils, food crops and fish around Obuasi, a mining town and its environs. In a study supported by UNIDO, Babut *et al.* (2003) studied Hg contamination in water, sediment, soil and food crops in the Apopre river basin at Dumasi, a well-known artisanal gold mining town in Ghana.

The fate of mercury in the soil is important not only to assess surface and groundwater quality, but also to understand mercury fluxes at the soil/air and water/air interfaces. The most important chemical retention mechanisms are sorption processes and precipitation.

Understanding the adsorption of mercury on soil from aqueous solution is necessary for tracing the fate of mercury in the biological environment and for assessing potential health effects and the impact of anthropogenic mercury emissions on the environment. Current estimates for anthropogenic mercury emission range from about 50 to 75% of the total annual mercury

emission to the atmosphere; recent modelling suggests that the present atmospheric mercury burden has increased by a factor of three during the last 100 years (Fitzgerald, 1995). Sorption or exchange has been described by either instantaneous equilibrium or a kinetic reaction where concentrations in solution and sorbed phases vary with time. Reviews of various forms of equilibrium and kinetic models are available in literature (Murali and Aylmore, 1983; Selim, 1989; Selim *et al.* 1990).

Nielsen *et al*. (1986) presented a comprehensive discussion of significant features of sorption-exchange reactions of the equilibrium and kinetic type. Linear, Freundlich, and one- and two-site Langmuir equations are perhaps the most commonly used to describe equilibrium reactions.

Mercury sorption in soils is often highly dependent on the Hg (II) species, which is largely determined by pH of soil, chloride concentration and redox potential (Schluter, 1997). The adsorption of Hg by soils can be influenced by a number of experimental as well as soil factors. One of the experimental variables which need to be established for adsorption of Hg by soils is the soil : solution ratio. Different soil: solution ratios have been used in Hg adsorption studies. For example, 1 : 10 (Aomine and Inoue, 1967; Khalid *et al*., 1977), 1 : 20 (Inoue and Aomine, 1969), 1 : 50 (Trost and Bisque, 1972; Hogg *et al*., 1978), and 1:100 (Trost and Bisque, 1972)

Soil pH and organic matter content are some of the most important soil properties which affect Hg adsorption. The influence of soil pH on Hg adsorption has been conflicting. Aomine and Inoue (1967) did not observe any pH influence on phenylmercury acetate (PMA) adsorption. But Inoue and Aomine (1969) observed a decrease of adsorption above pH 6.0, and attributed this to laws of cation exchange. On the other hand, Khalid *et al*. (1977) reported river sediments to adsorb more Hg (II) at pH 8.0 than at pH 5.0. This may be due to increased cation

exchange capacity (CEC) with increasing pH (Helling *et al*., 1964) assuming that cation exchange processes are involved. Alternatively, the apparent increase in adsorption may be a result of increased precipitation of Hg at higher pH values.

Soil organic matter is known to play a role in Hg adsorption, although its quantitative contribution is not clearly understood. Trost and Bisque (1972) and Estes *et al*. (1973) reported that surface soils, rich in organic matter, adsorbed significantly higher amounts of Hg as compared to their subsurface soils which contained relatively smaller quantities of organic matter. Fang (1978) found more adsorption of metallic Hg vapour in soils with high organic matter levels, although the highest adsorption did not necessarily occur in the soil with the highest level of organic matter (Landa, 1978). The results of Landa (1978) thus suggest that in addition to quantity, the nature of a soils' organic matter also influences adsorption of Hg. Lag and Steinnes (1978) found a positive correlation between total Hg and organic matter content of forest soils. Adsorption of Hg by organic matter is thought to take place via functional groups such as COOH and phenolic-OH, which are major constituents of organic matter (Lamar, 1968). It has been reported that the adsorption of 2-methoxyethylmercury chloride (Aretan) and $HgC1_2$ correlated with horizon wise variation in organic Carbon and pH in a clay soil, but not in the loam or sandy soils (Semu *et al*., 1985). These evidences show the importance of soil pH and organic Carbon in Hg adsorption. It is a well known fact that mercuric ions strongly bind to the organic matter present in soil (Yin *et al*., 1997a, b; Grigal, 2003), indicating that under these circumstances the metal has very low mobility, especially under low pH conditions (Yin *et al*., 1996). In acidic soils, mercury bound to humic material prevails (Schwesig *et al*., 1999). On the other hand, weakly bound species of mercury are also of environmental interest, since they are likely to be leached from soils, enhancing transport and toxicity.

Given the high levels of mercury in the soils of the artisanal gold mining areas and the health risks associated with the element, an insight into the sorption of mercury in this matrix is extremely important. Data on the sorption of inorganic Hg (II) on soils are available in literature (Schnoor, 1996; Yin *et al*, 1996; Schluter and Gath, 1997; Yin *et al*, 1997a; 1997b; Grigal, 2003) but so far none deals with Ghanaian soils. It is therefore important to determine sorption model for some Ghanaian soils within the mining environment.

The main river in the Ankobra Basin is River Ankobra which takes its source around Bibiani and passes through Bogoso and Prestea all of which are mining towns in Ghana. In addition, its major tributaries: river Mansi, river Bonsa and river Fure all pass through mining communities before joining the main Ankobra, which finally enters the Gulf of Guinea at Axim (Figure 1). There is therefore the possibility of mercury contamination of the environment as a result of artisanal gold mining activities close to the rivers but, the leachability of the mercury contaminant depends on the chemistry of the soil.

1.1 OBJECTIVES OF RESEARCH

The objectives of this study are:

i. To determine the relationship between total mercury and some soil characteristics.

ii. To determine the Hg (II) adsorption isotherms for some soils from the Ankobra Basin.

iii. To determine the model that best fits the experimental data.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 MERCURY

Mercury is one of the toxic heavy metals that contaminate much of the waters and soils. It travels easily through different environmental media, including the atmosphere, in a variety of chemical forms and is toxic to humans and biota even in extremely low concentrations (Schoellhamer, 1996).

2.1.1 Occurrence, Physical-Chemical and Toxicological Properties of Mercury

2.1.1.1 Occurrence

More than 25 mercury-containing minerals are known to occur in earth's mantle, yet the average crustal abundance of this element is only about 0.5 ppm (Schroeder and Munthe, 1998). Its principal ore is the mineral, cinnabar (HgS), which has been known and used by humankind for more than 2300 years. Major mercury deposits are located at Spain and Monte Amiata (Italy). In North America, significant cinnabar deposits occur in California (Pinchi Lake).

2.1.1.2 Physical – chemical Properties

Mercury (Hg) is found among the transition elements of the Periodic Table, in Group IIB along with zinc and cadmium. Hg^+ readily combines with noble metals such as, Au, Ag, Pt and Pd to form alloys ("amalgams"). Amalgamation with gold provides the basis for pre-concentration of Hg from samples of ambient air prior to analytical determination.

2.1.1.3 Toxicological Properties

The toxicity of Hg (all forms) via ingestion and dermal absorption, and the acute and sub -chronic toxicity of Hg vapour exposure via inhalation, have been extensively reviewed by Agency for Toxic Substances and Disease Registry (ATSDR) in 1994.

I. Carcinogenicity/mutagenicity

The potential carcinogenicity of Hg has been extensively reviewed by the International Agency for Research on Cancer (IARC) (1993) and by Boffetta *et al*. (1993). IARC (1993) concluded that metallic Hg and inorganic Hg compounds were not classifiable as to their carcinogenicity to humans. However, epidemiologic and experimental evidence are needed to confirm that Hg is not an occupational carcinogen.

II. Teratogenicity/reproductive toxicology

Most available information on the teratogenic and reproductive toxicity of Hg has been reviewed by WHO (1990, 1991) and ATSDR (1994). Cordier *et al*. (1991) reported an increased risk of spontaneous abortion in women whose husbands had urine Hg concentration in excess of 50 µg/L. The teratogenicity of methyl Hg is well known (WHO 1990). However, much less information is available related to Hg vapour ((WHO, 1991), Goering *et al*. (1992) and ATSDR (1994)).

III. Neurotoxicity

Both peripheral and central nervous system effects are associated with Hg vapour exposure. Overt clinical signs of nervous system impairment, including tremor and the various symptoms

associated with chronic mercurialism, generally occur at air levels exceeding 100 µg/m^3 (WHO, 1991) or in association with urine Hg concentrations of 100 µg/L or more (Echeverria *et al*. 1995). Below these levels which are known to cause clinical symptoms, 'pre-' or 'sub-' clinical impairment of peripheral nerve conduction, intention tremor of the extremities, and impacts on cognitive functions and mood state, have been reported (WHO, 1991).

Singer *et al* (1987) reported reduced median nerve conduction velocity in a group of 16 chlor-alkali workers relative to controls. A dose-dependent decrease in conduction velocity was observed with blood Hg concentration ($p<0.002$) and, to a weaker degree, with urine Hg concentration ($p<0.06$). Mean urine Hg concentration in exposed workers was 508 µg/L. Likewise, Levine *et al*. (1982) reported a dose- dependent increase in ulnar nerve distal latency (i.e. reduced nerve conduction velocity) in 18 male chloralkali workers with an average spot urine Hg level of 290 µg/L.

IV. Neurological/neuromuscular disease

Hg is a known Central Nervous System (CNS) toxicant (WHO 1990, 1991). Exposure to high levels of Hg can result in various neurological or neuromuscular diseases including Alzheimer's Disease (AD) (Lorscheider *et al*., 1995), Amyotrophic Lateral Sclerosis (ALS) (Kasarskis *et al*. 1987; Adams *et al*. 1983), multiple sclerosis (MS) (Clausen 1993) and Parkinson's Disease (PD) (Ngim and Devathason, 1989).

2.1.2 Sources of Mercury

Hg occurs from both natural and anthropogenic sources in the environment.

2.1.2.1 Natural Sources

Mercury is thought to be released from natural sources mainly as Hg- vapour, but mercury bound to particulate matter/aerosols may originate from some types of natural sources or processes.

I. Volcanic releases of Mercury

Mercury is initially released into the biosphere through volcanic activity. Mercury is present in the earth's crust at a concentration of 0.5 ppm (Schroeder and Munthe, 1998). Mercury typically forms the sulphide (HgS) because of the prevalence of sulphides in volcanic gases. In this fashion it is found naturally in deposits as the red suphides ore, cinnabar. It is commercially mined as this form. Volcanic sources emit an estimated global total of 60,000 kg of mercury per year (Fitzgerald, 1986).

II. Forest fires Biomass

Forest fires biomass, particularly trees and brush, accumulate and harbour 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), the 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. Forest fires and rain are responsible for the transport and deposition of mercury over much of the world's surface, regardless of its source (Central Valley Regional Water Quality Control Board (CVRWQCB), 1996).

III. Oceanic releases of Mercury

Oceanic releases of mercury is also a component of seawater and is released naturally through the evaporation of elemental mercury from the ocean's surface (Nriagu and Pacyna, 1988). 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 pushed towards more elemental mercury, which then releases more elemental mercury from the ocean's surface (Kim and Fitzgerald, 1986).

2.1.2.2 Anthropogenic Sources

Nriagu and Pacyna (1988) estimated world-wide anthropogenic mercury emissions for the year 1983 to have been in the range of 910- 6200 tonnes, with a median value of 3560 ton.

I. Industries use

Mercury is used in a broad array of more than 2,000 manufacturing industries and products (Kurita, 1987). These include barometers, thermometers, hydrometers, pyrometers, mercury arc lamps, switches, fluorescent lamps, mercury boilers, mercury salts, mirrors, catalysts for the oxidation of organic compounds, gold and silver extraction from ores, rectifiers, cathodes in electrolysis or electro-analysis, and in the generation of chlorine and caustic paper processing, batteries, dental amalgams, as a laboratory reagent, lubricants, caulks and coatings, in pharmaceuticals as a slimicide, in dyes, wood preservatives, floor wax, furniture polish, fabric softeners, and chlorine bleach (Volland, 1991).

It is estimated that the US exported about 32.5 tons of mercury in 2001, yielding a net domestic annual use of about 3,409 tons of mercury. Of this use, 50% to 56% was in the electrical

industry, 12% to 25% in chloralkali plants to generate chlorine and caustic soda, 10% to 12% was in paint manufacturing, and about 3% was used in the preparation of dental amalgams (Sills, 1992).

II Mining

It has been estimated that, in river drainages of the Mother Lode region alone, approximately 7,600 tons of refined quicksilver was inadvertently deposited in conjunction with the Gold Rush era mining (CVRWQCB, 1987). Additional mercury was used throughout the gold mining belt of the north-western and central Sierra Nevada. The majority of Coast Range mercury mines which supplied mercury for this practice have since been abandoned and remain unreclaimed.

III Coal-Fired Power Plants

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 of the order of 3,000 tons per year globally, about the same amount released through all industrial processes (Joensuu, 1971). The concentration of mercury in coal varies from 70 ng/g to 22800 ng/g. During the burning of coal, mercury is initially decomposed to elemental mercury and then, as the flue gas cools and exits the plant, majority of the mercury is quickly oxidized, probably catalytically due to the presence of other metals in the gas, to its water-soluble, ionic form, Hg^{2+}.

IV Gasoline and Oil Combustion

Crude petroleum is known to contain small but measurable amounts of mercury. A study performed by Shur and Stepp (1993) revealed that the average amount of mercury in petroleum

is 0.41 ppm. Another study on petroleum found a range of mercury concentration from 0.03 to 0.1 ppm (Speight, 1991). However, these studies also indicate minimum mercury concentrations in crude oil. 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 1,901 lbs. This value represents an annual discharge of 347 tons of mercury nationwide, assuming that all of the oil is combusted (CVRWQCB, 1996).

V. Smelting

The smelting of ores to yield pure metals is thought to release some mercury into the atmosphere. Most metal ores are thought to have higher concentrations of mercury than coal, although the volumes of ore that are smelted each year pale in comparison with the volume of coal burned for power generation (CVRWQCB, 1996).

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VI. Mildew Suppression, Laundry facilities

An infrequent and historical point source of mercury contamination has been the use of mercury compounds for mildew suppression by laundry facilities, which have a chronic problem with moisture and bacterial growth (Sills, 1992).

2.1.3 Environmental cycling of mercury

Once Hg species are released into the environment, they are expected to cycle between air and water/soil/vegetation media (Schroeder *et al*., 1989).

2.1.3.1 Atmospheric cycling of mercury

Atmospheric dispersion or transport of mercury is generally considered to be an environmental phenomenon on global, regional and local scales (Expert Panel, 1994).

The spatial scale will depend on the chemical and physical forms of the mercury and the rate of interconversion among species. The three predominant mercury species exhibit different transport characteristics. Mercury (II) is capable of being transported aerially for very long distances (tens of thousands of kilometers), mercury (II) species in the gas phase can be expected to be removed in the vicinity of a few tens to a few hundreds of kilometres from their source, and particulate-phase mercury, Hg(p), species are likely to be deposited at intermediate distances, depending on aerosol diameter or mass (Schroeder and Munthe, 1998)

2.1.3.2 Atmospheric reactions of mercury

Only a few chemical reactions of mercury, under conditions relevant to the atmosphere, have been studied in laboratory investigations. Oxidation processes for Hg involving ozone have been identified in the gas phase (Hall, 1995) and in the aqueous phase (Munthe, 1992).

Both gaseous and aqueous-phase processes are potentially important for the overall atmospheric cycling of mercury. Oxidation of Hg may, to some extent, be balanced by reduction processes occurring simultaneously in the atmosphere. To date, only one such process has been identified: the aqueous-phase reduction of Hg (I1) by S (IV) (Munthe *et al*., 1991). On a global scale the importance of this specific reaction is probably limited,

but other reduction processes may exist (for example, photochemically initiated reduction of Hg(I1) species). Atmospheric processes may also play a key role in the formation of particulate mercury species, Hg (p). Several investigators have proposed mercuric oxide, HgO, as the primary product of gas-phase oxidation of Hg by O_3 (Schroeder *et al*., 1991; Hall, 1995: Sommar, 1997).

The vapour pressure of HgO is very low and, if produced in the atmosphere, it will most likely be transformed into the solid state. A condensation of pure HgO is unlikely given the low concentrations in ambient air, so it will probably be sorbed by available aerosol surfaces. The nitrate radical reaction, on the other hand, is reported to yield only inorganic forms of mercury and could provide a competing reaction during night-time conditions.

EARTH'S SURFACE (water, soil, vegetation)
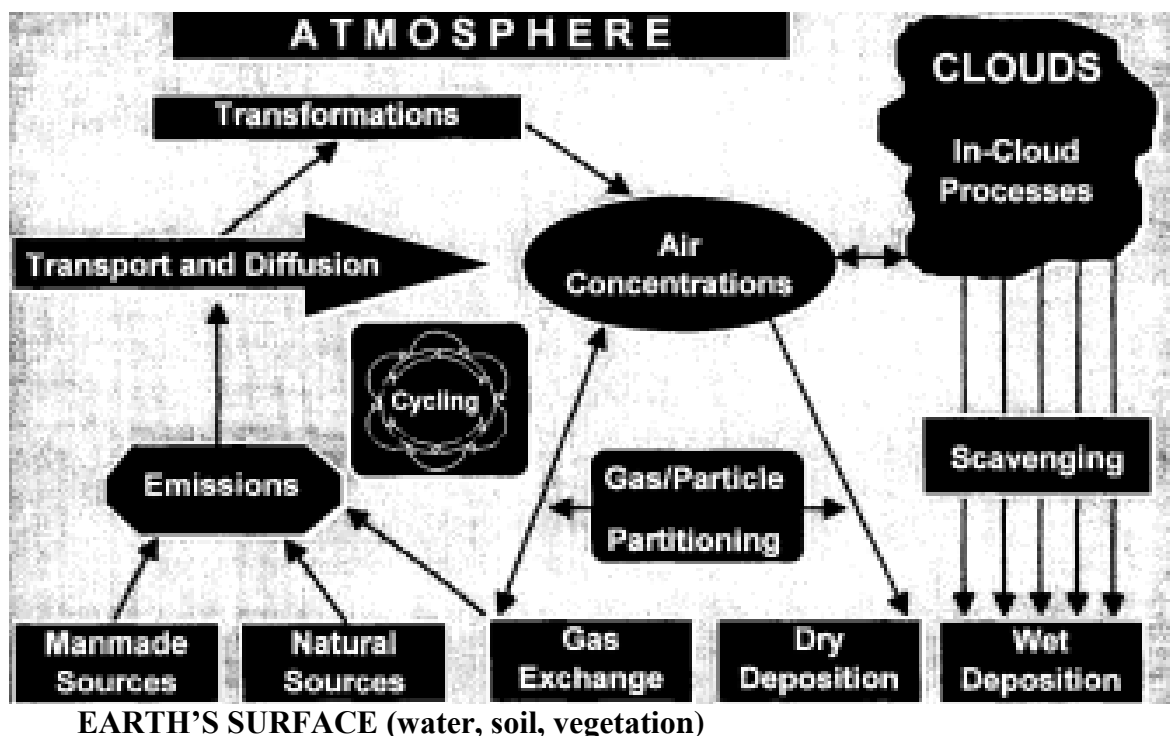
Figure 2.1: Conceptual framework of the atmospheric emissions-to-deposition cycle for mercury (Schroeder and Lane, 1988)

2.1.3.3 Air- surface exchange of mercury

In comparison to the other heavy metals, one of the major distinguishing features of Hg is the great extent to which it is re-circulated in the environment via the atmosphere. Since 1890, approximately 2×10^5 tonnes of Hg have been deposited to terrestrial soils (Expert Panel, 1994). The re-emission of mercury from this large pool may represent a significant global flux to the atmosphere. During the last 10 years, there have been a considerable number of scientific studies which have focused on air-surface exchange of Hg. These investigations have arisen out of a growing recognition of the importance and extent of intermediate transfer processes and environmental cycling involving Hg (and possibly methylated-Hg species also). Wet deposition (of dissolved Hg (II) species) and dry deposition (of particulate Hg) are generally considered to be uni-directional processes involving transfer of mercury from the atmospheric compartment to the earth's surface. However, air-surface exchange of Hg can occur bi-directionally, allowing re-emission or recycling of this trace element from a given surface to the atmosphere. If oxidized forms of Hg. i.e. Hg (II) species, are deposited on water, soil or vegetative surfaces they will tend to remain non-volatile and hence relatively immobile unless chemical, photolytic or biological reduction to the elemental form occurs.

Soils, especially the humus layer of forest soils, are often viewed as a "net sink" for the Hg pool present in the atmosphere (Lindqvist *et al*., 1984; 1991; Johansson *et al*., 1991). The studies by Lindberg and co-workers of biogeochemical cycling of Hg in the forest at Walker Branch Watershed (Tennessee) have shown that (at least for this forest ecosystem) the largest Hg pool resides in the soil (similar to the situation for most nutrients and other trace elements) and, furthermore, that about 75% of the total Hg soil pool is concentrated in the organic-rich A horizon, Nevertheless, some volatilization of mercury does occur at least during the warmer

times of the year from boreal forest soils (Schroeder *et al*., 1989; Xiao *et al*., 1991) from   soil lysimeters (Schluter *et al*., 1995a; 1995b) and from background forest soils in more temperate climatic regions (Lindberg *et al*., 1992; Kim *et al*., 1995) at emission rates in the order of l-10 ng m^{-2} h^{-1}.

2.1.4 Factors that influence Mercury Pollution

2.1.4.1 pH

The pH of inland surface waters has been found to dramatically affect the amount of mercury taken up by biota (Gilmour and Henry, 1991). Specifically, mercury in fish tissue is present predominantly as methyl mercury, so changes in the biogeochemistry of this compound of mercury may account for any increase in bioaccumulation. It has been determined that inorganic mercury binds to organic matter more strongly as the pH declines (Schindler *et al*., 1980), thus decreasing mercury's solubility. Conversely, in sediments a lower pH may increase the solubility of HgS (Ramal *et al*., 1995).

Alkalinity and pH affect the biogeochemistry of mercury in numerous ways, including the binding capacity of the various species, the rate of methyl mercury production, and even the uptake efficiency of methyl mercury by aquatic organisms (Cope *et al*., 1990; Slotton, 1991). The most important result of these combined effects is that methyl mercury is produced, transported, and accumulated by aquatic organisms significantly more efficiently at low alkalinity and pH; i.e., conditions to the acidic side of neutrality (< pH 7) (Winfrey and Rudd, 1990). Because of this, many thousands of lakes in north central and north eastern United States, central and eastern Canada, and northern Europe can, and do, develop mercury accumulations in edible fish well above health guidelines, from global atmospheric deposition alone and with no

local point sources. In California, the naturally moderate to high alkalinity of surface waters maintains the pH at levels typically well above acidic conditions. This is very fortunate, in light of the bulk mercury contamination that supplements global loads in many parts of the Estuary watershed. Under prevailing conditions of high alkalinity and above neutral pH, even grossly contaminated water bodies such as Clear Lake, frequently do not demonstrate edible fish mercury levels dramatically higher than those from relatively unpolluted, but acidic, waters. With hypothetical lower levels of alkalinity and pH, surface waters with bulk mercury contamination (i.e., much of the San Francisco Estuary watershed) could be expected to develop fish mercury accumulations far above those seen today.

2.1.4.2 Salinity

Salinity has been statistically linked to dissolved mercury concentrations in an inverse relationship, suggesting that local runoff may be an important source of dissolved mercury in the South Bay. As runoff increases and salinity decreases, the concentration of dissolved mercury increased (SFEI, 1993). Increasing salinity has also been associated with a decline in the rate of mercury methylation and in equilibrium methyl mercury concentrations (Compeau and Bartha, 1984).

2.1.4.3 Sulphate concentration

The microbial methylation of mercury is thought to proceed through the metabolic action of sulfur- reducing bacteria (SRB) in anoxic environments (Gilmour and Henry, 1991).

The concentration of sulphate in marine waters is approximately 28 mM, which is considerably higher than freshwater sulphur concentrations. In freshwater systems, it is clear that an increase in sulphur concentration increases sediment sulphate-reduction rates (Rudd *et al*., 1986).

However, there appears to be a window of sulphate concentration that promotes the highest mercury methylation rate. Optimum mercury methylation by SRB in sediments is at 200–500 mM. Above this range, the formation of sulphide appears to inhibit methylation (CVRWQCB, 1996).

2.1.4.4 Percentage Fines

In aquatic sediments, mercury and other heavy metal contamination is most strongly correlated with the proportion of fine particles. This is particularly the case when the heavy metal load entering the system is largely in a very diffuse, molecular form, such as in atmospheric deposition, mine leakage of dissolved metals, and direct introduction to the environment of liquid or vaporized elemental mercury. Fine sediment particles contain a disproportionate amount of surface area and adsorption sites, and thus tend to accumulate far greater concentrations of diffuse heavy metals than do larger sediment particles such as sand and gravel. In local research at a Sierra Nevada foothill reservoir, bottom sediment concentrations of mercury, as well as copper, zinc, and cadmium, were found to increase exponentially at average sediment grain sizes of less than 24 micrometers (Slotton *et al*., 1994; Slotton and Reuter, 1995).

2.1.4.5 Aerobic and Anaerobic Microenvironments

Each transformation of mercury from one valence state or one species to another takes place in specific micro environmental compartments. At the aerobic/anaerobic boundary in sediment, which is the limiting depth for oxygen penetration into the sediment, there is a redox potential discontinuity (RPD). In the oxygen-rich environment of the upper sediment, the electrochemical

potential is oxidizing, thus favouring oxygen metabolism and the ionized (soluble) states of metals (e.g. Hg^{+2}). Conversely, the oxygen-poor lower sediment exhibits a reducing electrochemical potential that favours sulphur metabolism by sulphur reducing bacteria (SRBs). Two products of microbial sulphur metabolism are HgS (which is highly insoluble) and CH_3Hg (which is the form of mercury most commonly found in tissue), when mercury is present in the sediment.

Where the water itself becomes anaerobic, methyl mercury production can increase dramatically and transfer rapidly and efficiently into the aquatic food web. Research at Davis Creek Reservoir in the Berryessa/Clear Lake historic mercury mining district found that the seasonally anoxic bottom waters of the reservoir provided a large annual pulse of methyl mercury to the reservoir food chain (Slotton 1991; Slotton *et al*. 1995). Piscivorous largemouth bass in this system accumulated fillet mercury at concentrations up to 10 times the 0.5 ppm health guideline. Both the proportions of total and dissolved mercury concentrations in the water and their absolute values can change due to shifts in the electrochemical potential of the sediment and/or water. Hydrological impacts such as the deposition of abnormally high volumes of silt, scouring, growth of algae or other oxygen-scavenging flora can dramatically alter mercury biogeochemistry and, consequently, the production, transformation, and concentration of the different mercury species.

2.2 ADSORPTION ISOTHERM

2.2.1 Definitions, Types and Characteristics of Adsorption Isotherms

2.2.1.1 Definition of Adsorption, Types and Characteristics

When a gas or vapour is brought into contact with a solid, part of it is taken up by the solid. The molecules that disappear from the gas or solution either enter the inside of the solid (termed absorption), or remain on the outside attached to the surface (termed adsorption).

When the phenomena occur simultaneously, the process is termed sorption (Atkins and de Paula, 2006). The solid that takes up the molecule is called adsorbent, and the gas, vapour or solute taken up on the surface is called adsorbate. Many organic and inorganic contaminants are removed from either gaseous or liquid solutions by adsorption on the very porous medium (solid phase) with large internal surfaces.

Adsorption is a reversible reaction; at a given solute concentration. Adsorbates can attach themselves onto surfaces in two ways; physisorption or chemisorptions. In physisorption (physical adsorption), there is a weak van der waals attraction of the adsorbates to the surface. During the process of physisorption, the chemical identity of the adsorbate remains intact. Physisorption is a spontaneous process ($\Delta G < 0$), since ΔS is negative, so ΔH be exothermic.

In chemisorption (chemical adsorption), the adsorbates stick to the solid by the formation of a chemical bond with the surface. This interaction is much stronger than physisorption and in general, chemisorption has more stringent requirements for the compatibility of adsorbate and surface than physisorption (Atkins and de Paula, 2006; Kadlec *et al*, 1970). The steps of adsorption can be summarized: solute diffuses near the solid surface, diffuses into the pores

of particle, then to the pore wall and adsorbs to the pore wall surface. Adsorption of dissolved contaminants is a complex phenomenon caused by several mechanisms, including London-Van der Waals forces, Coulomb forces, hydrogen bonding, ligand exchange, chemisorption, dipole- dipole forces, and hydrophobic forces. For example, hydrocarbons most commonly exhibit adsorption through the process of hydrophobic bonding. Thus adsorbents are characterized first by surface properties such as surface area, pore size distribution of micropores and polarity (hydrophilicity, hydrophobicity).

2.2.1.2 Definition of Adsorption Isotherm and Application

The relationship between the concentration of chemical adsorbed (S) and the concentration remaining in the solution (C) at equilibrium is referred to as the adsorption isotherm when the experiments are performed at constant temperature (Atkins and de Paula, 2006). Adsorption isotherms are widely used to characterize retention of chemicals in soils. The most important chemical processes affecting the behaviour and bioavailability of heavy metals in soils are those concerned with the sorption of metals from liquid phase onto solid phase (Alloway, 1990). Among all phenomena governing the mobility of substances in aqueous porous media and aquatic environments, the transfer of substances from a mobile phase (liquid or gaseous) to a solid phase is a universal phenomenon. That is the reason why the 'isotherm'', a curve describing the retention of a substance on a solid at various concentrations, is a major tool to describe and predict the mobility of this substance in the environment.

2.2.2 Adsorption Process

Adsorption processes can be operated on either a batch or continuous- flow basis.

2.2.2.1 Batch Processes

The batch method is far easier to use than any other method. The solid is shaken in the solution until the adsorption or desorption equilibrium is reached. Then, the remaining solute concentration is measured. The disadvantages are numerous. The solid/solution ratio is often either too high compared with the natural conditions in rivers, lakes or seas, or too low compared with the natural conditions of porous media. Moreover, the hydrodynamic conditions of natural porous media are not met. A long term experiment with continuous shaking can lead to side reactions (Sposito, 1984) such as the destruction of particles, which prevents the study of very slow reactions. As a consequence, the batch method is very useful as a preliminary experiment but extrapolation to porous media requires other investigations.

2.2.2.2 Continuous– Flow Adsorption Systems

Most continuous– flow adsorption systems are operated as single column or multiple fix-bed adsorption columns in series. Furthermore, they may be operated in either the upflow and packed or expanded or down-flow mode. In down flow systems, the adsorbent can serve for adsorption and for filtration of suspended solids and make adsorption less efficient. Adsorption columns behave in much the same way as ion exchange columns during operation (Limousin *et al*., 2007). Continuous –flow adsorption systems are capable of treating large volume of wastewater and are widely used for both municipal and industrial applications. The use of upflow or down flow columns in series are used to optimize adsorbent usage and operating costs.

2.2.3 Classification of Adsorption isotherms

The performance of an adsorbent for adsorption of a specific adsorbate and also valuable information (e.g. the theoretical capacity of the sorbent exhaustion) can be obtained from plotting an adsorption isotherm (Hinz, 2001).

The first systematic attempt to interpret adsorption isotherms for gas –solid equilibria was introduced by Brunauer *et al* in 1940 (Findenegg, 1984). They classified isotherms into six types which is presented in Figure 2.2. The Type I isotherm characterizes microporus adsorbents. Types II and III describe adsorption on macroporus adsorbents with strong and weak adsorbate-adsorbent interactions respectively. The Type IV and V represent adsorption isotherm with hysteresis. Finally, Type VI has steps. The Brunauer classification has the deficiencies of being incomplete and gives incorrect impression that adsorption isotherms are always monotonic functions of pressure. This is because it only takes into account adsorption at subcritical temperatures (Findenegg, 1984).
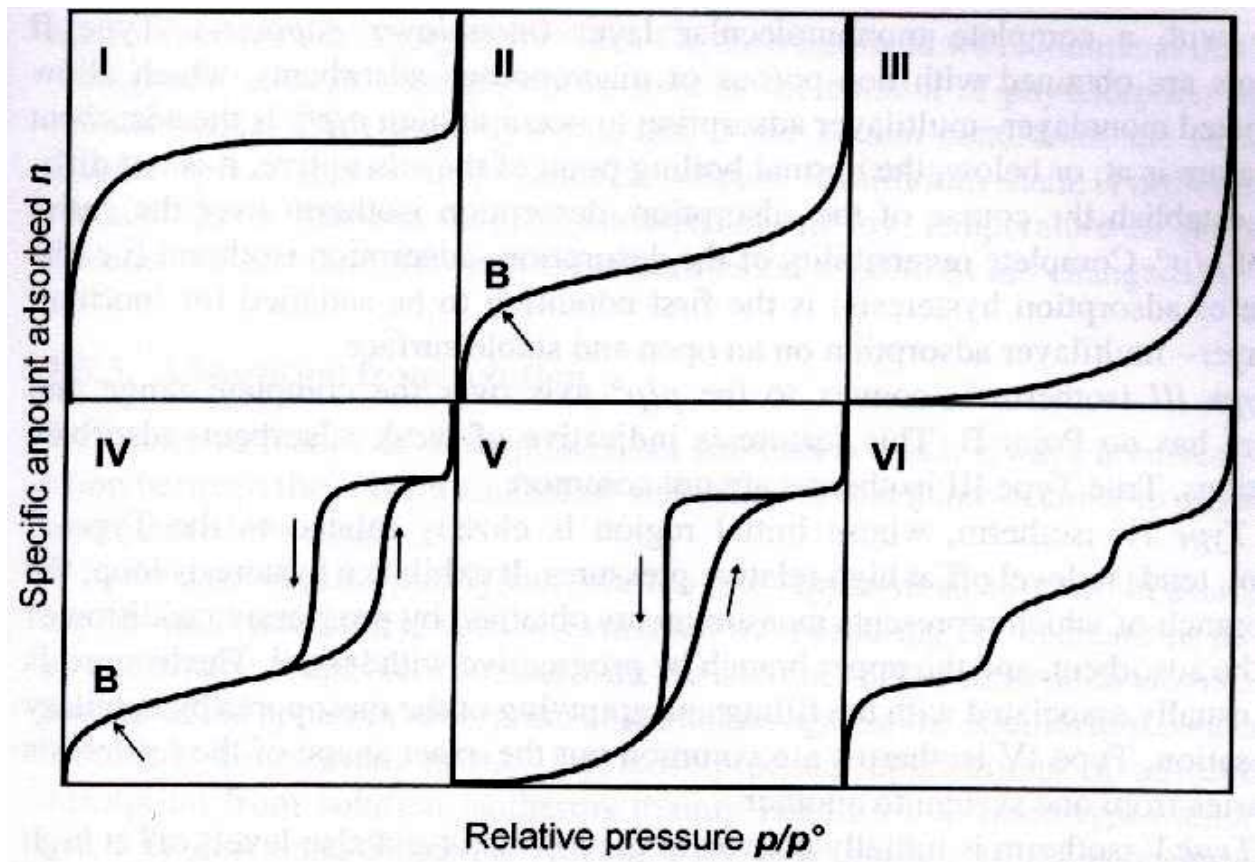
Figure 2.2: The Brunauer classification of adsorption isotherm (Findenegg, 1984).

Giles *et al.* in 1974 related the shape of the adsorption isotherm to adsorption mechanisms for a solute – solvent adsorbent system. The isotherm classification of Brunauer *et al*, describes adsorption from gas phase, whiles the isotherm of Giles *et al*, are taken from liquid-solid systems.

Giles *et al*. (1974) classified sorption isotherms based on their initial slopes and curvatures. They distinguished between high affinity (H), Langmuir (L), constant partition (C), and sigmoidal-shaped (S) isotherm classes as shown in Figure 2.2. This classification is based on pure observation and does not reveal the processes that lead to different isotherm shapes.

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2.2.3.1 The "C" isotherm

The curve is a line of zero-origin (Figure 2.2a). It means that the ratio between the concentration of the compound remaining in solution and adsorbed on the solid is the same at any concentration. This ratio is usually named ''distribution coefficient'' or ''partition coefficient'': Kd or Kp, (L kg1). The ''C'' isotherm is often seen as an easy-to-use approximation (for a narrow range of concentration or very low concentrations such as observed for trace pollutants) rather than an accurate description. But the simplicity of this isotherm must not justify its use without verification, otherwise it could lead to erroneous conclusions. For example, if the solid has a limited quantity of adsorption sites, the isotherm could be nonlinear because of a possible saturation plateau (Limousin *et al*., 2007).

2.2.3.2 The ''L'' isotherm

The ratio between the concentration of the compound remaining in solution and adsorbed on the solid decreases when the solute concentration increases, providing a concave curve (Figure 2.2b). It suggests a progressive saturation of the solid. One usually makes two sub-groups: (i) the curve reaches a strict asymptotic plateau (the solid has a limited sorption capacity), and (ii) the curve does not reach any plateau (the solid does not show clearly a limited sorption capacity). But it often appears practically difficult to know if an isotherm belongs to the first or to the second sub-group (Limousin *et al*., 2007).

2.2.3.3 The ''H'' isotherm

This is only a particular case of the ''L'' isotherm, where the initial slope is very high (Figure 2.2c). This case was distinguished from the others because the compound exhibits sometimes

such a high affinity for the solid that the initial slope cannot be distinguished from infinity, even if it does not make sense from a thermodynamic point of view (Tóth, 1995).

2.2.3.4 The ''S'' isotherm

The curve is sigmoidal and thus has got a point of inflection (Figure 2.2d). This type of isotherm is always the result of at least two opposite mechanisms. Non-polar organic compounds are a typical case: they have a low affinity with clays. But as soon as a clay surface is covered by these compounds, other organic molecules are adsorbed more easily (Karimi-Lotfabad *et al*., 1996; Pignatello, 2000). This phenomenon is called ''cooperative adsorption'' (Hinz, 2001) and is also observed for surfactants (Smith *et al*., 1990; Smith and Galan, 1995; Groisman *et al*., 2004). The presence of a soluble ligand can also provide a sigmoidal isotherm for metallic species. At low metal concentrations, the adsorption is limited by the presence of the ligand. The ligand must be saturated and then the adsorption occurs normally (Sposito, 1984). The point of inflection illustrates the concentration for which the adsorption overcomes the complexation.
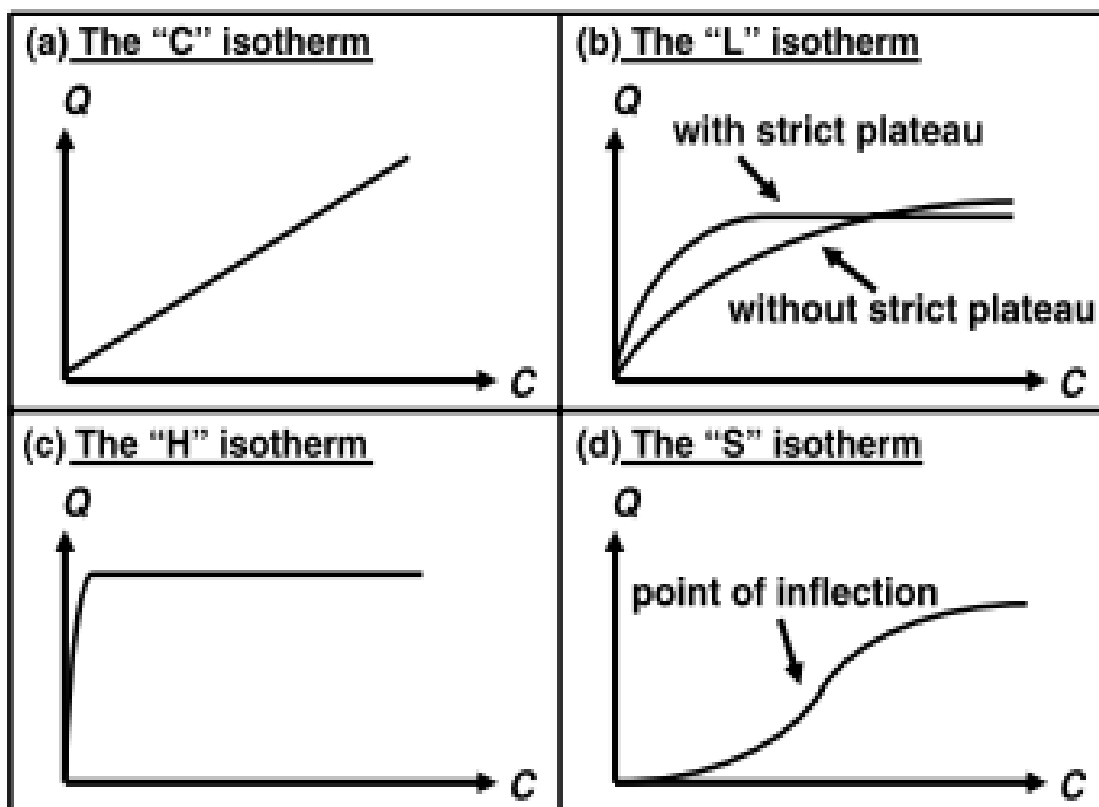
Fig 2.3: The Giles classification of adsorption isotherms (Giles *et al.*, 1974).

Where '**Q**' is the concentration of solute adsorbed on solid and '**C**' is concentration of solute remaining in solution.

2.2.4 Equilibrium-Based Adsorption Isotherm Models

There is an array of equilibrium-based models that have been used to describe adsorption on soil surfaces. These include the widely used Freundlich equation, a purely empirical model, the Langmuir equation, and double layer model

2.2.4.1 Simple Freundlich model.

The concave isotherm (''L'' or ''H'' isotherms) is the most widely met isotherm. This model is empirical (Coles and Yong, 2006) and is based on the following relation between the adsorbed quantity Q and the remained solute concentration (C):

$$Q = FC^n$$

with F (L kg-1) and n (dimensionless) being two constants (n < 1). This equation is easily linearized as

$$\log Q = \log F + n \log C$$

A graph with log C as x-axis versus log Q as y-axis provides a line of slope n and intercepts the y-axis at log F. According to the Freundlich equation, the isotherm does not reach a plateau as C increases.

2.2.4.2 The Langmuir models

Langmuir model is based on reaction hypotheses (Langmuir, 1918). The solid is assumed to have a limited adsorption capacity, Q_{max}. All the adsorption sites (i) are assumed to be identical, (ii) each site retains one molecule of the given compound and (iii) all sites are energetically and sterically independent of the adsorbed quantity.

Since activities of adsorbed species are not clearly defined thermodynamically, the mass action law cannot be directly applied to this reaction. Nevertheless, it has been proposed to assume the surface activity coefficients equal to unity and to calculate the activities with conditional stability constant, where Q is the solid concentration of the retained compound on the solid and Q_{max}- Q is the solid concentration of the free adsorptive site. Therefore, the ''Langmuir'' isotherm is:

$$Q = Q_{max}\frac{LC}{1+LC}$$

It can be linearized as:

$$\frac{Q}{C} = QmaxL - LQ$$

The constant L (Langmuir energy) corresponds to the affinity of the compound for the solid, while Qmax corresponds to the adsorption capacity of the solid.

A graph with Q as x-axis and Q/C as y-axis provides a line of slope L and intercepts the y-axis at $Q_{max}L$. According to the initial assumptions, the isotherm reaches a plateau Q_{max} (contrary to the Freundlich isotherm). The constant $Q_{max}L$ is the initial slope of the isotherm and QmaxL is often used as a distribution coefficient (K_d) when the concentrations are low enough to justify this approximation.

2.2.4.3 Linear model

In order to model transport of contaminants through the subsurface, a linear adsorption isotherm is usually used because of its simplicity (Sharma and Reddy, 2004).

The distribution coefficient, K_d is the slope of the line of linear sorption or the ratio of the equilibrium sorbed contaminant to the solution contaminant (Martinez *et al.*, 2006). Since this ratio can be significantly smaller at higher contaminant concentrations, if K_d is employed for concentrations outside of the linear range then contaminant migration will be underestimated (Yong, 2001).

2.3 SORPTION OF IONS ON SOILS

Adsorption, surface precipitation, and polymerization are all examples of sorption, a general term used when the retention mechanism at a surface is unknown. There are various sorption mechanisms involving both physical and chemical processes that could occur at soil mineral surfaces.

2.3.1 Retention Mechanism

There are various sorption mechanisms involving both physical and chemical processes that could occur at soil mineral surfaces. Adsorption isotherms generally exhibit one of four characteristic shapes, depending on the retention mechanism (Spark, 1989).

2.3.1.1 Adsorption

Adsorption is one of the most important chemical processes in soils. It determines the quantity of plant nutrients, metals, pesticides, and other organic chemicals retained on soil surfaces and therefore is one of the primary processes that affects transport of nutrients and contaminants in soils. Adsorption also affects the electrostatic properties, e.g., coagulation and settling, of suspended particles and colloids (Stumm, 1992).

2.3.1.2 Precipitation

The formation of metal hydroxide surface precipitates appears to be an important way to sequester metals. The mechanism for the formation of metal hydroxide surface precipitates is not clearly understood but it is clear that the type of metal ion determines whether metal hydroxide surface precipitates form, and the type of surface precipitate formed, i.e., metal hydroxide or

mixed metal hydroxide, is dependent on the sorbent type. The precipitation could be explained by the combination of several processes (Yamaguchi *et al*., 2001).

First, the electric field of the mineral surface attracts metal ions, e.g., Ni, through adsorption, leading to a local super saturation at the mineral–water interface. Second, the solid phase may act as a nucleation center for polyhydroxy species and catalyze the precipitation process (McBride, 1994).

Third, the physical properties of water molecules adsorbed at the mineral surface are different from those of free water (Sposito, 1989), causing a lower solubility of metal hydroxides at the mineral–water interface. With time Al, which is released by weathering of the mineral surface, slowly diffuses into the octahedral layer of the mineral and partially replaces the metal (e.g., Ni) in the octahedral sites. A Ni–Al LDH, which is thermodynamically favoured over α-Ni hydroxide, is formed.

The formation of metal hydroxide surface precipitates appears to be an important way to sequester metals. As the surface precipitates age, metal release is greatly reduced. Thus, the metals are less prone to leaching and as the amount of cation or anion sorbed on a surface (surface coverage or loading, which is affected by the pH at which sorption occurs) increases, sorption can proceed from mononuclear adsorption to surface precipitation (a three-dimensional phase). There are several thermodynamic reasons for surface precipitate formation: (1) the solid surface may lower the energy of nucleation by providing sterically similar sites (McBride, 1991); (2) the activity of the surface precipitate is <1 (Sposito, 1986); and (3) the solubility of the surface precipitate is lowered because the dielectric constant of the solution near the surface is less than that of the bulk solution (O'Day *et al*., 1994). There are several types of surface precipitates. They can arise via polymeric metal complexes (dimers,

trimers, etc.) that form on mineral surfaces and via the sorption of aqueous polymers (Chisholm-Brause, 1990). Homogeneous precipitates can form on a surface when the solution becomes saturated and the surface acts as a nucleation site. When adsorption attains monolayer coverage, sorption continues on the newly created sites, causing a precipitate on the surface (Farley *et al*., 1985; McBride, 1991).

When the precipitate consists of chemical species derived from both the aqueous solution and dissolution of the mineral, it is referred to as a coprecipitate. The composition of the co-precipitate varies between that of the original solid and a pure precipitate of the sorbing metal. The ionic radius of the sorbing metal and sorbent ions must be similar for coprecipitates to form. Thus Co (II), Mn (II), Ni (II), and Zn (II) form coprecipitates on sorbents containing Al (III) and Si (IV) but not Pb (II), which is considerably larger (0.12 nm). Coprecipitate formation is most limited by the rate of mineral dissolution, rather than the lack of favourable thermodynamic conditions (McBride, 1994; Scheidegger *et al*., 1998). If the formation of a precipitate occurs under solution conditions that would, in the absence of a sorbent, be undersaturated with respect to any known solid phase, this is referred to as surface-induced precipitation (Towle *et al*., 1997).

Thus there is often a continuum between surface complexation (adsorption) and surface precipitation. This continuum depends on several factors: (1) ratio of the number of surface sites to the number of metal ions in solution; (2) the strength of the metal oxide bond; and (3) the degree to which the bulk solution is undersaturated with respect to the metal hydroxide precipitate (McBride, 1991). At low surface coverages, surface complexation (e.g., outer- and inner-sphere adsorption) tends to dominate.

As surface coverage increases, nucleation occurs and results in the formation of distinct entities or aggregates on the surface. As surface loadings increase further, surface precipitation becomes the dominant mechanism. For example, Fendorf and Sparks (1994) used XAFS, FTIR, and HRTEM to study Cr (III) sorption on Si oxide. At low Cr (III) surface coverage (<20%), adsorption was the dominant process with an inner-sphere monodentate complex formation.

2.3.1.3 Surface Ion exchange

Ion exchange, the interchange between an ion in solution and another ion in the boundary layer between the solution and a charged surface, truly has been one of the hallmarks in soil chemistry. Since the pioneering studies in the middle of the 19th century (Way, 1850), many important studies have occurred on various aspects of both cation and anion exchange in soils. The sources of cation exchange in soils are clay minerals, organic matter, and amorphous minerals. The sources of anion exchange in soils are clay minerals, primarily 1:1 clays such as kaolinite, and metal oxides and amorphous materials. The ion exchange capacity is the maximum adsorption of readily exchangeable ions (diffuse ion swarm and outer-sphere complexes) on soil particle surfaces (Sposito, 2000). Ion exchange involves electrostatic interactions between a counter ion in the boundary layer between the solution and a charged particle surface and counter ions in a diffuse cloud around the charged particle. It is usually rapid, diffusion-controlled, reversible, and stoichiometric, and in most cases there is some selectivity of one ion over another by the exchanging surface. The rate of ion exchange in soils is dependent on the type and quantity of inorganic and organic components and the charge and radius of the ion being considered (Sparks, 1989). With clay minerals like kaolinite, where only external exchange sites are present, the rate of ion exchange is rapid.

With 2:1 clay minerals that contain both external and internal exchange sites, particularly with vermiculite and micas where partially collapsed interlayer space sites exist, the kinetics is slower. In these types of clays, ions such as K+ slowly diffuse into the partially collapsed interlayer spaces and the exchange can be slow and tortuous. The charge of the ion also affects the kinetics of ion exchange. Generally, the rate of exchange decreases as the charge of the exchanging species increases (Helfferich, 1962).
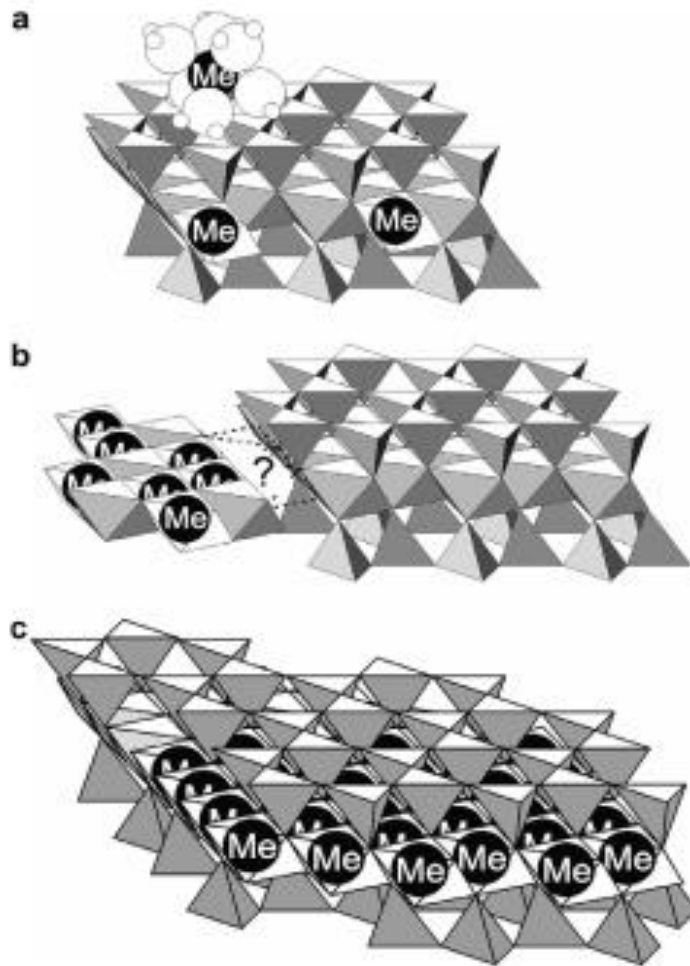
Figure 2.4: Different sorption mechanisms of metal ions (Me) on clay minerals

Fig 2.3 illustrate different sorption mechanisms of metal ions (Me) on clay minerals by (a) adsorption by outer sphere surface complex on exchange sites located on basal planes (hydrated metal) and as inner sphere surface complexes on the edges (dehydrated metal); or (b) inclusion of the metal into crystal structure by coprecipitation; or (c) precipitation of a new solid phase (Schlegel *et al*., 1999).

2.3.2 Factors which Affect Sorption Process

2.3.2.1 Surface Functional Groups

Surface functional groups in soils play a significant role in adsorption processes. A surface functional group is "a chemically reactive molecular unit bound into the structure of a solid at its periphery such that the reactive components of the unit can be bathed by a fluid" (Sposito, 1989). Surface functional groups can be organic (e.g. carboxyl, carbonyl, phenolic) or inorganic molecular units. The major inorganic surface functional groups in soils are the siloxane surface groups associated with the plane of oxygen atoms bound to the silica tetrahedral layer of a phyllosilicate and hydroxyl groups associated with the edges of inorganic minerals such as kaolinite, amorphous materials, and metal oxides, oxyhydroxides, and hydroxides (Spark, 2000).

The water molecule is unstable and can be exchanged for an inorganic or organic anion (Lewis base or ligand) in the solution, which then bonds to the metal cation. This process is called ligand exchange (Stumm, 1992).

The Lewis acid sites are present not only on metal oxides such as on the edges of gibbsite or goethite, but also on the edges of clay minerals such as kaolinite. There are also singly coordinated OH groups on the edges of clay minerals. At the edge of the octahedral sheet, OH groups are singly coordinated to Al^{3+}, and at the edge of the tetrahedral sheet they are

singly coordinated to Si^{4+}. These edge OH groups are called silanol (SiOH) and aluminol (AlOH), respectively (Sposito, 1989; Stumm, 1992).
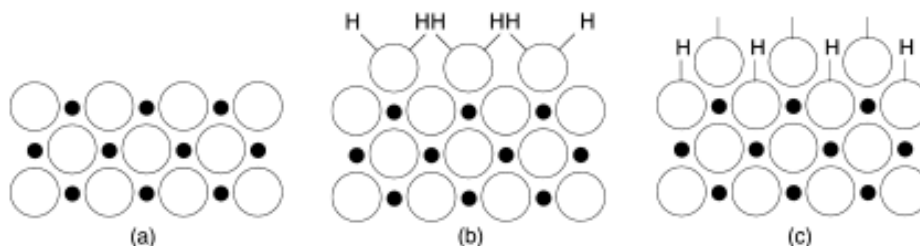
Figure 2.5: Cross section of the surface layer of a metal oxide

Figure 2.4, depicts cross sections of the surface layer of a metal oxide with (•) representing Metal ions, and (O) representing oxide ions. In (a), the metal ions in the surface layer have a reduced coordination number and exhibit Lewis acidity. With (b), in the presence of water, the surface metal ions may coordinate with the H_2O molecules. While in (c), dissociative chemisorption leads to a hydroxylated surface (Schindler, 1981).

Spectroscopic analyses of the crystal structures of oxides and clay minerals show that different types of hydroxyl groups have different reactivities. Goethite (α-FeOOH) has four types of surface hydroxyls whose reactivities are a function of the coordination environment of the O in the FeOH group (Sparks, 1989). Clay minerals have both aluminol and silanol groups. Kaolinite has three types of surface hydroxyl groups: aluminol, silanol, and Lewis acid sites. When the interaction of a surface functional group with an ion or molecule present in the soil solution creates a stable molecular entity, it is called a surface complex. The overall reaction is referred to as surface complexation.

There are two types of surface complexes that can form outer-sphere and inner-sphere. Figure 2.4 shows surface complexes between metal ions and siloxane ditrigonal cavities on 2:1 clay minerals. Such complexes can also occur on the edges of clay minerals. If a water molecule is present between the surface functional group and the bound ion or molecule, the surface complex is termed outer-sphere (Sposito, 1989).

Environmental factors such as pH, surface loading, ionic strength, type of sorbent, and time all affect the type of sorption complex or product. Outer-sphere complexes involve electrostatic coulombic interactions and are thus weak compared to inner-sphere complexes in which the binding is covalent or ionic. Outer-sphere complexation is usually a rapid process that is reversible, and adsorption occurs only on surfaces of opposite charge to the adsorbate.

Inner-sphere complexation is usually slower than outer-sphere complexation and is often not reversible, and can increase, reduce, neutralize, or reverse the charge on the sorptive regardless of the original charge. Adsorption of ions via inner-sphere complexation can occur on a surface regardless of the surface charge. It is important to remember that outer- and inner-sphere complexations can, and often do, occur simultaneously.

The effects of ionic strength on sorption are often used as indirect evidence for whether an outer-sphere or inner-sphere complex forms (Hayes and Leckie, 1986). For example, strontium [Sr (II)] sorption on γ-Al_2O_3 is highly dependent on the ionic strength of the background electrolyte, $NaNO_3$, while Co(II) sorption is unaffected by changes in ionic strength . The lack of ionic strength effect on Co(II) sorption would suggest formation of an inner-sphere complex, which is consistent with findings from molecular scale spectroscopic analyses (Hayes and Katz, 1996; Towle *et al*., 1997). The strong dependence of Sr (II) sorption on ionic

strength, suggesting outer-sphere complexation, is also consistent with spectroscopic findings (Katz and Boyle-Wight, 2001).

2.3.2.2 Soil organic matter (SOM)

Soil organic matter complexes can also occur with clay minerals coated with metal oxides such as Al and Fe oxides. Useful reviews on this topic can be found in a number of sources (Mortland, 1970; Greenland, 1971; Mortland *et al*., 1986; Schnitzer, 1986). Clays tend to stabilize SOM, and a correlation is often observed between the clay content and SOM. Some organic substances bridge soil particles together, resulting in stable aggregates. In some soils, particularly those high in humic substances (HS), all of the clay may be coated with the HS. It has been estimated that from 52 to 98% of all C in soils occurs as clay–SOM complexes (Stevenson, 1982). Even though such a complex exists, the organic surface is still reactive and can retain ions and other materials such as pesticides.

Other organic acids, organic amine cations, and amino acids can also interact with clays. Organic acids are negatively charged in the pH range of most soils but they are pH-dependently charged; some adsorption can occur through H bonding and van der Waals forces. When the pH is below the pKa of the acidic group, and when the organic acid is in the undissociated form, organic materials such as proteins and charged organic cations can also be adsorbed in the interlayers of expansible layer silicates like montmorillonite.

The types of interactions involved in SOM–clay complexes include physical adsorption or interactions via van der Waals forces, electrostatic interactions (cation and anion exchange processes), cation and anion bridges whereby the polyvalent metal forms a bridge between the organic molecule and the inorganic surface to which it is bound (clay mineral–metal–HS), often

referred to as coordination complexes, chemical adsorption, and H bonding. Two or more of these mechanisms may occur simultaneously, depending on the type of organic material, the nature of the exchangeable ion on the clay surface, the surface acidity, and the moisture content of the system (Schnitzer, 1986).

Physical adsorption or retention via van der Waals forces is weak and results from changes in the electric charge density of individual atoms. An electrically positive fluctuation in one atom causes an electrically negative fluctuation in a neighboring atom, resulting in a net attractive force. Adsorption due to physical forces occurs with neutral polar and nonpolar molecules, particularly those with high molecular weight (Schnitzer, 1986).

Electrostatic bonding can occur via cation or anion exchange or protonation. The cationic property of a weakly basic organic molecule is strongly pH-dependent. Thus, this mechanism is dependent on the basic character of the organic molecule, the pH of the system, the properties of the organic cation or chain length, and the type of cation on the clay surface. Sorption of HS on negatively charged clays occurs only when polyvalent metal cations such as Al^{3+}, Fe^{3+}, and Ca^{2+} are present on the clay exchanger since they can neutralize the negative charge on the clay and the charge on the deprotonated organic functional group, e.g., COO–. Calcium is weakly held as a cation bridge and can be easily displaced, whereas Al^{3+} and Fe^{3+} are usually bound nonelectrostatically and are difficult to remove (Schnitzer, 1986). It is probably through this latter mechanism and through coordination that fulvic acid (FA) and humic acid (HA) are primarily retained in soils (Stevenson, 1982).

Hydrogen bonding results from linkage between two electronegative atoms through bonding with a single H^+ ion. The H^+ ion is a bare nucleus with a plus one (+ 1) charge and a propensity to share electrons with those atoms that contain an unshared electron pair such as O. The

hydrogen bond is weaker than ionic or covalent bonds, but stronger than van der Waals attractive forces (Stevenson, 1982).

2.3.2.3 pH

Sorption of metal ions is pH-dependent and is characterized by a narrow pH range where sorption increases to nearly 100% and traditionally known as an adsorption edge. The pH position of the adsorption edge for a particular metal ion is related to its hydrolysis or acid–base characteristics.

One can measure the relative affinity of a cation for a sorbent or the selectivity. The properties of the cation, sorbent, and the solvent affect the selectivity. With monovalent alkali metal cations, electrostatic interactions predominate and the general order of selectivity is $Li^+ <$ $Na^+ < K^+ < Rb^+ < Cs^+$ (Kinniburgh and Jackson, 1981). This order is related to the size of the hydrated radius. The ion in the above group with the smallest hydrated radius, Cs+, can approach the surface the closest and be held the most tightly.

However, on some hydrous oxides, the reverse order is often observed. This has been particularly noted for some hydrous metal oxides. The reason for this selectivity is not well understood, but may be related to the effect of the solid on water that is present on the oxide surface (Kinniburgh and Jackson, 1981) or to variation in the solution matrix.

With divalent ions there is little consistency in the selectivity order. The type of surface and the pH both appear to have major effects on the selectivity sequence. Differences in the H^+/Mn^+ could cause reversals in selectivity since the ion with the higher H^+/Mn^+ stoichiometry would be favored at higher pH (Kinniburgh and Jackson, 1981).

CHAPTER THREE

3. MATERIALS AND METHODS

3.1 THE STUDY AREA

The study was carried out on the Ankobra Basin. The main river is River Ankobra which takes its source around Bibiani and passes through Bogoso and Prestea all of which are mining towns in Ghana. In addition, its major tributaries: River Mansi, River Bonsa and River Fure all pass through mining communities before joining the main Ankobra, which finally enters the Gulf of Guinea at Axim. Figure 3.1 shows the geographical layout of the Ankobra River and sampling sites.
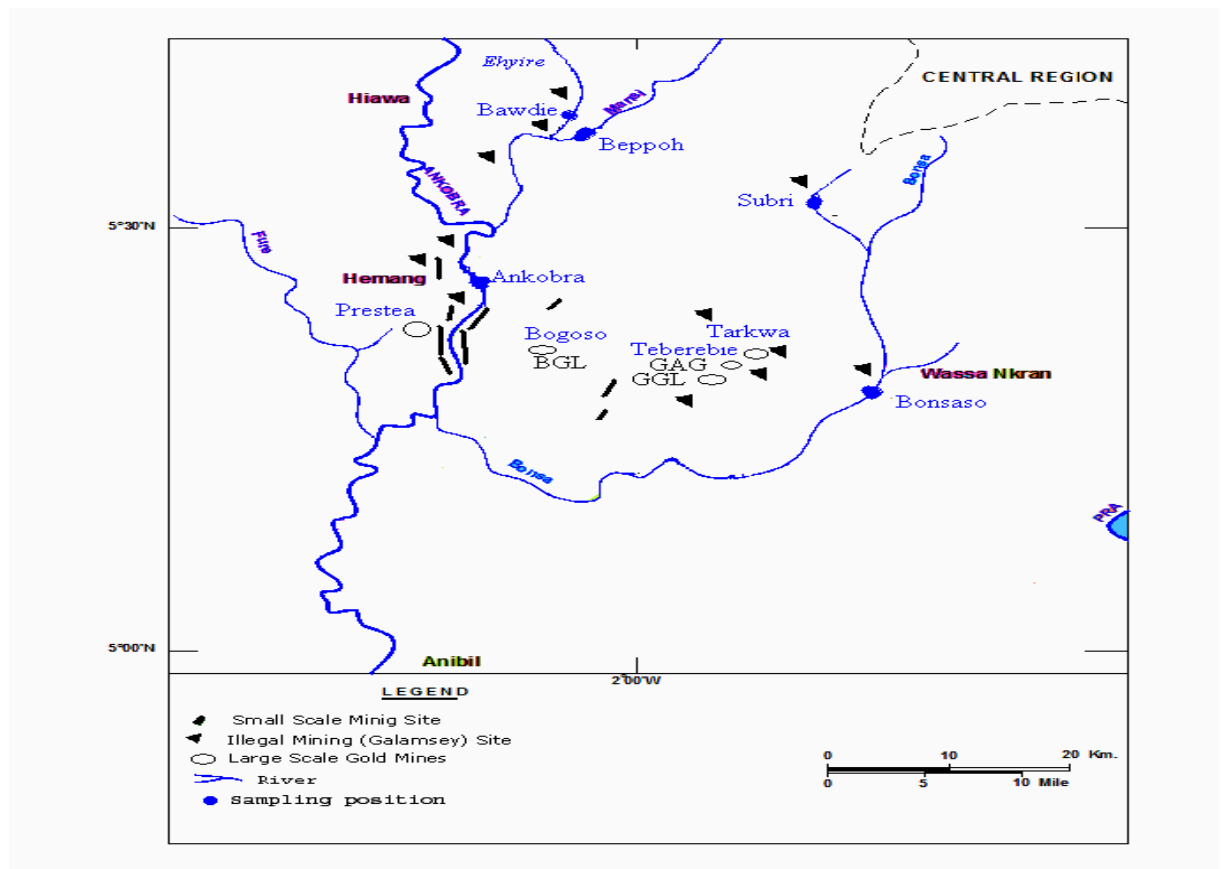
Figure.3.1 The geographical layout of the Ankobra Basin and sampling sites (Modified from Kortatsi, 2004)

3.2 GEOLOGY OF THE AREA

Ankobra basin is one of the main mining areas in Ghana. The major minerals mined in this area include gold, manganese, bauxite and diamond. Gold mining in this basin dates to about 500 years but written records have restricted the period to 120 years (Marston *et al*., 1992). The intense and uncontrolled mining activities in the basin have led to environmental degradation, including the pollution of surface water sources. Ankobra River, for instance, is documented to be highly polluted due to mining activities (Golow and Adzei, 2002).

The Ankobra basin is approximately 8,400 km^2 and lies between latitudes 4.8^o N and 6.5^o N, and longitudes 1.6^o W and 2.3^o W (Figure.3.1). Physically, the Ankobra basin comprises series of ridges, which in some places reached the height of 200 m above sea level and separated by steep sided flat-bottomed valleys that vary in altitude from 46 m in the south to approximately 76 m in the north. Most of the valleys are parallel to one another and to the strike of the rocks. Heavy rainfall and forest vegetation that prevent sheet erosion have reduced the whole area into highly dissected and uniformly moderate relief with a gentle slope to the south (Service, 1938). Erosion is mainly restricted to river channels that cut up the plateau surfaces, and the hills are usually capped with iron-pan (laterite) and bauxite (Dickson and Benneh, 1980).

The geomorphology of the Tarkwa-Prestea area consists of a series of ridges and valleys parallel to each other and to the strike of the rocks. The strike of the rock are generally in north-south direction (Kortatsi, 2004). Both the Tarkwaian and Birimian systems are folded along axes that trend northeast. The general type of topography reflects underlying geology (Kortatsi, 2004). The area has three main gold deposits. Placer or alluvial deposit, non-sulphidic paleplacer or free milling ore and oxidized ore (Kortatsi, 2004).

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Alluvial deposits occur in streams draining areas with auriferous deposits where the bedrock only is slightly metamorphosed and intruded by Dixcove granite particularly in Biriminan rock areas (Kortatsi, 2004). Non-sulphidic paleplacer ore occurs mainly in hard rock. It is particularly associated with Banket conglomerates of Tarkwa formation (Kortatsi 2004). Oxidized ore occurs in weathered rocks and is derived from sulphides, arsenopyrite, realgar (AsS), opiment (As_2S_3) pyrites etc (Kortatsi, 2004).

3.3 APPARATUS

- Automatic Mercury Analyzer Model HG-5000 (Sanso Seisakusho Co., Ltd, Japan), equipped with mercury lamp operated at a wavelength of 253.7 nm was used for the determinations. The signals were obtained on a Yokogawa strip chart recorder Model 3021 as peak heights. Recorder chart speed was 20 cm h^{-1} and range was 100mv.

- Pyrex 50 ml graduated stoppered test tube (26 x 200mm).

- Aluminium top hot plate, HP 1- 2, 457 x 305 x 150 mm (Clifton, UK). Aluminium Heating Blocks, 95 x 75 x 50 mm each with 6 round holes. Each hole is 28 x 47mm. The heating blocks were placed on top of the hot plate and the tubes inserted into the holes. The hot plate could accommodate 12 heating blocks allowing for the digestion of a maximum of 72 samples.

3.4 REAGENTS

All reagents used were of analytical reagent grade (BDH Chemicals Ltd, Poole, England) unless otherwise stated. Double distilled water was used for the preparation of all solutions.

- Mercury stock standard solution (1000 mg L^{-1}) was prepared by dissolving 0.0677 g of $HgCl_2$ in the acid mixture of HNO_3: H_2SO_4: $HClO_4$ (1:5:1) in a 50 ml digestion flask with heating on a hot plate at a temperature of 200 °C for thirty (30) minutes. The solution was then diluted to 50 ml with water. Blank solutions were also prepared alongside. The working standard solutions were freshly prepared by serial dilution of appropriate aliquot of the stock solution using blank solution.

- Stannous Chloride solution (10% w/v) was prepared by dissolving 10 g of $SnCl_2.2H_2O$ in 100 ml 1 M HCl solution. The solution was aerated with nitrogen gas at 50mlmin^{-1} for 30 min to expel any elemental mercury from it.

- Potassium permanganate solution (0.5% w/v) was prepared by dissolving 0.5g of $KMnO_4$ in distilled water and made to a final volume of 100ml.

- Potassium dichromate solution (1M) was prepared by dissolving 49.024g of dry $K_2Cr_2O_7$ in 800ml of distilled water and diluted to 1000ml.

- Conc. Sulphuric acid, analytical reagent grade (BDH Chemicals Ltd, Poole, England)

- Ferrous ammonium sulphate solution (0.2M) was prepared by dissolving 78.390g ferrous ammonium sulphate in 50ml conc. H_2SO_4 and diluted to 1000ml with distilled water

- Ferroin Indicator solution (phenanthroline monohydrate- ferrous sulphate) $[C_{12}H_8N_2]_3FeSO_4$ was prepared by dissolving 1.485g of 1,10 phenanthroline monohydrate ($C_{12}H_8N_2.H_2O$) in 100ml of 0.025M ferrous sulphate (0.695g of ferrous sulphate, FeSO4. 7H$_2$O in 100ml of distilled water).

All glassware used for dilution, storage and experiments were cleaned with detergent solution, rinsed with distilled water and soaked in 10% (v/v) HNO_3 overnight. They were rinsed with

distilled water followed by 0.5% (w/v) KMnO$_4$ and finally rinsed with distilled water and dried before use.

3.5 SAMPLING AND SAMPLE PREPARATION

Seven (7) surface soil samples (0 – 10 cm) were collected close to the main River Ankobra and its major tributaries at Ankobra (AA), Bonsa (BB), Subri (SS), Beppoh (BM), Bawdie (BE), Teberebie (TB) and Efuanta (EB) using a plastic trowel. Samples were randomly collected from both sides of the river, air dried and passed through a 2 mm sieve.

3.6 DETERMINATION OF SOIL pH

Soil suspension for soil pH determination was prepared using the ratio of 1: 2.5 (w/v) soil: water (McLean, 1982).

3.7 GRANULOMETRIC DETERMINATION

Particle size distribution was determined using hydrometer method (Gee and Bauder, 1986) as follows:

An amount of 50g of air dried, 2-mm sieved soil was placed in a 300-ml Erlenmeyer flask.

 Hundred (100) ml of 5% sodium hexametaphosphate (Calgon) was added. It was shaken until well mixed and allowed to stand overnight. The contents were transferred into a dispersing cup with an electric mixer which was filled to a level of about 2 inches from the top with distilled water. The cup was then attached to the mixer and stirred for 2 minutes.

The soil suspension was transferred quantitatively from the dispersing cup to a 1-L graduated cylinder, rinsed with distilled water, and made to the mark. The soil was mixed with a plunger until a uniform suspension was obtained. The plunger was gently removed and the time noted immediately. A hydrometer was placed gently into the suspension immediately after removing

the plunger and readings were taken at the end of 40 seconds, and at the end of 6.9 hours. The hydrometer was removed and the procedure was repeated twice. The average was calculated and recorded.

Calculation:

% silt + clay = corrected 40-s (g/L) / oven dry weight of soil sample (g/L) *100

% sand = 100% - % silt + clay

% clay = corrected 6 h52 m (g/L) / oven dry weight of soil (g/L) *100

% silt = % silt + clay - % clay

3.8 ORGANIC MATTER CONTENT

Organic matter content was determined using the dichromate oxidation method (Nelson and Sommers, 1975) as follows:

An amount of 0.5 g of the air dried 2 mm sieved soil was weighed into a block digestion tube (50 ml). Five (5) ml potassium dichromate solution (1 M) and 7.5 ml conc. H_2SO_4 were added.

The tube was placed in a pre-heated block at 155 $^\circ$C for exactly 30 minutes, removed and allowed to cool. The digest was quantitatively transferred into a 100 ml conical flask using distilled water and 0.3 ml of the ferroin indicator solution was added. It was well swirled and titrated with ferrous ammonium sulphate solution, to an intermediate endpoint of greenish colour then to brick red endpoint. The titre was recorded and corrected with the mean of 2 reagent blanks (T).

Calculation:

$$\% \text{ Organic Carbon} = \frac{T \times 0.2 \times 0.3}{\text{Sample weight}}$$

% Organic Matter = (% OC x 1.72) x 0.58

3.9 DIGESTION PROCEDURE FOR DETERMINATION OF TOTAL MERCURY IN SOIL

The soil samples were digested for total mercury determination by an open flask procedure developed at the National Institute for Minamata Disease (NIMD) in Japan by Akagi and Nishimura (1991) as shown in chart 3.1. In the procedure, 0.5g of soil was weighed into 50 ml digestion flask and 1 ml H_2O, 2 ml HNO_3-$HClO_3$ (1:1) and 5 ml H_2SO_4 were added in turns. The mixture was then heated at a temperature of 200^0C for 30 minutes. The sample solution was then cooled and diluted to 50 ml with double distilled water. Solutions of volumes 25 µl, 50 µl and 100µl of 1µg ml^{-1} standard Hg solution were also subjected to the same digestion procedure. The concentrations of the standard solution digests obtained were 0.5, 1.0 and 2.0 ng ml^{-1}, were used to calibrate the mercury analyser. Blanks were prepared in a similar manner but without the analyte.

Sample (0.5 g of soil in 50 ml digestion flask)

        H_2O, 1ml

        HNO_3: $HClO_4$ (1:1), 2 ml

        H_2SO_4, 5 ml

        Heat at $200^o C$ for 30 min

Digested Sample

        Cool to room temperature

        Make up to 50 ml with H_2O

Sample Solution, 5 ml

        10% $SnCI_2$, 0.5 ml

CV-AAS (Analyzer)
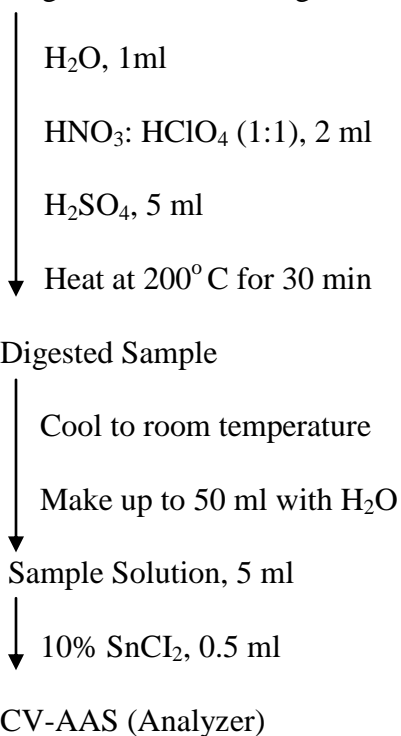
Chart 3.1 Analytical procedure for total mercury determination in soil samples

3.10 DETERMINATION OF EQUILIBRIUM TIME FOR SORPTION

One (1) gram of soil sample (BE) was accurately weighed in triplicate into a 15 ml centrifuge tube and 10 ml of 80 μg/l Hg (II) solution was added. The tubes containing the suspensions were then shaken with an electronic shaker at different times over twenty-four hours. Suspensions were taken after 30 mins, 1 hrs, 1.5 hrs, 2 hrs, 6 hrs, 10 hrs, 14 hrs, 18 hrs and 22 hrs. Each suspension was centrifuged at a speed of 4000 rpm for 15 minutes. The supernatant was analysed for total mercury. Amount sorbed was calculated from the difference between the initial concentration of Hg (II) solution and the equilibrium concentration.

3.11 SORPTION STUDIES

One (1) gram of each soil sample was accurately weighed in triplicate into a 15 ml centrifuge tube and 10 ml of a known concentration of Hg (II) solution was added. The tubes containing the suspensions were then shaken with an electronic shaker for 90 minutes (equilibration time) at a speed of 1000 rpm. The suspension was centrifuged at a speed of 4000 rpm for 15 minutes. The supernatant was analysed for total mercury. Amount sorbed was calculated from the difference between the initial concentration of Hg (II) solution and the equilibrium concentration.

3.12 DETERMINATION OF MERCURY

Determination of mercury in the supernatants and soil digests were carried out using Cold Vapour Atomic Absorption Spectrophotometer with an Automatic Mercury Analyzer model HG-5000 (Sanso Seisakusho co., Ltd, Japan) developed at National Institute for Minamata Disease (NIMD).

The analyzer is an instrument designed specifically for the measurement of mercury using the cold vapour technique. It makes use of the batch mercury cold vapour generating system. The

analyzer consists of an air circulation pump, a reaction vessel, $SnCl_2$ dispenser, an acidic gas trap and a four-way stop-cock with tygon tubes to which is attached a ball valve. The operations of the ball valve and the air circulation pump are controlled by a microprocessor. A schematic diagram of the system is shown in Figure 3.2.

For the determination, 5 ml of the sample solution was introduced into the reaction vessel using a micropipette (1-5 ml). The reaction vessel is immediately stoppered tightly and 0.5 ml of 10% (w/v) $SnCl_2.2H_2O$ in 1 M HCl is added from a dispenser for the reduction reaction. During this time, air is circulated through the four-way stopcock to allow the mercury vapour to come to equilibrium and the acidic gases produced by the reaction also swept into the sodium hydroxide solution. After 30 seconds, the four-way stopcock is rotated through 90^0 and the mercury vapour is swept into the absorption cell. Response is recorded on the strip chart recorder as very sharp peaks. Peak heights were used for computation of total mercury concentration.

Figure 3.2 Apparatus for mercury analyses by Cold Vapour Atomic Absorption Spectrophotometry

3.13 STATISTICAL ANALYSIS

The data obtained in this study were subjected to statistical analysis using Microsoft Excel. Linear regression and correlation analysis were used to assess correlation between initial total mercury concentrations in soil, amount sorbed and soil characteristics.

CHAPTER FOUR

4. RESULTS AND DISCUSSIONS

4.1 TOTAL MERCURY IN THE SOIL SAMPLES

Total mercury (THg) concentrations were determined in surface soils from the Ankobra basin in the south- western part of Ghana. In all, a total of seven soil samples were collected close to the main river Ankobra and its major tributaries at Ankobra (AA), Bonsa (BB), Subri (SS), Beppoh (BM), Bawdie (BE), Teberebie (TB) and Efuanta (EB) and analyzed for total mercury. Summary of results of soil total mercury concentration (THg), soil pH, soil organic matter (OM) and particle size distribution are presented in Table 4.1. Each THg value is the mean of three replicate samples ± standard deviation. The THg of the soils ranged from 0.051µg/g to 0.366µg/g with an average of 0.15µg/g. The total Hg content measured in this study was below the level set by US EPA (200µg/g). Considering the sampling sites, soil from Efuanta (EB) had the highest mean THg with 0.366µg/g compared to the others. Samples from Ankobra (AA) had the second highest mean THg (0.195µg/g) which is about half that of samples from Efuanta (EB). Soil samples from Bawdie (BM) had the lowest T Hg content (0.051µg/g).

Table 4. 1: Result of THg in soil and some soil characteristics

Sample	THg (µg/g)	Sand (%)	Silt (%)	Clay (%)	O M (%)	pH	Texture
Ankobra (AA)	0.195± 0.003	39.65	46.48	13.88	2.25	6.61	Loam
Bonsa (BB)	0.058± 0.001	64.84	9.65	25.52	2.67	5.54	Sandy clay loam
Subri (SS)	0.081± 0.002	24.04	22.72	29.38	1.79	7.54	Clay
Beppoh (BM)	0.051± 0.003	14.09	51.28	26.49	0.38	8.06	Silty clay loam
Bawdie (BE)	0.167± 0.001	70.29	16.62	9.39	0.52	5.06	Sandy loam
Teberebie (TB)	0.116± 0.001	90.52	2.77	3.31	0.09	6.49	Sand
Efuanta (EB)	0.366± 0.004	46.28	38.12	13.84	3.58	6.61	Loam

Previous studies have revealed that, the soil in the Tarkwa area consists of mostly silty-sands with minor patches of laterite, mainly on hilly areas (Kuma and Younger, 2001). The texture of the soils used in this study are found to be loam for Efunta (EB) and Ankobra (AA), clay for Subri (SS), sand for Teberebie (TB), sandy loam for Bawdie (BE), silty clay loam for Beppoh (BM) and sandy clay loam for Bonsa (BB).

The THg data from this study was subjected to Pearson correlation analysis to determine the relationship between mercury concentrations in the soil samples and some soil characteristics. The results are presented in Table 4.2 in the form of correlation coefficients.

Table 4. 2: Correlation coefficients for relationships between THg in various surface soils from Ankobra basin and some soil characteristics

	THg (μg/g)	pH	OM	Clay (%)	Sand (%)	Silt (%)
THg (μg/g)		-0.19	0.57	-0.47	0.09	0.27
pH	-0.19		-0.11	0.48	-0.76	0.59
OM	0.57	-0.11		0.26	-0.20	0.23
Clay (%)	-0.47	0.48	0.26		-0.76	0.31
Sand (%)	0.09	-0.76	-0.2	-0.76		-0.81
Silt (%)	0.27	0.59	0.23	0.31	-0.81	

4. 2 EFFECT OF SOME SOIL CHARACTERISTICS ON THg

4.2.1 Soil organic matter

Soil organic matter is known to play a role in Hg adsorption, although its quantitative contribution is not clearly understood (Semu and Singh, 1987). The THg correlated positively (r = 0.57) with the OM in the soil. This indicates increasing Hg concentration with increasing organic matter content. Nater and Grigal (1992) also found a positive correlation between total Hg and organic matter content of forest soils across the north-central USA (r = 0.51).

4.2.2 Percentage soil clay

Zhong and Wang (2008) found that, the percentages of extracted Hg were comparable among coated or uncoated quartz, calcium carbonate, Fe and Mn oxides (42- 60%), but lower in clay (15- 23%), suggesting that the clay content in the sediments decreased Hg extraction. Elimination of the clay content from the sediments increased the Hg extraction (from 30% to 55%), consistent with the low bioavailability of Hg in clay. One possibility for this is the strong association between organic matter and clay since Hg was found to be predominately bound to organic matter.

Biester *et al* (2001) also found that high clay content in soils inhibited the leachability of Hg and Parkpian *et al* (2001) also reported that the high content of clay in sediments made Hg less bioavailable. In this study, it was found that percentage soil clay had slight negative correlation ($r = -0.47$, $p< 0.05$) with THg concentration. This could suggest that soil with high content of clay would have low level of Hg.

4.2.3 Soil pH

The pH of the soils in this study had no significant correlation ($r = -0.19$, $p< 0.05$) with the THg concentration. This could suggest that soil pH has no direct effect on THg concentration in soil. Despite several investigations on soil pH values as one of the two most important factors which may significantly influence Hg geochemistry under various conditions including soil transport, transformation processes, and also exchange/release flux via the interface, no significant

correlation has been established between pH values and Hg concentration in soil (Semu and Singh, 1987) which this study has also corroborated.

4. 3 DETERMINATION OF EQUILIBRIUM PERIOD

In sorption studies, it is very important to equilibrate the adsorbent and adsorbate long enough to ensure that steady state had been reached. However, one should be careful that the equilibrium process is not so lengthy that precipitation or dissolution reactions occur (Sposito, 1984). Additionally, the degree of agitation used in the equilibration process should be forceful enough to effect good mixing but not so vigorous that adsorbent modification would occur (Spark, 1989). Soil organic matter is known to play a role in Hg adsorption, although its quantitative contribution is not clearly understood. Trost and Bisque (1972) and Estes *et al* (1973) reported that surface soils, rich in organic matter, adsorbed significantly higher amounts of Hg at longer periods of equilibration as compared to their subsurface soils which contained relatively smaller quantities of organic matter. Equilibration period for sorption should, therefore, be very useful. In this study, the period required to attain equilibrium was determined using soil sample from Efuanta (EB) because it has the highest organic matter. The sorption of Hg in the soil exhibited an initial rapid sorption within 1 hour; followed by a slight decrease in amount sorbed and then a steady rate of sorption over the rest of the 24 hour period. This experiment indicated that a period of 90 min is sufficient to attain equilibrium for all of the Hg (II) solutions. This equilibration period obtained is in agreement with 90 minutes equilibration period published by Miretzky *et al* (2005). The amount of Hg (II) sorbed against time of shaking is presented in Fig 4.1.
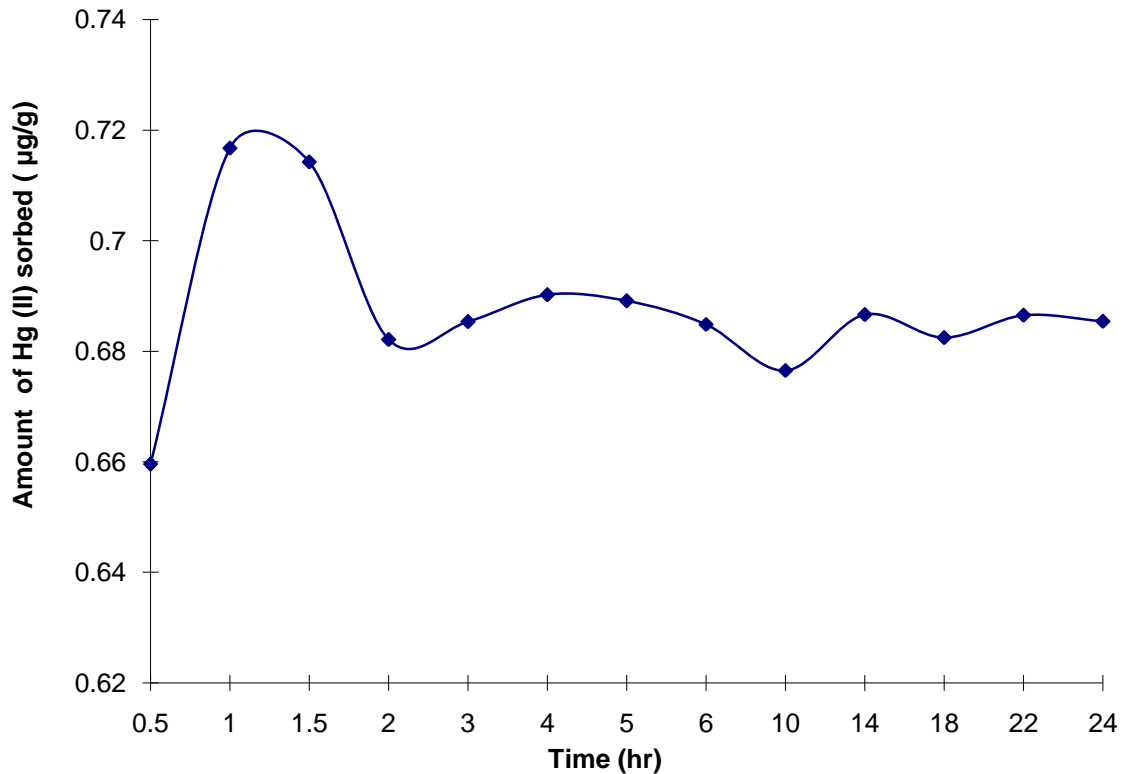
Fig 4. 1: Amount of Hg sorbed against time of shaking

4.4 THE EFFECT OF Hg (II) CONCENTRATION ON SORPTION

Apart from a few contradictory studies (Koss and Kim, 1990), sorption is often observed to increase with the solute concentration. The main reasons proposed for this phenomenon called "solid effect" are (i) the occupied volume of the suspended particles (Celorie *et al*., 1989) and (ii) their aggregation (Voice *et al.,* 1983; Di Toro *et al*., 1986) that would prevent an optimal sorption of the solutes. It has been found that, the ratio of solid mass versus solution volume should theoretically not influence the proportion of adsorbed compound. And most of the time, this parameter does not effectively influence the shape of the isotherm if it remains in the same order of magnitude. The results of this study corroborate the observations that the amount of Hg (II) sorbed increased with increase in the concentration of the mercury solutions

4.5 QUALITATIVE DESCRIPTION OF SORPTION ISOTHERMS

Sorption isotherms are widely used to characterize retention of chemicals in soils. The shape of the isotherm provides information on the strength by which the sorbate is held onto the soil. Isotherms also allow comparison of the relative amount of sorbate that soils can retain under given circumstances and determination of the maximum sorption capacity of a sorbent (Harter, 1991). Sorption isotherms for Hg (II) on seven soils were constructed by plotting the amount of Hg (II) sorbed versus the equilibrium concentration of Hg (II) remaining in solution.

Giles *et al*, (1974) classified sorption isotherms based on their initial slopes and curvatures. They distinguished between high affinity (H), Langmuir (L), constant partition (C), and sigmoidal – shaped (S) isotherm classes. For an S-type isotherm the slope initially increase with adsorptive concentration, but eventually decreases and becomes zero as vacant adsorbent sites are filled. This type of isotherm indicates that at low concentrations the surface has a low affinity for the adsorptive, which increases at higher concentrations.

The H-type isotherm is indicative of strong adsorbate - adsorbate interactions such as inner-sphere complexes. The C-type isotherms are indicative of a partitioning mechanism whereby adsorptive ions or molecules are distributed or partitioned between the interfacial phase and the bulk solution phase without any specific bonding between the adsorbent and adsorbate.

All the soils in this study had an L - type isotherm according to the classification of Giles *et al* (1974). This type of isotherm is characterized by concave curve provided by the ratio between the concentrations of the Hg (II) remaining in solution and sorbed on the soil which decreases when the solute concentration increases. The L- shaped isotherm is characterized by a decreasing slope as concentration increases since vacant adsorption sites decrease as the adsorbent becomes covered. This provides a concave curve. Such adsorption behavior could be explained by the

high affinity of the adsorbent for the adsorptive at low concentrations, which then decreases as concentration increases.

It suggests a progressive saturation of the solid, but the curve does not reach any plateau (the soil does not show clearly a limited sorption capacity). This means that the theoretical monolayer has not been completed and the monolayer sorption could be as a result of different retention mechanisms, new sites, or the development of a fresh surface where retention can take place (Harter, 1991). The graph showing the amount sorbed versus the equilibrium concentration for all the soils is presented in the figure 4. 2.
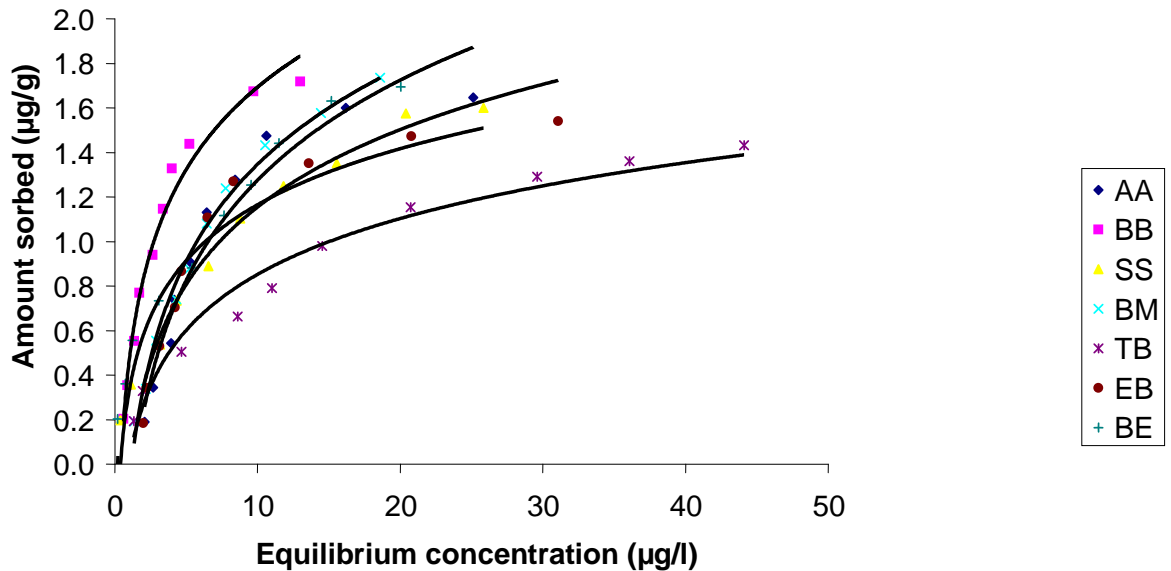
Figure 4. 2 Amount sorbed against equilibrium concentration.

In this study, there was a sharp increase in the rate of sorption with increase in initial concentration of Hg (II) for the various soil samples. For instance, for soil from Bonsa (BB), increase in equilibrium concentration led to sharp increase in amount sorbed to a point (amount sorbed = 1.437 µg/g) where it further increased slightly. For soil sample from Ankobra (AA)

increase in initial concentration led to increase in amount sorbed to a maximum point (1.600) where further increase in concentration of Hg (II) resulted in no significant effect on amount sorbed. This was observed for all the soils, except for soil sample from Teberebie (TB) where increase in concentration led to a slight increase in the amount sorbed.

Generally, increase in initial concentration of the Hg (II) resulted in an increase in the amount sorbed for the soil samples. However, the extent of increase varies with regards to the initial concentrations. For instance, increase in concentration from 80 µg/l to 100 µg/l led to increase in amount sorbed for BE by 0.32, for BB the increase was higher (0.39). The increase in concentration resulting to a decrease in the amount of solute sorbed suggests a progressive saturation of the soil surface.

4. 6 QUANTITATIVE DESCRIPTION OF SORPTION ISOTHERM

Traditionally, the sorption of ions by soils has been quantitatively described by parameters obtained either directly from isotherms or by least square analysis with Linear, Langmuir and Freundlich isotherms.

The data from this study was subjected to Linear, Langmuir and Freundlich models to determine sorption parameters and identify the model which gives the best fit. Linear isotherm was used to show the relationship between concentrations of Hg (II) remaining in solution and amount sorbed on the soil. The Linear sorption isotherm assumes that the sorbed concentration is directly proportional to the dissolved concentration.

The linear equation is described by:

$C_s = K_d C_e$

Where Cs is the amount sorbed per unit weight of soil (µg/g); K_d is the linear distribution coefficient (L/Kg); and C_e is the equilibrium concentration (µg/l).

The plot showing the linear model for all the soils shows that soil from Bonsa (BB) had the highest amount of Hg sorbed at the various concentrations followed by Beppoh (BM) while soil from Teberebie (TB) had the lowest amount of Hg sorbed. The plot showing the linear model for all the soils is presented in Figure 4.3 and Table 4.3 presents the linear distribution coefficients and parameters for all the soils deduced from the application of the linear model.
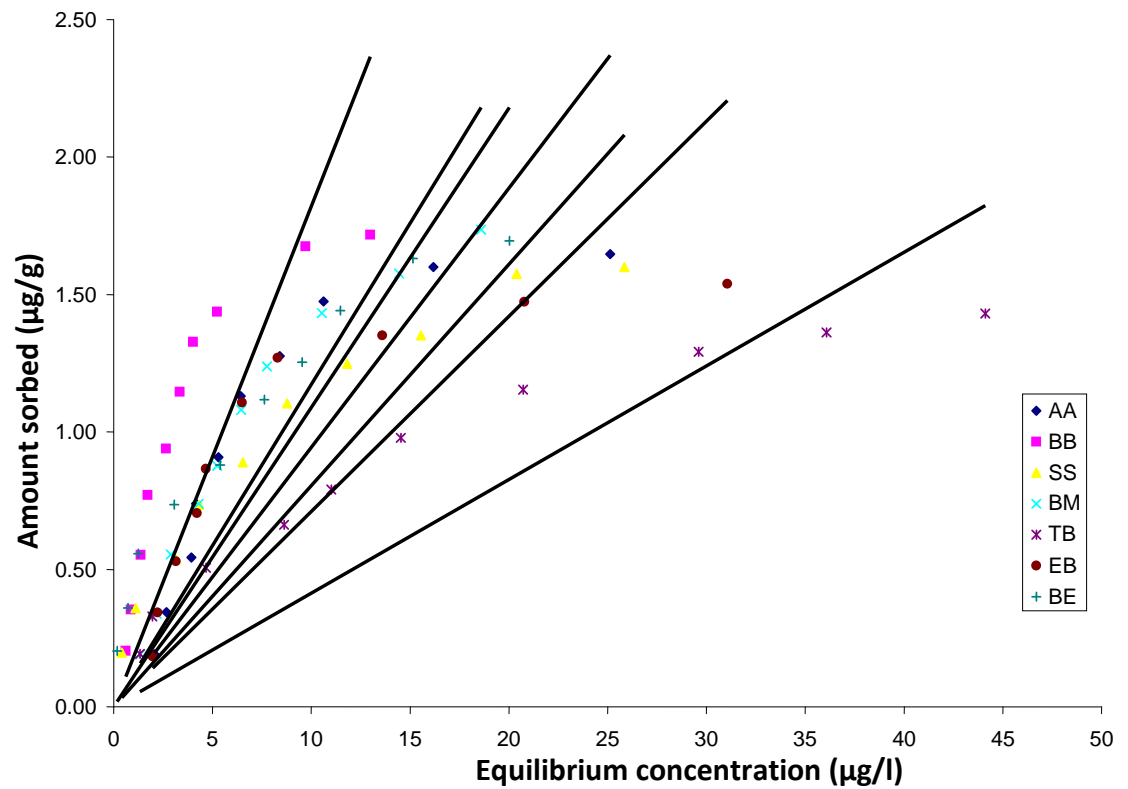
Figure 4. 3: Linear model for Ankobra basin soils

Table 4. 3: Parameters for the linear equation

Sample	Equation	K_d (L/Kg)	R^2
Ankobra (AA)	y = 0.0943x	94.3	0.36
Bonsa (BB)	y = 0.1822x	182.2	0.28
Subri (SS)	y = 0.0805x	80.5	0.57
Beppoh (BM)	y = 0.1172x	117.2	0.74
Bawdie (BE)	y = 0.1089x	108.9	0.62
Teberebie (TB)	y = 0.071x	71.0	0.03
Efuanta (EB)	y = 0.0414x	41.4	0.55

The distribution coefficient (K_d), which is the slope of a simple linear model, is often used to characterize the mobility of trace metals in aquatic environment: where low K_d values imply that most of the metal remains in solution, and high K_d values indicate that the metal has great affinity for the soil (Anderson and Christensen, 1988). In this study, distribution coefficient (K_d) ranged from 41.4 µg/g (TB) to 182.2 µg/g (BB) which is presented in Table 4.3. Although, soil from Efuanta (EB) had the highest THg and OM, it did not have the highest distribution coefficient (K_d = 71 L/Kg). This could mean that soils with high OM do not necessarily have high distribution coefficients, because distribution coefficient depends on other factors. In this study, it was observed that soils with relatively high % clay and relatively low THg had higher distribution coefficients. These include soil from Bonsa (BB) with K_d value of 182.2 L/Kg (% clay = 25.52, THg = 0.058 µg/g) and soil from Bawdie (BM) which had K_d value of 108.9 (% clay = 26.49, T Hg = 0.051 µg/g).

The ratio of organic to mineral matter in particulates affects both K_d and particulate T Hg concentration, with stronger binding associated with higher organic content (Mason and

Sullivan, 1998)   With regards to soil properties, a strong positive correlation was found to exist between the linear distribution coefficient and % clay ($r = 0.65$, $p < 0.05$), and a slight positive correlation between distribution coefficient and organic matter ($r = 0.35$, $p < 0.05$). No correlation was found between the distribution coefficient and soil pH ($r = -0.17$, $p < 0.05$). Ranking the soils by their K_d values, it is observed that, Bonsa (BB) >Beppoh (BM) >Bawdie (BE) > Ankobra (AA) > Subri (SS) > Efuanta (EB) >Teberebie (TB). This could suggest that soil with similar soil characteristics like Bonsa (BB) would sorb Hg (II) better than the others and hence could help minimize leaching of Hg into the aquatic environment.

Table 4.4: The correlation coefficient for relationship between distribution coefficient and some soil characteristics

	(%) Clay	OM	pH	Log K_d (l/Kg)
Clay (%)		0.26	0.48	0.65
OM	0.26		-0.11	0.35
pH	0.48	-0.11		-0.17
Log K_d (L/Kg)	0.65	0.35	-0.17	

The Langmuir isotherm model suggests that sorption occurs on homogeneous surface by monolayer sorption without interaction between sorbed ions. The linear form of Langmuir isotherm equation is represented by the following equation:

$Q_e/C_e = bK - KQ_e$

Where C_e is the equilibrium concentration (µg/l), Q_e is the amount sorbed (µg/g), b is the maximum Hg(II) ions uptake per unit mass of soil (µg/g) related to adsorption capacity. In

short, K reflects the retention intensity and the number of available sites for a sorbate. Figure 4.4, presents the linearized form of Langmuir model after the experimental data was fitted. The values of b and K were evaluated from the slope and intercept respectively for the seven isotherm lines and presented in Table 4.5.
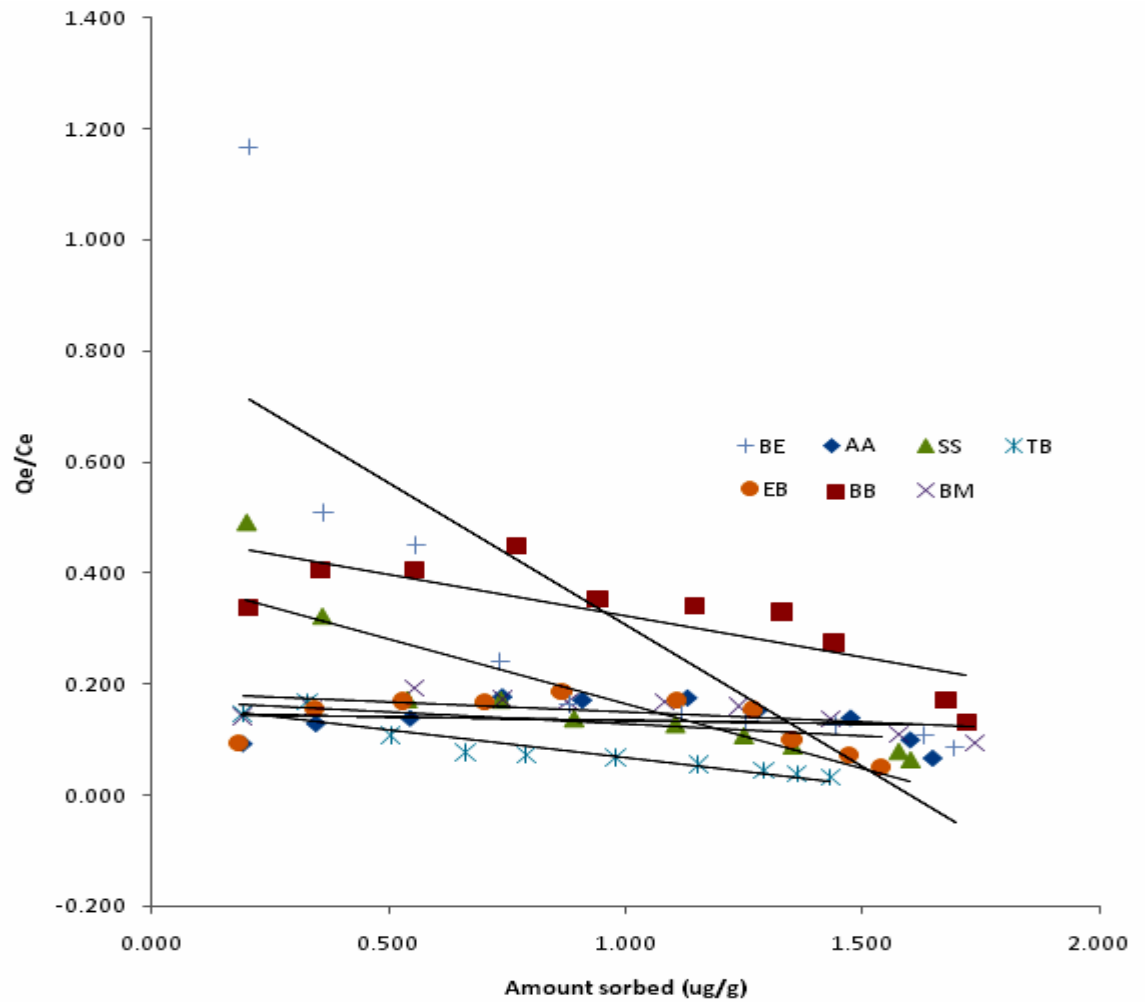
Figure 4.4: Langmuir model for Ankobra basin soils

Table 4.5: Parameters for the Langmuir equation

Sample code	Equation	b	k	R^2
AA	y= -0.012x +0.146	12.16	0.012	0.03
BB	y= -0.149x +0.472	3.16	0.149	0.63
SS	y =-0.232x +0.397	1.71	0.232	0.75
BM	y =-0.036x +0.184	5.11	0.036	0.41
TB	y =-0.098x +0.166	1.69	0.098	0.88
EB	y =-0.044x +0.172	3.91	0.044	0.19
BE	y =-0.510x +0.817	1.60	0.510	0.64

The Langmuir adsorption capacity for the seven Ankobra Basin soils for Hg ranged from 1.60 L/Kg to 12.16 L/Kg (Table 4.5). The Langmuir Energy for these soils for Hg ranged from 0.012 to 12.16. The Langmuir energy reflects the retention intensity and the number of sites available for a sorbate.

With regards to soil properties, negative correlation was found to exist between the Langmuir adsorption energy and soil pH ($r = -0.58$, $p < 0.05$), and correlation between Langmuir adsorption energy and organic matter was insignificant ($r = -0.19$, $p < 0.05$). No correlation was found between Langmuir adsorption capacity and soil characteristics.

Table 4.6: Correlation coefficients for relationship between Langmuir parameters and some soil characteristics

	Clay (%)	OM	pH	b	K
Clay (%)		0.26	0.48	-0.11	-0.08
OM	0.26		-0.11	0.03	-0.19
pH	0.48	-0.11		0.18	-0.58
B	-0.11	0.03	0.18		-0.56
K	-0.08	-0.19	-0.58	-0.56	

The Freundlich model is a case for heterogeneous surface energies and it gives an exponential distribution of active sites. This form of the equation was used to relate the amount of inorganic Hg sorbed on soil. The linear form of this model is represented by:

$\log Q_e = \log a + n \log C_e$

Where C_e is the equilibrium concentration and Q_e is the amount sorbed ($\mu g/g$).

The Freundlich constants a and n, which respectively indicate the adsorption capacity and the adsorption intensity, were calculated from the intercept and slope of plot of $\log Q_e$ versus $\log C_e$ which is presented in Figure 4.5 and the parameters presented in Table 4.7.
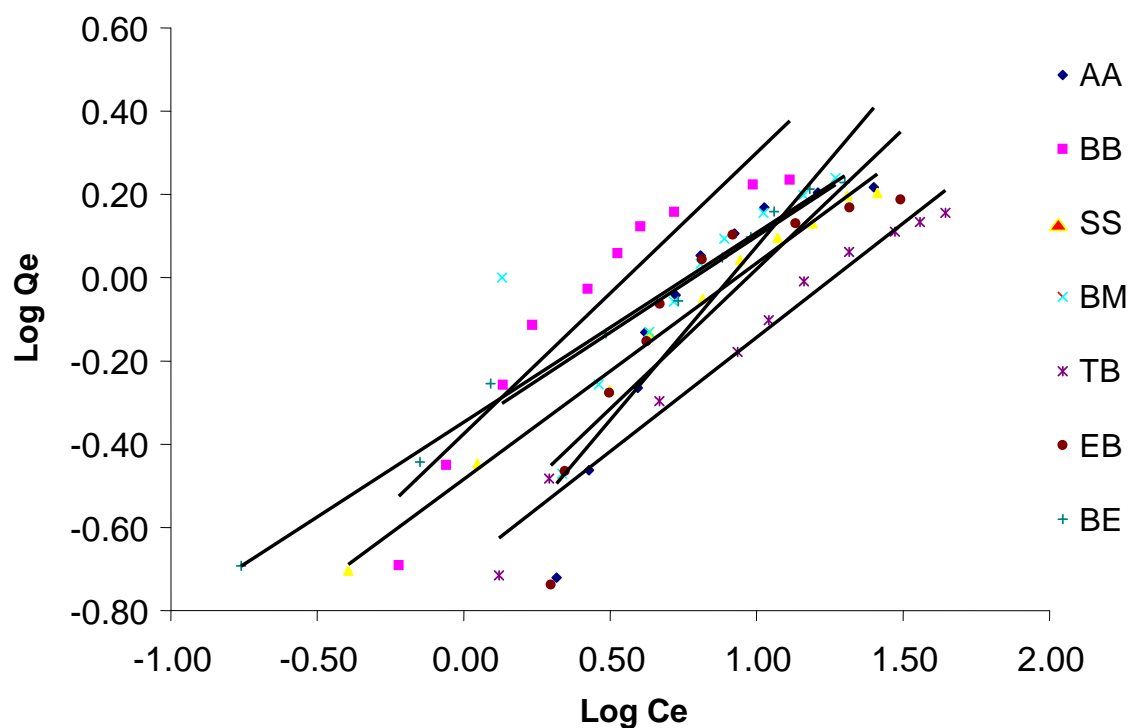
Figure 4. 5: Freundlich model for Ankobra basin soils

Table 4. 7: Parameters for the Freundlich equation

Sample Code	Equation	a	n	R^2
Ankobra (AA)	y = 0.8329x- 0.758	0.175	0.833	0.37
Bonsa (BB)	y = 0.6747x- 0.3749	0.422	0.675	0.90
Subri (SS)	y = 0.5196x- 0.4849	0.327	0.511	0.99
Beppoh (BM)	y = 0.4611x- 0.3623	0.434	0.461	0.58
Efuanta (EB)	y = 0.04552x- 0.3473	0.450	0.455	0.99
Bawdie (BE)	y = 0.6705x – 0.6498	0.224	0.671	0.78
Teberebie (TB)	y = 0.5483x- 0.6919	0.203	0.548	0.98

The Freundlich binding capacities for the Ankobra Basin soils for Hg ranged from 0.175 to 0.45

(Table 4.7), with the Freundlich adsorption intensity of the soils for Hg ranging from 0.455 to

0.833 (Table 4.7). With regards to soil properties, a slight positive correlation was found to exist

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between the linear distribution coefficient and % clay (r = 0.49, p < 0.05), and a strong positive correlation between Freundlich adsorption intensity and organic matter (r = 0.69, p < 0.05). Correlation was insignificant between the Freundlich binding capacities and soil pH (r = -0.17, p < 0.05). Similarly, correlation between Freundlich binding capacities and organic matter was insignificant (r = -0.29, p < 0.05).

Table 4. 8: Correlation coefficients for relationship between Freundlich constant and some soil characteristics

	(%) Clay	OM	pH	a	n
(%) Clay		0.26	0.48	0.49	-0.11
OM	0.26		-0.11	-0.29	0.69
pH	0.48	-0.11		-0.17	-0.16
a	0.49	-0.29	-0.17		-0.63
n	-0.11	0.69	-0.16	-0.63	

The goodness of fit of an experimental data is measured by the determination coefficients (R^2) (Zaid and Mohammed, 2008). The R^2 for the isotherms studied, has been presented in Table 4.9. Considering the R^2 of this study, it could be deduced that, the Freundlich model showed the best fit followed by Langmuir model and the Linear model in the stated order. Miretzky *et al* (2005) also in a similar study deduced that, the Freundlich model showed a better fit than the Langmuir model. This could be due to similarities in soil characteristics. The better fitness of the Freundlich model compared to the other models could be attributed to the heterogeneous surface energies and exponential distribution of active sites which are characteristics of soils.

The affinity constant between the compound and the organic carbon is often well correlated to any partition coefficient by a logarithmic relationship. In a Freundlich adsorption isotherm system, the value of n is determined experimentally from the slope of the line which is equal to 1/n.

According to, Ansari *et al* (2009) adsorbents with n values near 1.0 are valid for many organic contaminants while lower values (0.4-0.6) are valid for heavy metals and phosphorus. All the soils had an exponent (n) lower than one, indicating that these soils could be good sorbents for Hg (II).

Table 4. 9: Summary of the Freundlich and Langmuir constants and enthalpy for adsorption of Hg on soils from Ankobra Basin

CODE	OM	pH	Linear		Langmuir			Freundlich			
			K_d	R^2	b	K	R^2	a	n	R^2
Ankobra (AA)	2.25	6.61	94.3	**0.36**	12.16	0.012	**0.03**	0.175	0.833	**0.37**
Bonsa (BB)	2.67	5.54	182.2	**0.28**	3.16	0.149	**0.63**	0.422	0.675	**0.90**
Subri (SS)	1.79	7.54	80.5	**0.57**	1.71	0.232	**0.75**	0.327	0.511	**0.99**
Beppoh (BM)	0.38	8.06	117.2	**0.74**	5.11	0.036	**0.41**	0.434	0.461	**0.58**
Bawdie (BE)	0.52	5.06	108.9	**0.62**	1.60	0.510	**0.64**	0.450	0.455	**0.99**
Teberebie (TB)	3.58	6.61	71.0	**0.03**	1.69	0.098	**0.88**	0.224	0.671	**0.78**
Efuanta (EB)	0.09	6.49	41.4	**0.55**	3.91	0.044	**0.19**	0.203	0.548	**0.98**

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS.

From the analysis carried out, the following conclusions may be deduced from the results obtained.

- The THg of the soils ranged from 0.051µg/g to 0.366µg/g with an average of 0.15µg/g. The total Hg content measured in this study for all the soils was below the level set by US EPA (200µg/g).

- THg correlated positively (r = 0.57) with the OM in the soil. This indicates increasing Hg concentration with increasing organic matter content. It was found that percentage soil clay had slightly significant negative correlation (r = -0.47) with THg concentration.

- This study showed that a period of 90 min is sufficient to attain equilibrium between Hg (II) solution and soil.

- In the study, all soils had an L - type isotherm according to the classification of Giles *et al* (1974) and the distribution coefficient (K_d) ranged from 41.4 µg/g to 182.2 µg/g.

- The Freundlich model showed a better fit followed by Langmuir model and Linear model. All the soils had adsorption intensity (n) lower than one, indicating that the soils could be good sorbents for Hg (II).

5.2 RECOMMENDATIONS

This recommendation is made as a result of the outcome of this research.

- The same soil samples used in this study should be used to study the kinetics and factors affecting Hg (II) adsorption in soils to predict mercury transport and fate in soils.

- Further soil characteristics should be determined to identify the relationship between them and the total mercury.

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APPENDIX

Table A1: Sampling Information

Sample code	Location	River	Date of sampling
AA	Ankobra	Ankobra	27/05/09
BB	Bonsa	Bonsaso	27/05/09
SS	Subri	Subri	3/07/09
BM	Beppoh	Mansi	3/07/09
BE	Bawdie	Ehyireso	3/07/09
TB	Teberebie	Bedeabewo	2/07/09
EB	Efunta	Bonsa	2/07/09

$y = 15712x + 1113.2$

$R^2 = 0.9973$
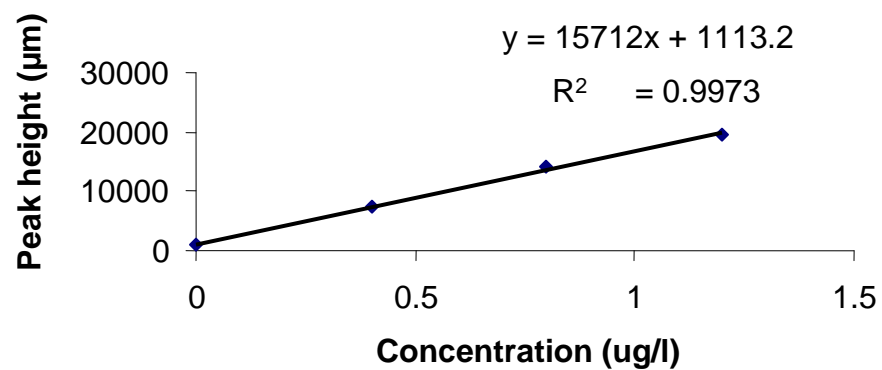
Fig A1: Standard curve for Hg(II)

Table A2: Determination of period sufficient to attain equilibrium

Rotary shaker at 1400rpm   conc. of Hg used: 51.2µg/l (det'd from instrument)
Centrifuge at the speed of 4000 for 5min.

Time (min)	Wgt of soil (g)	Raw Peak Height (mm)	Actual Peak Height(mm)	T. Hg conc. in supernatant (µg/l)	Conc. Sorbed (µg/l)	Amt. sorbed (µg/g)
60						
	1.0055	6	3	0.06	0.58	0.58
	1.0269	6	3	0.06	0.58	0.56
	1.1449	6	3	0.06	0.58	0.51
						0.55
90						
	1.2297	18	15	0.3	0.34	0.28
	1.0007	19	16	0.32	0.32	0.32
	1.0198	18	15	0.3	0.34	0.33
						0.31
120						
	1.0048	8	5	0.1	0.54	0.54
	1.0603	7	4	0.08	0.56	0.53
	1.0448	8	5	0.1	0.54	0.52
						0.53
360						
	1.0311	7	4	0.08	0.56	0.54
	1.0932	6	3	0.06	0.58	0.53
	1.0018	6	3	0.06	0.58	0.58
						0.55
600						
	1.0148	8	5	0.1	0.54	0.53
	1.0112	8	5	0.1	0.54	0.53
	1.0156	8	5	0.1	0.54	0.53
						0.53
840						
	1.0648	6	3	0.06	0.58	0.54
	1.0033	6	3	0.06	0.58	0.58
	1.0478					
						0.56
1080						
	1.1213					
	1.0419	6	3	0.06	0.58	0.56
	1.0656	6	3	0.06	0.58	0.54
						0.55
1320						
	1.037	6	3	0.06	0.58	0.56
	1.0096	6	3	0.06	0.58	0.57
	1.021	6	3	0.06	0.58	0.57
						0.57

Table A3: Actual concentration of Hg(II) prepared

PREPARED CONC. (μg/l)	PEAK HEIGHT	PEAK HEIGHT	AVERAGE P. HEIGHT	CONC OF Hg in 50 ml (μg/l)	ACTUAL CONC (μg/l)
20	17842.112	17838.106	17840.109	1.065	21.292
40	18895.108	18897.106	18896.107	1.132	37.727
60	16605.026	16595.02	16600.023	0.986	59.378
80	16845.941	16841.695	16843.818	1.001	79.967
100	16345.492	16339.49	16342.491	0.969	96.928
120	16996.458	16989	16992.729	1.011	120.893
140	16852.425	16840.139	16846.282	1.001	139.852
160	16898.184	16896.196	16897.19	1.005	159.965
180	16785.445	16781.441	16783.443	0.997	179.378
200	16574.548	16570.546	16572.547	0.984	196.784

Table A4: Sorption data for sample: AA (Ankorbra River)

Code	Initial amt of Hg (II) added (ng)	Peak height	Peak height	Average P. height	Conc. in 50 ml (ug/l)	amt of Hg in supernatant (ng)	amt sorbed (ng)	mass of soil (g)	amt sorbed/wgt (ng/g)
20 1	212.919	2687.062	2974.552	2830.807	0.109	21.864	191.055	1.010	189.16
20 2	212.919	2724.542	2718.982	2721.762	0.102	20.476	192.443	1.010	190.54
20 3	212.919	2721.762	2625.752	2673.757	0.099	19.865	193.054	1.010	191.14
						20.735			190.28
40 1	377.268	2100.265	1923.777	2012.021	0.057	19.069	358.199	1.010	354.65
40 2	377.268	2409.763	2561.343	2485.553	0.087	29.115	348.153	1.010	344.71
40 3	377.268	2584.831	2685.747	2635.289	0.097	32.291	344.977	1.030	334.93
						26.825			344.76
60 1	593.776	2118.901	2150.181	2134.541	0.065	39.159	554.617	1.000	554.62
60 2	593.776	2175.479	2062.323	2118.901	0.064	38.559	555.217	1.050	528.78
60 3	593.776	2167.703	2156.049	2161.876	0.067	40.207	553.569	1.010	548.09
						39.308			543.83
80 1	799.668	1861.451	1895.345	1878.398	0.049	38.899	760.770	1.050	724.54
80 2	799.668	1960.381	1906.521	1933.451	0.052	41.698	757.970	1.010	750.47
80 3	799.668	1992.689	1979.329	1986.009	0.056	44.369	755.299	1.020	740.49
						41.655			738.50
100 1	969.278	1967.674	1933.722	1950.698	0.053	53.303	915.975	1.010	906.91
100 2	969.278	1992.337	1925.903	1959.12	0.054	53.839	915.439	1.010	906.38
100 3	969.278	1977.586	1876.698	1927.142	0.052	51.804	917.474	1.010	908.39
						52.982			907.22
120 1	1208.926	1957.525	1952.249	1954.887	0.054	64.079	1144.848	1.010	1133.51
120 2	1208.926	1936.77	1991.436	1964.103	0.054	64.780	1144.146	1.020	1121.71
120 3	1208.926	1953.321	1963.581	1958.451	0.054	64.350	1144.576	1.010	1133.24
						64.403			1129.49
140 1	1398.522	2049.538	2036.664	2043.101	0.059	82.659	1315.863	1.010	1302.83
140 2	1398.522	2016.89	2082.186	2049.538	0.060	83.232	1315.290	1.050	1252.66
140 3	1398.522	2080.206	2090.148	2085.177	0.062	86.400	1312.122	1.030	1273.91
						84.097			1276.47
160 1	1599.653	2182.647	2084.175	2133.411	0.065	103.395	1496.258	1.000	1496.26
160 2	1599.653	2192.289	2117.277	2154.783	0.066	105.561	1494.092	1.020	1464.80
160 3	1599.653	2101.143	2283.435	2192.289	0.069	109.362	1490.291	1.020	1461.07
						106.106			1474.04
180 1	1793.781	2568.061	2460.799	2514.43	0.089	160.400	1633.382	1.030	1585.81
180 2	1793.781	2525.763	2610.359	2568.061	0.093	166.539	1627.242	1.020	1595.34
180 3	1793.781	2500.052	2500.052	2500.052	0.088	158.754	1635.027	1.010	1618.84
						161.897			1599.99
200 1	1967.839	3007.904	3176.596	3092.25	0.126	251.916	1715.924	1.090	1574.24
200 2	1967.839	3153.138	3111.784	3132.461	0.129	257.034	1710.805	1.030	1660.98
200 3	1967.839	3092.25	2979.16	3035.705	0.122	244.718	1723.121	1.010	1706.06
						251.223			1647.09

Table A5: Sorption data for sample: BB (Bonsaso River)

Code	Initial amt of Hg (II) added (ng)	Peak height	Peak height	Average P. height	Conc. in 50 ml (ug/l)	amt of Hg in supernatant (ng)	amt sorbed (ng)	mass of soil (g)	amt sorbed/wgt (ng/g)
20 1	212.919	1586.242	1587.323	1586.783	0.030	6.028	206.891	1.010	204.842
20 2	212.919	1583.51	1581.381	1582.446	0.030	5.973	206.946	1.000	206.946
20 3	212.919	1585.264	1585.446	1585.355	0.030	6.010	206.909	1.040	198.951
						6.004			203.580
40 1	377.268	1508.408	1508.789	1508.599	0.025	8.388	368.880	1.040	354.692
40 2	377.268	1545.414	1546.167	1545.791	0.028	9.177	368.091	1.070	344.010
40 3	377.268	1520.682	1518.306	1519.494	0.026	8.620	368.648	1.010	364.998
						8.729			354.567
60 1	593.776	1482.972	1468.581	1475.777	0.023	13.901	579.875	1.000	579.875
60 2	593.776	1477.799	1473.803	1475.801	0.023	13.902	579.874	1.060	547.051
60 3	593.776	1459.803	1444.164	1451.984	0.022	12.989	580.787	1.090	532.832
						13.598			553.252
80 1	799.668	1485.564	1476.05	1480.807	0.023	18.687	780.981	1.000	780.981
80 2	799.668	1402.465	1420.773	1411.619	0.019	15.170	784.498	1.030	761.648
80 3	799.668	1436.231	1482.512	1459.372	0.022	17.598	782.070	1.020	766.736
						17.152			769.788
100 1	969.278	1559.394	1558.4	1558.897	0.028	28.367	940.911	1.010	931.595
100 2	969.278	1516.727	1510.968	1513.848	0.025	25.499	943.779	1.000	943.779
100 3	969.278	1514.835	1516.184	1515.51	0.026	25.605	943.673	1.000	943.673
						26.490			939.682
120 1	1208.926	1553.328	1582.099	1567.714	0.029	34.603	1174.324	1.020	1151.298
120 2	1208.926	1587.56	1575.483	1581.522	0.030	35.654	1173.272	1.060	1106.861
120 3	1208.926	1504.042	1520.962	1512.502	0.025	30.399	1178.527	1.000	1178.527
						33.552			1145.562
140 1	1398.522	1549.373	1545.802	1547.588	0.028	38.613	1359.909	1.040	1307.605
140 2	1398.522	1549.597	1544.417	1547.007	0.028	38.561	1359.961	1.010	1346.496
140 3	1398.522	1597.784	1598.536	1598.16	0.031	43.108	1355.414	1.020	1328.837
						40.094			1327.646
160 1	1599.653	1670.932	1670.372	1670.652	0.035	56.496	1543.157	1.090	1415.740
160 2	1599.653	1605.36	1601.521	1603.441	0.031	49.684	1549.969	1.070	1448.569
160 3	1599.653	1611.932	1614.171	1613.052	0.032	50.658	1548.995	1.070	1447.659
						52.279			1437.323
180 1	1793.781	1956.238	1958.412	1957.325	0.054	96.627	1697.154	1.010	1680.350
180 2	1793.781	1971.422	1963.469	1967.446	0.054	97.786	1695.995	1.010	1679.203
180 3	1793.781	1939.039	1984.382	1961.711	0.054	97.129	1696.652	1.020	1663.384
						97.181			1674.312
200 1	1967.839	2106.627	2169	2137.814	0.065	130.424	1837.415	1.080	1701.310
200 2	1967.839	2134.926	2164.132	2149.529	0.066	131.916	1835.923	1.070	1715.816
200 3	1967.839	2119.618	2105.249	2112.434	0.064	127.194	1840.645	1.060	1736.458
						129.845			1717.861

Table A6: Sorption data for sample: SS (Subri river)

Code	Initial amt of Hg (II) added (ng)	Peak height	Peak height	Average P. height	Conc. in 50 ml (ug/l)	amt of Hg in supernatant (ng)	amt sorbed (ng)	mass of soil (g)	amt sorbed/wgt (ng/g)
20 1	212.919	1432.759	1436.956	1434.858	0.020	4.094	208.824	1.020	204.730
20 2	212.919	1453.265	1453.475	1453.37	0.022	4.330	208.589	1.110	187.918
20 3	212.919	1401.601	1407.299	1404.45	0.019	3.707	209.212	1.040	201.165
						4.044			197.938
40 1	377.268	1682.804	1641.534	1662.169	0.035	11.646	365.622	1.030	354.972
40 2	377.268	1615.555	1615.238	1615.397	0.032	10.654	366.614	1.030	355.936
40 3	377.268	1606.273	1671.206	1638.74	0.033	11.149	366.119	1.010	362.494
						11.150			357.801
60 1	593.776	1927.546	1908.923	1918.235	0.051	30.866	562.911	1.030	546.515
60 2	593.776	1983.786	1997.724	1990.755	0.056	33.646	560.130	1.040	538.586
60 3	593.776	1905.835	1891.256	1898.546	0.050	30.111	563.665	1.070	526.790
						31.541			537.297
80 1	799.668	1969.206	1962.788	1965.997	0.054	43.352	756.316	1.040	727.227
80 2	799.668	1935.358	1947.516	1941.437	0.053	42.104	757.564	1.030	735.499
80 3	799.668	1995.767	1975.236	1985.502	0.056	44.344	755.324	1.020	740.514
						43.266			734.414
100 1	969.278	2104.787	2133.992	2119.39	0.064	64.040	905.238	1.020	887.488
100 2	969.278	2124.967	2197.952	2161.46	0.067	66.717	902.561	1.010	893.625
100 3	969.278	2164.332	2125.479	2144.906	0.066	65.664	903.614	1.020	885.897
						65.473			889.003
120 1	1208.926	2271.219	2223.679	2247.449	0.072	86.352	1122.575	1.020	1100.563
120 2	1208.926	2259.365	2278.485	2268.925	0.074	87.987	1120.939	1.030	1088.291
120 3	1208.926	2295.485	2268.535	2282.01	0.074	88.983	1119.943	1.000	1119.943
						87.774			1102.932
140 1	1398.522	2449.763	2435.867	2442.815	0.085	118.190	1280.332	1.050	1219.364
140 2	1398.522	2414.461	2380.934	2397.698	0.082	114.180	1284.342	1.010	1271.626
140 3	1398.522	2472.856	2496.14	2484.498	0.087	121.895	1276.627	1.020	1251.595
						118.088			1247.528
160 1	1599.653	2612.463	2619.691	2616.077	0.096	152.311	1447.341	1.050	1378.420
160 2	1599.653	2692.556	2685.745	2689.151	0.100	159.717	1439.936	1.110	1297.240
160 3	1599.653	2635.137	2641.125	2638.131	0.097	154.546	1445.107	1.050	1376.292
						155.525			1350.651
180 1	1793.781	2896.223	2897.428	2896.826	0.114	204.173	1589.609	1.000	1589.609
180 2	1793.781	2890.23	2894.656	2892.443	0.113	203.671	1590.110	1.000	1590.110
180 3	1793.781	2894.077	2896.897	2895.487	0.113	204.019	1589.762	1.030	1543.458
						203.954			1574.392
200 1	1967.839	3168.313	3102.852	3135.583	0.129	257.432	1710.408	1.120	1527.150
200 2	1967.839	3127.514	3119.993	3123.754	0.128	255.926	1711.913	1.060	1615.012
200 3	1967.839	3189.154	3156.053	3172.604	0.131	262.144	1705.695	1.030	1656.015
						258.500			1599.392

Table A7: Sorption data for sample: BM (Mansi river)

Code	Initial amt of Hg (II) added (ng)	Peak height	Peak height	Average P. height	Conc. in 50 ml (ug/l)	amt of Hg in supernatant (ng)	amt sorbed (ng)	mass of soil (g)	amt sorbed/wgt (ng/g)
20 1	212.919	2086.694	2155.071	2120.883	0.064	12.827	200.092	1.05	190.564
20 2	212.919	2100.306	2104.148	2102.227	0.063	12.589	200.330	1.05	190.790
20 3	212.919	2269.794	2326.681	2298.238	0.075	15.084	197.835	1.04	190.225
						13.500			190.526
40 1	377.268	2123.184	2177.269	2150.227	0.066	22.001	355.267	1.02	348.301
40 2	377.268	2007.93	2217.2	2112.565	0.064	21.202	356.066	1.09	326.666
40 3	377.268	2213.641	2076.14	2144.891	0.066	21.888	355.380	1.05	338.458
						21.697			337.808
60 1	593.776	1848.87	1851.231	1850.051	0.047	28.251	565.525	1.02	554.436
60 2	593.776	1852.687	1856.532	1854.61	0.047	28.426	565.350	1	565.350
60 3	593.776	1896.562	1898.604	1897.583	0.050	30.074	563.702	1.04	542.021
						28.917			553.936
80 1	799.668	1922.262	1915.907	1919.085	0.051	40.967	758.701	1.02	743.825
80 2	799.668	1966.574	1923.886	1945.23	0.053	42.296	757.372	1.02	742.521
80 3	799.668	2006.635	2018.265	2012.45	0.057	45.714	753.954	1.03	731.995
						42.992			739.447
100 1	969.278	1907.861	1924.658	1916.26	0.051	51.111	918.166	1.02	900.163
100 2	969.278	1921.424	1924.214	1922.819	0.052	51.529	917.749	1.06	865.801
100 3	969.278	1964.257	1963.09	1963.674	0.054	54.129	915.149	1.06	863.348
						52.256			876.438
120 1	1208.926	1975.448	1981.944	1978.696	0.055	65.891	1143.035	1.1	1039.123
120 2	1208.926	1944.92	1910.167	1927.544	0.052	61.997	1146.929	1.05	1092.313
120 3	1208.926	1957.414	1985.215	1971.315	0.055	65.329	1143.597	1.03	1110.288
						64.406			1080.575
140 1	1398.522	2100.347	2017.131	2058.739	0.060	84.049	1314.473	1.09	1205.938
140 2	1398.522	1995.738	1993.723	1994.731	0.056	78.360	1320.162	1.05	1257.297
140 3	1398.522	1907.351	1902.754	1905.053	0.050	70.388	1328.134	1.06	1252.956
						77.599			1238.731
160 1	1599.653	2200.636	2198.27	2199.453	0.069	110.088	1489.565	1.06	1405.250
160 2	1599.653	2140.776	2146.981	2143.879	0.066	104.456	1495.197	1.02	1465.880
160 3	1599.653	2114.72	2118.985	2116.853	0.064	101.717	1497.936	1.05	1426.606
						105.420			1432.578
180 1	1793.781	2353.501	2370.004	2361.753	0.079	142.922	1650.859	1.01	1634.514
180 2	1793.781	2386.351	2382.463	2384.407	0.081	145.516	1648.265	1.05	1569.776
180 3	1793.781	2387.299	2374.252	2380.776	0.081	145.100	1648.681	1.08	1526.556
						144.513			1576.949
200 1	1967.839	2589.898	2579.759	2584.829	0.094	187.325	1780.514	1.02	1745.602
200 2	1967.839	2573.734	2579.149	2576.442	0.093	186.258	1781.581	1.04	1713.059
200 3	1967.839	2565.875	2559.152	2562.514	0.092	184.485	1783.354	1.02	1748.386
						186.023			1735.682

Table A8: Sorption data for sample: TB (Teberebe river)

Code	Initial amt of Hg (II) added (ng)	Peak height	Peak height	Average P. height	Conc. in 50 ml (ug/l)	amt of Hg in supernatant (ng)	amt sorbed (ng)	mass of soil (g)	amt sorbed/wgt (ng/g)
20 1	212.919	2126.537	2132.829	2129.683	0.065	12.939	199.980	1.06	188.66
20 2	212.919	2184.576	2152.977	2168.777	0.067	13.437	199.482	1.05	189.98
20 3	212.919	2166.13	2140.266	2153.198	0.066	13.238	199.681	1	199.68
						13.205			192.77
40 1	377.268	2056.498	2041.414	2048.956	0.060	19.852	357.416	1.09	327.90
40 2	377.268	2029.141	2035.503	2032.322	0.058	19.499	357.769	1.08	331.27
40 3	377.268	2027.922	2025.945	2026.934	0.058	19.385	357.883	1.09	328.33
						19.579			329.17
60 1	593.776	2337.903	2325.043	2331.473	0.078	46.709	547.067	1.08	506.54
60 2	593.776	2323.928	2376.185	2350.057	0.079	47.422	546.354	1.08	505.88
60 3	593.776	2301.618	2308.531	2305.075	0.076	45.697	548.079	1.09	502.82
						46.610			505.08
80 1	799.668	2806.066	2798.254	2802.16	0.107	85.859	713.810	1.08	660.94
80 2	799.668	2809.223	2819.433	2814.328	0.108	86.477	713.191	1.08	660.36
80 3	799.668	2807.448	2808.885	2808.167	0.108	86.164	713.504	1.07	666.83
						86.167			662.71
100 1	969.278	2802.124	2809.164	2805.644	0.108	107.717	861.561	1.09	790.42
100 2	969.278	2895.461	2812.134	2853.798	0.111	110.781	858.497	1.09	787.61
100 3	969.278	2869.477	2864.05	2866.764	0.112	111.607	857.671	1.08	794.14
						110.035			790.72
120 1	1208.926	3043.397	3042.445	3042.921	0.123	146.912	1062.015	1.08	983.35
120 2	1208.926	3010.574	3015.328	3012.951	0.121	144.630	1064.296	1.09	976.42
120 3	1208.926	3009.67	3004.656	3007.163	0.121	144.190	1064.736	1.09	976.82
						145.244			978.86
140 1	1398.522	3448.057	3441.998	3445.028	0.148	207.277	1191.245	1.06	1123.82
140 2	1398.522	3445.83	3443.139	3444.485	0.148	207.229	1191.293	1.02	1167.93
140 3	1398.522	3450.576	3430.769	3440.673	0.148	206.890	1191.632	1.02	1168.27
						207.132			1153.34
160 1	1599.653	4035.687	4049.437	4042.562	0.186	296.881	1302.772	1	1302.77
160 2	1599.653	4045.3	4014.764	4030.032	0.186	295.611	1304.042	1.01	1291.13
160 3	1599.653	4026.329	4033.628	4029.979	0.186	295.605	1304.048	1.02	1278.48
						296.032			1290.79
180 1	1793.781	4258.256	4256.214	4257.235	0.200	359.899	1433.882	1.09	1315.49
180 2	1793.781	4238.291	4267.496	4252.894	0.200	359.402	1434.379	1.03	1392.60
180 3	1793.781	4286.601	4281.925	4284.263	0.202	362.993	1430.788	1.04	1375.76
						360.765			1361.28
200 1	1967.839	4563.588	4584.94	4574.264	0.220	440.563	1527.276	1.06	1440.83
200 2	1967.839	4598.105	4589.455	4593.78	0.222	443.047	1524.792	1.06	1438.48
200 3	1967.839	4561.796	4572.312	4567.054	0.220	439.645	1528.194	1.08	1414.99
						441.085			1431.43

Table A9: Sorption data for sample: EB (Efunta –Bonsa river)

Code	Initial amt of Hg (II) added (ng)	Peak height	Peak height	Average P. height	Conc. in 50 ml (ug/l)	amt of Hg in supernatant (ng)	amt sorbed (ng)	mass of soil (g)	amt sorbed/wgt (ng/g)
20 1	212.919	2564.413	2789.196	2676.8045	0.100	19.903	193.016	1.000	193.02
20 2	212.919	2629.542	2735.839	2682.6905	0.100	19.978	192.941	1.080	178.65
20 3	212.919	2683.829	2620.87	2652.3495	0.098	19.592	193.327	1.090	177.36
						19.825			183.01
40 1	377.268	2187.111	2090.317	2138.714	0.065	21.756	355.512	1.040	341.84
40 2	377.268	2180.1	2181.082	2180.591	0.068	22.645	354.623	1.040	340.98
40 3	377.268	2171.401	2136.619	2154.01	0.066	22.081	355.187	1.030	344.84
						22.161			342.55
60 1	593.776	1904.176	1909.108	1906.642	0.050	30.421	563.355	1.060	531.47
60 2	593.776	1920.005	1954.016	1937.0105	0.052	31.586	562.190	1.030	545.82
60 3	593.776	1923.005	1988	1955.5025	0.054	32.294	561.482	1.100	510.44
						31.434			529.24
80 1	799.668	1922.799	1988.962	1955.8805	0.054	42.838	756.830	1.090	694.34
80 2	799.668	1901.376	1965.233	1933.3045	0.052	41.690	757.978	1.090	695.39
80 3	799.668	1951.697	1929.065	1940.381	0.053	42.050	757.618	1.050	721.54
						42.193			703.76
100 1	969.278	1856.337	1819.169	1837.753	0.046	46.115	923.163	1.090	846.94
100 2	969.278	1849.131	1811.892	1830.5115	0.046	45.654	923.624	1.060	871.34
100 3	969.278	1875.465	1872.166	1873.8155	0.048	48.410	920.868	1.050	877.02
						46.726			865.10
120 1	1208.926	1945.425	1949.145	1947.285	0.053	63.500	1145.426	1.050	1090.88
120 2	1208.926	1943.062	1994.393	1968.7275	0.054	65.132	1143.794	1.020	1121.37
120 3	1208.926	1984.594	1985.445	1985.0195	0.055	66.373	1142.553	1.030	1109.28
						65.002			1107.17
140 1	1398.522	2055.145	2056.454	2055.7995	0.060	83.788	1314.734	1.040	1264.17
140 2	1398.522	2027.043	2029.976	2028.5095	0.058	81.362	1317.160	1.050	1254.44
140 3	1398.522	2057.123	2052.779	2054.951	0.060	83.713	1314.809	1.020	1289.03
						82.954			1269.21
160 1	1599.853	2511.428	2516.5	2513.964	0.089	141.963	1457.890	1.090	1337.51
160 2	1599.653	2501.764	2514.167	2507.9655	0.089	141.355	1458.298	1.080	1350.28
160 3	1599.653	2137.586	2541.967	2339.7765	0.078	124.309	1475.344	1.080	1366.06
						135.875			1351.28
180 1	1793.781	2943.454	2953.634	2948.544	0.117	210.093	1583.688	1.080	1466.38
180 2	1793.781	2918.708	2929.972	2924.34	0.115	207.322	1586.459	1.070	1482.67
180 3	1793.781	2916.791	2915.439	2916.115	0.115	206.381	1587.400	1.080	1469.82
						207.932			1472.95
200 1	1967.839	3536.468	3540.448	3538.458	0.154	308.714	1659.125	1.080	1536.23
200 2	1967.839	3537.961	3540.332	3539.1465	0.154	308.802	1659.037	1.080	1536.15
200 3	1967.839	3567.834	3598.101	3582.9675	0.157	314.380	1653.459	1.070	1545.29
						310.632			1539.22

Table A10: Sorption data for sample: BE (Ehyireso river)

Code	Initial amt of Hg (II) added (ng)	Peak height	Peak height	Average P. height	Conc. in 50 ml (ug/l)	amt of Hg in supernatant (ng)	amt sorbed (ng)	mass of soil (g)	amt sorbed/wgt (ng/g)
20 1	212.919	1244.216	1244.873	1244.545	0.008	1.672	211.247	1.080	195.599
20 2	212.919	1295.226	1226.275	1260.751	0.009	1.878	211.041	1.010	208.951
20 3	212.919	1284.623	1202.541	1243.582	0.008	1.660	211.259	1.030	205.106
						1.737			203.219
40 1	377.268	1441.56	1450.743	1446.152	0.021	7.064	370.204	1.030	359.422
40 2	377.268	1445.446	1474.564	1460.005	0.022	7.358	369.910	1.020	362.657
40 3	377.268	1448.948	1420.799	1434.874	0.020	6.824	370.444	1.030	359.654
						7.082			360.578
60 1	593.776	1494.467	1443.93	1469.199	0.023	13.649	580.127	1.040	557.814
60 2	593.776	1436.442	1414.167	1425.305	0.020	11.966	581.810	1.050	554.104
60 3	593.776	1402.433	1425.709	1414.071	0.019	11.536	582.240	1.040	559.847
						12.384			557.255
80 1	799.668	1727.004	1735.152	1731.078	0.039	31.410	768.258	1.040	738.710
80 2	799.668	1702.052	1723.211	1712.632	0.038	30.472	769.196	1.070	718.875
80 3	799.668	1701.445	1700.645	1701.045	0.037	29.883	769.785	1.030	747.364
						30.588			734.983
100 1	969.278	1965.136	1970.073	1967.605	0.054	54.379	914.899	1.040	879.710
100 2	969.278	1936.373	1923.297	1929.835	0.052	51.975	917.303	1.060	865.380
100 3	969.278	1980.718	1990.559	1985.639	0.056	55.527	913.751	1.020	895.834
						53.960			880.308
120 1	1208.926	2112.069	2117.009	2114.539	0.064	76.233	1132.693	1.020	1110.483
120 2	1208.926	2117.813	2112.433	2115.123	0.064	76.278	1132.648	1.020	1110.440
120 3	1208.926	2117.497	2118.771	2118.134	0.064	76.507	1132.419	1.000	1132.419
						76.339			1117.781
140 1	1398.522	2185.465	2184.445	2184.955	0.068	95.269	1303.253	1.010	1290.350
140 2	1398.522	2182.602	2184.814	2183.708	0.068	95.158	1303.364	1.050	1241.299
140 3	1398.522	2193.071	2184.016	2188.544	0.068	95.588	1302.934	1.060	1229.183
						95.338			1253.611
160 1	1599.853	2216.161	2241.399	2228.78	0.071	113.060	1486.793	1.010	1472.072
160 2	1599.653	2268.334	2230	2249.167	0.072	115.126	1484.527	1.060	1400.497
160 3	1599.653	2220.314	2298.543	2259.429	0.073	116.166	1483.487	1.020	1454.399
						114.784			1442.323
180 1	1793.781	2440.949	2442.763	2441.856	0.085	152.092	1641.689	1.000	1641.689
180 2	1793.781	2453.612	2410.437	2432.025	0.084	150.967	1642.814	1.020	1610.602
180 3	1793.781	2412.32	2459.113	2435.717	0.084	151.389	1642.392	1.000	1642.392
						151.483			1631.561
200 1	1967.839	2698.258	2700.142	2699.2	0.101	201.884	1765.955	1.080	1635.144
200 2	1967.839	2686.945	2691.598	2689.272	0.100	200.620	1767.219	1.040	1699.249
200 3	1967.839	2680.239	2660.139	2670.189	0.099	198.191	1769.648	1.010	1752.127
						200.232			1695.506